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Kinetics of free-surface decomposition of magnesium, strontium and barium carbonates analyzed thermogravimetrically by the third-law method

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Abstract

The results of our thermogravimetric experiments on the decompositions of $MgCO_3$, $SrCO_3$ and $BaCO_3$ 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 for these carbonates (218, 286 and $302\,kJ\,mol^{-1}$) are much higher than the enthalpies of equilibrium reactions (up to solid oxide and CO_2) and the values accepted by TA community as the reference data. At the same time, these data are in a good agreement with the mechanism of congruent dissociative evaporation of carbonates with the simultaneous condensation of low-volatility oxides. Differences in the magnitudes of the τ parameter responsible for the consumption of condensation energy by the reactant are revealed. Instead of expected 0.50, the magnitudes of the τ parameter for Mg, Sr and Ba carbonates are as follows: 0.47, 0.42 and 0.10.
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1. Introduction

The mechanism and kinetics of thermal decomposition of alkaline earth carbonates has been dealt with a large number of studies summed up in the past in a fundamental review [1] and monographs [2,3]. The advent of the physical approach [4] to the interpretation of the decomposition kinetics offered a fresh look at the old problems associated with the absence of quantitatively substantiated models of carbonate decomposition and some unusual features in their decomposition. The physical approach has been successively applied to compare the experimental literature data on the kinetics of carbonate decomposition with their theoretical values calculated on the basis of the physical approach [5]. Later on, the new methodology based on the so-called third-law method was proposed [6], which improved significantly the reliability in the determination of the most important characteristic in decomposition kinetics: the E parameter. The third-law method has been used recently for a thorough experimental investigation of free-surface decomposition kinetics of calcite [7] and dolomite [8].

The present work is a logic extension of these publications [7,8] and it is devoted to experimental investigations of kinetics and mechanisms of carbonate decomposition for other alkaline earth metals: magnesium, strontium and barium. The final goal of this project is to obtain eventually the whole picture of decomposition kinetics for this important class of solids. As before [4–8], the experimental values of the E parameter will be compared with the theoretical ones for assumed decomposition reactions. The methods of their determination and calculation were described in detail elsewhere [6–8]. Therefore, only some final relationships will be presented below.

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 and B with simultaneous

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condensation of low-volatility species A, that is

$$S(s) \rightarrow aA(g) \downarrow + bB(g) \qquad (1)$$

the E parameter for reaction (1) is equal to [4]:

$$E = \frac{\Delta_r H_T^\circ}{\nu} \qquad (2)$$

Here ν is the total number of moles of gaseous products, $(a+b)$, and $\Delta_r H_T^\circ$ 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 a low-volatility product A to the reactant, we introduce into the calculations of the enthalpy of decomposition reaction (1) an additional term, $\tau a \Delta_c H_T^\circ(A)$, where the coefficient τ corresponds to the fraction of the condensation energy consumed by the reactant [4]. Thus, we can write

$$\Delta_r H_T^\circ = a \Delta_f H_T^\circ(A) + b \Delta_f H_T^\circ(B) - \Delta_f H_T^\circ(S)$$
$$+ \tau a \Delta_c H_T^\circ(A) \qquad (3)$$

For equal temperatures of the solid phases (product and reactant), one may expect equipartition of energy between the two phases, i.e. $\tau = 0.50$. For the majority of substances investigated up to now, the condition $\tau = 0.50$ is found to be valid.

The magnitudes of thermodynamic functions (the entropy and enthalpy) for the components of decomposition reactions and for the reactions as a whole (given in italics) at different temperatures are listed in Tables 1–3. A possible error (S.D.) in these calculations of $\Delta_r H_T^\circ$ values is within 4–5 kJ mol^{-1}.

