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Thermochimica Acta 410 (2004) 47–55

thermochimica acta

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Peculiarities of $CaCO_3$, $SrCO_3$ and $BaCO_3$ decomposition in CO_2 as a proof of their primary dissociative evaporation

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Received 7 January 2003; received in revised form 17 May 2003; accepted 7 July 2003

Abstract

The results of thermogravimetric experiments on the decompositions of $CaCO_3$, $SrCO_3$ and $BaCO_3$ in the presence of CO_2 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. The values obtained (495, 569 and 605 kJ mol^{-1}) are twice as much compared with the values of the E parameter obtained for these carbonates earlier in the absence of CO_2. This fact together with the invariance of the E parameter with partial pressure of CO_2 (P_{CO_2}) and a hyperbolic dependence of the rate of decomposition on P_{CO_2} is in excellent agreement with the theoretical predictions deduced from the mechanism of decomposition that includes the primary stage of dissociative evaporation of reactant.

Keywords: Alkaline earth carbonates; Dissociative evaporation; Effect of CO_2; Kinetics; Solid decomposition; Third-law method

1. Introduction

The peculiarities of thermal decomposition of alkaline earth carbonates in atmosphere of CO_2 were studied over the last 70 years in many works [1–11]. However, there is no agreement in quantitative and even in qualitative interpretation of kinetics for this reaction. As illustration, we present in Table 1 the results of determination of the E parameter for decomposition of calcite in the presence of CO_2 obtained by different workers. As can be seen, in most of the publications [1–6], increase of CO_2 pressure is accompanied by increase of the E parameter, which in some cases reaches 2000–4000 kJ mol^{-1}. In contrast to these results, a rather constant values of the E parameter were observed in [7,8] under variation of CO_2 pressure, though the absolute magnitudes of E in the latter works differ more than two and a half times. The serious discrepancy was also observed in the dependence of absolute values of decomposition rate of $CaCO_3$ on CO_2 pressure. In contrast to the observation of hyperbolic rate law ($\propto 1/P_{CO_2}$) in [9,10], Darroudi and Searcy [11] found close to linear decrease of the decomposition rate with the background pressure of CO_2. At the same time, as discussed later, the peculiarities of thermal decomposition of carbonates in atmosphere of CO_2 can be used as a very strong argument *pro et contra* one or other mechanism of decomposition, in particular, the mechanism of thermal decomposition based on the primary dissociative evaporation of reactant with simultaneous condensation of the low-volatile product [12–16].

The objectives of this work are in experimental determination of the E parameter for decomposition of $CaCO_3$, $SrCO_3$ and $BaCO_3$ in the presence of CO_2 and in subsequent comparison of these data with the values of the E parameters in the absence of CO_2 and with corresponding predictions of theory. The choice of the reactants was defined, on the one hand, by high accuracy of their E parameters determined in [8,16] in the absence of CO_2 and, on the other hand, by the difference in the fraction of the condensation energy consumed by these carbonates during decomposition (see Section 2.3). (Magnesite was excluded because of the uncertainty in composition of available materials.) The third-law method as the most reliable method of calculation of the E parameter will be used. This method was described in detail elsewhere [14–16]. Therefore, only some final relationships describing the theoretical values of the E parameter under different conditions (in the absence

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doi:10.1016/S0040-6031(03)00372-1

Table 1
Investigations of the effect of CO_2 pressure on the E parameter for $CaCO_3$ decomposition

Authors	Year	Variation of P'_{CO_2} (atm)	Point number	Variation of the E parameter ($\mathrm{kJ\,mol^{-1}}$)	Measurement technique	Calculation method
Zawadzki and Bretsznajder [1]	1935	0.0013–0.059	6	186–1536	Isothermal	Arrhenius plots
Tagawa and Sudo [2]	1958	0–0.53	5	160–360	Isothermal	Arrhenius plots
Mauras [3]	1960	0.032–0.26	4	708–1580	Non-isothermal	Arrhenius plots
Gallagher and Johnson [4]	1976	1.0	1	565–3830[a]	Non-isothermal	Arrhenius plots
Caldwell et al. [5]	1977	0 and 0.05	2	201 and 950	Isothermal	Arrhenius plots
		0–1.0	3	213–2142	Non-isothermal	Arrhenius plots
Maciejewski and Baldyga [6]	1985	0.02–0.06	3	310–460	Isothermal	Arrhenius plots
Criado et al. [7]	1995	0.013–0.20	4	191 ± 5	Non-isothermal	Arrhenius plots
		0.20	1	187	Isothermal	Arrhenius plots
L'vov et al. [8]	2002	4×10^{-6} to 8×10^{-5}	5	493 ± 5	Isothermal	Third-law

[a] At different heating rates and sample size.

and in the presence of CO_2) and equations, which are necessary for their experimental determination by the third-law method, will be presented below.

2. Theoretical

The main concept in the physical approach [12–16] to the interpretation of kinetics 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 carbonates, this difference consists in the decomposition of MCO_3 into molecules of CO_2 and low-volatility gaseous molecules of MO, which subsequently condense with the formation of solid MO.