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

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

$$\Delta_r H_T^\circ = T(\Delta_r S_T^\circ - R \ln K_P) \qquad (4)$$

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

$$K_P = P_A^a P_B^b \qquad (5)$$

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 (5), Eq. (4) can be reduced to the following equation:

$$E = T \left(\frac{\Delta_r S_T^\circ}{\nu} - R \ln P_{eq} \right) \qquad (6)$$

Table 1
Thermodynamic functions for MgCO$_3$ decomposition [9]

Function[a]	Temperature (K)		
	500	600	700
S_T°(MgO(g))	230.9	238.0	244.6
S_T°(MgO(s))	48.6	57.1	64.5
S_T°(CO$_2$)	234.8	243.2	250.6
S_T°(MgCO$_3$)	110.7	129.6	146.7
$\Delta_r S_T^\circ$	*355.0 ± 0.6*	*351.6 ± 0.6*	*348.5 ± 0.6*
$\Delta_r S_T^\circ/\nu$	*177.5 ± 0.3*	*175.8 ± 0.3*	*174.3 ± 0.3*
$\Delta_f H_T^\circ$(MgO(g))	48.5	52.4	56.7
$\Delta_f H_T^\circ$(MgO(s))	−583.6	−579.0	−574.2
$\Delta_c H_T^\circ$(MgO)	−632.1	−631.4	−630.9
$\Delta_f H_T^\circ$(CO$_2$)	−375.5	−370.9	−366.0
$\Delta_f H_T^\circ$(MgCO$_3$)	−1058.9	−1048.6	−1037.4
$\Delta_r H_T^{\circ}$[b]	*434.8 ± 4*	*433.3 ± 4*	*431.6 ± 4*
$\Delta_r H_T^\circ/\nu$[b]	*217.4 ± 2*	*216.7 ± 2*	*215.8 ± 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.
[b] At $\tau = 0.47$ (see Section 4.4 on choosing this magnitude).

Table 2
Thermodynamic functions for SrCO$_3$ decomposition [9]

Function[a]	Temperature (K)	
	800	900
S_T°(SrO(g))	264.8	269.1
S_T°(SrO(s))	104.9	111.4
S_T°(CO$_2$)	257.4	263.5
S_T°(SrCO$_3$)	196.8	210.5
$\Delta_r S_T^\circ$	*325.4 ± 2*	*322.1 ± 2*
$\Delta_r S_T^\circ/\nu$	*162.7 ± 1*	*161.1 ± 1*
$\Delta_f H_T^\circ$(SrO(g))	14.6	18.3
$\Delta_f H_T^\circ$(SrO(s))	−554.1	−548.6
$\Delta_c H_T^\circ$(SrO)	−568.7	−566.9
$\Delta_f H_T^\circ$(CO$_2$)	−361.0	−355.7
$\Delta_f H_T^\circ$(SrCO$_3$)	−1154.6	−1143.0
$\Delta_r H_T^{\circ}$[b]	*569.3 ± 4*	*567.5 ± 4*
$\Delta_r H_T^\circ/\nu$[b]	*284.7 ± 2*	*283.8 ± 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.
[b] At $\tau = 0.42$ (see Section 4.4 on choosing this magnitude).

Table 3
Thermodynamic functions for BaCO$_3$ decomposition [9]

Function[a]	Temperature (K)	
	1100	1200
S_T°(BaO(g))	281.8	285.0
S_T°(BaO(s))	140.9	145.9
S_T°(CO$_2$)	274.4	279.3
S_T°(BaCO$_3$)	275.3	289.1
$\Delta_r S_T^\circ$	*280.9 ± 2*	*275.2 ± 2*
$\Delta_r S_T^\circ/\nu$	*140.5 ± 1*	*137.6 ± 1*
$\Delta_f H_T^\circ$(BaO(g))	−87.6	−83.9
$\Delta_f H_T^\circ$(BaO(s))	−493.6	−487.7
$\Delta_c H_T^\circ$(BaO)	−406.0	−403.8
$\Delta_f H_T^\circ$(CO$_2$)	−344.9	−339.3
$\Delta_f H_T^\circ$(BaCO$_3$)	−1077.7	−1061.9
$\Delta_r H_T^{\circ}$[b]	*604.6 ± 5*	*598.3 ± 5*
$\Delta_r H_T^\circ/\nu$[b]	*302.3 ± 2.5*	*299.2 ± 2.5*

[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.
[b] At $\tau = 0.10$ (see Section 4.4 on choosing this magnitude).

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. Tables 1–3 contain these values for all the carbonates under investigation.

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

$$P_{eq} = \frac{(2\pi MRT)^{1/2} J}{\gamma M} \tag{7}$$

Here M is the molar mass of the gaseous product (CO_2) and $\gamma = 101325\,Pa\,atm^{-1}$ is the conversion factor from Pascal's to atmospheres used to calculate partial pressures in chemical thermodynamics. As can be seen from a consideration of Eq. (6), 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. (6) 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 equal to

$$T_s = T_h \frac{E_{true}}{E_{exp}} \tag{8}$$

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

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 height was used as a sample container. The powdered sample introduced into a crucible was leveled and pressed manually (about $1\,kg\,mm^{-2}$) into a flat pellet. The total (outer) 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 powder measured separately).

To reduce the self-cooling effect, the sample chamber was evacuated to a residual pressure of about $n \times 10^{-4}$ atm (low vacuum) by a two-stage rotation pump. Pressure was measured with a thermal-conduction manometer. For comparison, some experiments were performed in high vacuum (at $n \times 10^{-8}$ 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 intermediate one (20 K lower than the desired temperature) was $10\,K\,min^{-1}$ and from intermediate 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 for 10–20 min) did not exceed ±0.2 K. A single measurement of the decomposition rate took entirely about 90 min, except the case of $MgCO_3$ decomposition at 670 K when because of the additional acceleratory period the total measurement time raised up to 150 min.

The absolute value of the decomposition rate for powder samples was estimated using the method proposed in our previous work [8]. 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 correction (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), as was shown in [8], does not depend on the temperature, residual pressure of air in the reactor, grain size and mass of a powder sample.

4. Results and discussion

4.1. Magnesium carbonate

The experimental conditions and the results of calculation of the E parameter by the third-law method are presented in Table 4. As can be seen from a comparison of results at different temperatures, the self-cooling effect is small but appreciable: the E values systematically increase with temperature. The average value of the E parameter at 670 K is equal to $217.8 \pm 0.4\,kJ\,mol^{-1}$ (two points). If we assume that this value is true, than in accordance with Eq. (8) the sample temperature at 711 and 690 K is, respectively, 9 and 6 K lower.

In addition to these results, some data from the literature can be used for the calculation of the E parameter by the third-law method. Fox and Soria-Ruiz [10] investigated the decomposition of $MgCO_3$ with a fast scanning mass analyzer of the quadrupole mass filter type. The absolute rate of decomposition of natural crystals of magnesite was measured

Table 4
Experimental conditions and results of calculation of the E parameter for $MgCO_3$ decomposition by the third-law method

Sample[a]	Vacuum (atm)	T (K)	m_0 (mg)	S_0 (mm^2)	α_m[b]	S_m[c] (mm^2)	$\Delta m/\Delta t$[d] (μg s^{-1})	J_{corr}[e] (kg m^{-2} s^{-1})	P_{eq} (atm)	$\Delta_r S_T^\circ/\nu$[f] (J mol^{-1} K^{-1})	E (kJ mol^{-1})
Powder	4×10^{-4}	711.0	20	58.2	0.147	52.3	1.283	8.76×10^{-6}	7.94×10^{-8}	174.2	220.5
Powder	4×10^{-4}	690.6	20	58.2	0.037	56.8	0.567	3.57×10^{-6}	3.19×10^{-8}	174.5	219.6
Powder	4×10^{-4}	670.8	20	58.2	0.064	55.7	0.283	1.82×10^{-6}	1.60×10^{-8}	174.8	217.4
Powder	4×10^{-4}	670.7	20	58.2	0.072	55.4	0.237	1.53×10^{-6}	1.35×10^{-8}	174.8	218.3

[a] The apparent density of pellets, prepared from this powder, is equal to 1959 kg m^3.
[b] The decomposition degree by the time of measurement.
[c] The surface area by the time of measurement calculated by the equation $S_m = S_0(1 - \alpha_m)^{2/3}$.
[d] Measured in the interval from 70 to 80 min at 711 and 690 K and from 130 to 140 min at 670 K (the acceleratory period of decomposition occupied about 60 min).
[e] $J_{corr} = (\Delta m/\Delta t)/(2.8 S_m)$.
[f] Interpolated for different temperatures taking into account the values listed in Table 1.

in ultrahigh vacuum (about 1 pbar) in the isothermal conditions in the interval 453–563 K (four orders of magnitude change in the rate of decomposition). At 453 K, $J \cong 1.8 \times 10^{11}$ molecules m^{-2} s^{-1} = 7.2×10^{-15} kg m^{-2} s^{-1} [10]. Using Eqs. (6) and (7), we receive $E = 220.9$ kJ mol^{-1}. This value is in excellent agreement with our results. The E parameter measured in this work [10] by the second-law method was equal to 176 ± 3 kJ mol^{-1} (11 points). This difference is a typical feature of the self-cooling of magnesite sample at temperatures higher than 453 K. Indeed, at 563 K, $J \cong 1.8 \times 10^{15}$ molecules m^{-2} s^{-1} = 7.2×10^{-11} kg m^{-2} s^{-1} [10] and $E = 229.0$ kJ mol^{-1}. From Eq. (8) we receive that the true temperature of magnesite sample was 20 K lower than the temperature of the furnace.

4.2. Strontium carbonate

The experimental conditions and the results of calculation of the E parameter for the $SrCO_3$ decomposition by the third-law method are presented in Table 5. All measurements have been performed at about 908 K. The equivalent pressure varied near 1×10^{-8} atm. At this high temperature and rather low decomposition rate, the sample self-cooling was negligible and values of the E parameter did not depend on the residual pressure of air in the reactor. The average value is equal to 285.5 ± 1.3 kJ mol^{-1} (four points). Any

literature data on the absolute decomposition rate of $SrCO_3$ are unknown. Zemtsova et al. [11] determined the E parameter for the $SrCO_3$ isothermal decomposition by the Arrhenius plots method in high vacuum in the range from 888 to 993 K (nine points). The value obtained (279 kJ mol^{-1}) is in good agreement with our result.

4.3. Barium carbonate

The experimental conditions and the results of calculation of the E parameter for the $BaCO_3$ decomposition by the third-law method are presented in Table 6. As expected, the values of the E parameters increase with temperature. The averaged value at 1077 K is equal to 302.1 ± 1.5 kJ mol^{-1} (four points).

Basu and Searcy [12] measured the absolute rates of $BaCO_3$ decomposition in the range from 1163 to 1210 K by a torsion-Langmuir technique. At 1163 K, the equivalent pressure $P_{eq} = 4.5 \times 10^{-8}$ atm. Using Eq. (6), we receive $E = 324.0$ kJ mol^{-1}. This value is in agreement with our result at highest temperature and obviously is overestimated due to the self-cooling effect. The latter conclusion is supported by the low value of the E parameter (225.9 ± 6.7 kJ mol^{-1}) obtained in this work [12] by the second-law method (26 points). If we assume that the true value of the E parameter at 1163 K is equal to 302 kJ mol^{-1}, than in accordance with Eq. (8) the sample temperature in this case was 79 K lower.

Table 5
Experimental conditions and results of calculation of the E parameter for $SrCO_3$ decomposition by the third-law method

Sample[a]	Vacuum (atm)	T (K)	m_0 (mg)	S_0 (mm^2)	α_m[b]	S_m[c] (mm^2)	$\Delta m/\Delta t$[d] (μg s^{-1})	J_{corr}[e] (kg m^{-2} s^{-1})	P_{eq} (atm)	$\Delta_r S_T^\circ/\nu$[f] (J mol^{-1} K^{-1})	E (kJ mol^{-1})
Powder	8×10^{-8}	907.8	40	61.8	0.0057	61.5	0.180	1.04×10^{-6}	1.07×10^{-8}	161.0	284.7
Powder	8×10^{-8}	907.1	40	61.8	0.0064	61.5	0.173	1.01×10^{-6}	1.03×10^{-8}	161.0	284.8
Powder	1×10^{-4}	908.7	40	61.8	0.0121	61.3	0.127	7.38×10^{-7}	7.60×10^{-9}	161.0	287.5
Powder	1×10^{-4}	908.7	40	61.8	0.0228	60.8	0.173	1.02×10^{-6}	1.05×10^{-8}	161.0	285.1

[a] The apparent density of pellets, prepared from this powder, is equal to 2613 kg m^3.
[b] The decomposition degree by the time of measurement.
[c] The surface area by the time of measurement calculated by the equation $S_m = S_0(1-\alpha_m)^{2/3}$.
[d] Measured in the interval from 70 to 80 min in high vacuum and from 90 to 100 min in low vacuum.
[e] $J_{corr} = (\Delta m/\Delta t)/(2.8 S_m)$.
[f] Interpolated for 908 K taking into account the values listed in Table 2.

Table 6
Experimental conditions and results of calculation of the E parameter for $BaCO_3$ decomposition by the third-law method

Sample[a]	Vacuum (atm)	T (K)	m_0 (mg)	S_0 (mm^2)	α_m[b]	S_m[c] (mm^2)	$\Delta m/\Delta t$[d] ($\mu g\,s^{-1}$)	J_{corr}[e] ($kg\,m^{-2}\,s^{-1}$)	P_{eq} (atm)	$\Delta_r S_T^\circ/\nu$[f] ($J\,mol^{-1}\,K^{-1}$)	E ($kJ\,mol^{-1}$)
Powder	3×10^{-8}	1232	40	63.9	0.59	35.3	4.59	4.64×10^{-5}	5.54×10^{-7}	136.7	316.0
Powder	3×10^{-8}	1154	40	63.9	0.279	51.4	2.49	1.73×10^{-5}	2.00×10^{-7}	139.0	308.4
Powder	3×10^{-8}	1115	40	63.9	0.188	55.6	1.33	8.54×10^{-6}	9.70×10^{-8}	140.1	305.9
Powder	3×10^{-8}	1076	40	63.9	0.109	59.2	0.79	5.37×10^{-6}	5.99×10^{-8}	141.2	301.7
Powder	2×10^{-4}	1077	40	63.9	0.115	58.9	0.960	5.82×10^{-6}	6.50×10^{-8}	141.2	300.3
Powder	2×10^{-4}	1077	40	63.9	0.092	60.0	0.647	3.385×10^{-6}	4.30×10^{-8}	141.2	304.0
Powder	2×10^{-4}	1077.5	40	63.9	0.102	59.5	0.773	4.64×10^{-6}	5.18×10^{-8}	141.2	302.4

[a] The apparent density of pellets, prepared from this powder, is equal to $2177\,kg\,m^3$.
[b] The decomposition degree by the time of measurement.
[c] The surface area by the time of measurement calculated by the equation $S_m = S_0(1 - \alpha_m)^{2/3}$.
[d] Measured in the interval from 70 to 80 min at 1232 K and from 60 to 70 min at other temperatures.
[e] $J_{corr} = (\Delta m/\Delta t)/(2.8 S_m)$.
[f] Interpolated for the temperatures used taking into account the values listed in Table 3.

Table 7
Specific enthalpies and the E parameters for decomposition of carbonates

Carbonate	Temperature (K)[a]	Equilibrium products	$\Delta_r H_T^\circ/\nu$ ($kJ\,mol^{-1}$)	Primary products	τ	$\Delta_r H_T^\circ/\nu$ ($kJ\,mol^{-1}$)	E ($kJ\,mol^{-1}$)	Reference
$MgCO_3$	690	$MgO(s) + CO_2$	97 ± 2	$MgO(g)\downarrow + CO_2$	0.47	216 ± 2	217.8 ± 0.4	This work
$CaMg(CO_3)_2$	790	$MgO(s) + CaO(s) + 2CO_2$	164 ± 3	$MgO(g)\downarrow + CaO(g)\downarrow + 2CO_2$	0.50	245 ± 3	245.0 ± 0.6	[8]
$CaCO_3$	890	$CaO(s) + CO_2$	171 ± 1	$CaO(g)\downarrow + CO_2$	0.50	253 ± 2	255.1[b]	[7]
$SrCO_3$	940	$SrO(s) + CO_2$	238 ± 1	$SrO(g)\downarrow + CO_2$	0.42	283 ± 2	285.5 ± 1.3	This work
$BaCO_3$	1060	$BaO(s) + CO_2$	242 ± 4	$BaO(g)\downarrow + CO_2$	0.10	303 ± 3	302.1 ± 1.5	This work

[a] Temperature (rounded off to two figures) that corresponds to $P_{eq} = 3 \times 10^{-8}$ atm.
[b] This magnitude was received instead of the original value $261.0\,kJ\,mol^{-1}$ [7] after correction of the absolute rate of decomposition calculated in [7] by Eq. (7), where the molar mass of $CaCO_3$ was erroneously used instead of molar mass of CO_2.

In case of our measurement at 1232 K, the sample temperature was 54 K lower.

4.4. Interpretation of kinetics

In Table 7, we compare the kinetic data (the E parameters) for Mg, Sr and Ba carbonates received in this work with the specific enthalpies ($\Delta_r H_T^\circ/\nu$) for two different decomposition reactions. (For completeness, we included in this table the corresponding data for calcite and dolomite obtained earlier [7,8].) The first of these reactions proceeds, in accordance with the traditional approach [1–3], up to the equilibrium products. The second one, in agreement with the physical approach [4,5], proceeds through formation of intermediate *gaseous* oxides and their simultaneous condensation. The following conclusions can be deduced from these data:

1. Contrary to the widely accepted opinion [1–3], the E parameters for all alkaline earth carbonates are much higher than the enthalpies of equilibrium reactions. For calcite and dolomite, the difference between corresponding values is equal to about $80\,kJ\,mol^{-1}$ and for magnesite reaches $120\,kJ\,mol^{-1}$.
2. The values of the E parameter and decomposition temperature successively increase from $MgCO_3$ to $BaCO_3$. As

expected, the average magnitude of T/E ratio (3.3 ± 0.2) is in agreement with the theoretically predicted value for $P_{eq} = 3 \times 10^{-8}$ atm [6].
3. In the framework of the physical approach, the obtained values of the E parameter are interpreted as the specific enthalpies of primary gasification reaction with consideration for the partial transfer of condensation energy of low-volatility oxides to the reactant. The values of τ factor indicated in Table 7 (and Tables 1–3) correspond to the condition: $\Delta_r H_T^\circ/\nu \cong E$.
4. In contrast to the expectation that the τ factor for all reactants is close to 0.50, this factor in cases of $MgCO_3$ and, especially, of $SrCO_3$ and $BaCO_3$ decomposition is significantly smaller (0.47, 0.42 and 0.10, respectively). This fact deserves special consideration and it will be discussed later [13].

5. Conclusions

The third-law method was applied in this work to investigation of decomposition kinetics of powder samples of Mg, Sr and Ba carbonates. The much lower dependence on the self-cooling effect and the order of magnitude higher precision of this method compared to the second-law and Arrhenius plots methods permitted for the first time over the long

story of these investigations to obtain reliable data on the E parameters. They are in good agreement with the E parameters for $MgCO_3$ and $BaCO_3$ (single crystals), which were calculated from the absolute decomposition rates reported in the literature [10,12]. However, these data, together with the corresponding results for calcite and dolomite obtained in our previous works [7,8], are systematically higher (by 40–80 kJ mol^{-1} for Mg, Ca, Sr and Ba carbonates) than the values accepted by TA community as the most reliable (reference) data [2,3].

The new data are also much higher than the enthalpies of equilibrium reactions (up to solid oxide and CO_2). For this reason, the widely accepted identification of carbonate decomposition reactions as reversible should be refused. At the same time, these data are in agreement with the mechanism of congruent dissociative evaporation of carbonates with the simultaneous condensation of low-volatility oxides. The interpretation of the E parameter as the specific enthalpies of primary gasification reaction with consideration for the partial transfer of condensation energy of low-volatility oxides to the reactant revealed some differences in the values of τ factor for different carbonates. In contrast to $CaCO_3$ and $CaMg(CO_3)_2$, for which $\tau = 0.50$, the magnitudes of the τ parameter for $MgCO_3$, $SrCO_3$ and $BaCO_3$ are equal to 0.47, 0.42 and 0.10, respectively. The reason of this difference will be discussed in [13].

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