The equilibrium character of decomposition reactions has received recently [14] a strong confirmation. The mean ratio of the initial temperature of decomposition, T_{in}, to the E parameter for 100 different substances ($3.6 \pm 0.4\,\mathrm{kJ\,mol^{-1}}$) taken from the literature practically coincides with the value ($3.6 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$) predicted from equilibrium thermodynamics. The great advantage of the physical approach relative to the standard (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.

2.1. Decomposition rate

In the case of a compound S decomposed into gaseous products A and B with simultaneous condensation of low-volatility species A, i.e.

$$\mathrm{S\,(s)} \rightarrow a\mathrm{A\,(g)} \downarrow + b\mathrm{B\,(g)} \tag{1}$$

the flux of each product (A or B), which ultimately determines the rate of decomposition, can be expressed through the so-called equivalent partial pressure P_{eq} (in atm) of this product corresponding to the hypothetical equilibrium of reaction (1) in the form

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

where M is the molar mass of product. Here $\gamma = 101\,325\,\mathrm{Pa\,atm^{-1}}$ is the conversion factor from atmospheres to pascals. This relationship derived as shown here by Langmuir is usually called the Hertz–Langmuir equation.

2.2. Equilibrium pressure of product for dissociative evaporation

The partial pressure, P_A, of product A can be calculated from the equilibrium constant, K_P, for reaction (1). In the absence of reaction products in the reactor atmosphere, the situation corresponding to the *equimolar* evaporation mode, the partial pressure P_A can be expressed [12] as

$$P_A^e = a\left(\frac{K_P}{F}\right)^{1/\nu}\left(\frac{M_A}{M_B}\right)^{b/2\nu} = \frac{a}{F^{1/\nu}}\left(\frac{M_A}{M_B}\right)^{b/2\nu}\exp\frac{\Delta_r S_T^\circ}{\nu R}\exp\left(-\frac{\Delta_r H_T^\circ}{\nu RT}\right) \tag{3}$$

where

$$F \equiv a^a b^b \tag{4}$$

$$\nu = a + b \tag{5}$$

and

$$K_P = P_A^a P_B^b \tag{6}$$

Here $\Delta_r H_T^\circ$ and $\Delta_r S_T^\circ$ are, respectively, the changes of the enthalpy and entropy in reaction (1).

If the partial pressure P'_B of one of the gaseous component (B) greatly exceeds the equivalent pressure P_B of the same component released in the decomposition and if, in addition to that, the magnitude of P'_B remains constant in the process of decomposition, we call such an evaporation mode *isobaric*. In this case

$$P^{\rm i}_{\rm A}=\frac{K_P^{1/a}}{(P'_{\rm B})^{b/a}}=\frac{1}{(P'_{\rm B})^{b/a}}\exp\frac{\Delta_{\rm r}S^\circ_T}{aR}\exp\left(-\frac{\Delta_{\rm r}H^\circ_T}{aRT}\right) \qquad (7)$$

2.3. Theoretical calculation of the E parameter

Eqs. (2)–(7) can be used for the calculation of the E parameter, entering the Arrhenius equation

$$k = A\exp\left(-\frac{E}{RT}\right) \qquad (8)$$

As can be seen from Eqs. (3) and (7), the E parameter for reaction (1) should be different for the equimolar and isobaric modes of decomposition, i.e.,

$$E^{\rm e} = \frac{\Delta_{\rm r}H^\circ_T}{\nu} = \frac{\Delta_{\rm r}H^\circ_T}{a+b} \qquad (9)$$

for the equimolar mode and

$$E^{\rm i} = \frac{\Delta_{\rm r}H^\circ_T}{\nu - b} = \frac{\Delta_{\rm r}H^\circ_T}{a} \qquad (10)$$

for the isobaric mode. In both cases, the E parameter corresponds to the *specific enthalpy*, i.e. the enthalpy of the decomposition reaction reduced to 1 mol 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 (1) an additional term, $\tau a\,\Delta_{\rm c}H^\circ_T({\rm A})$, where the coefficient τ corresponds to the fraction of the condensation energy consumed by the reactant. Thus, we can write

$$\begin{aligned}\Delta_{\rm r}H^\circ_T &= a\,\Delta_{\rm f}H^\circ_T({\rm A}) + b\,\Delta_{\rm f}H^\circ_T({\rm B}) - \Delta_{\rm f}H^\circ_T({\rm S})\\ &\quad + \tau a\,\Delta_{\rm c}H^\circ_T({\rm A})\end{aligned} \qquad (11)$$

For equal temperatures of the solid phases, one may expect equipartition of energy between the two phases, i.e. $\tau = 0.50$. For the majority of substances investigated up to now (among them $CaCO_3$), the condition $\tau = 0.50$ is found to be valid. At the same time for $SrCO_3$ and $BaCO_3$, τ is equal to 0.42 and 0.10, respectively [16].

The magnitudes of thermodynamic functions (the entropy and enthalpy) for the components of decomposition reactions and for the reactions as a whole (given in bold) at different temperatures are listed in Tables 2–4. A possible error (S.D.) in these calculations of $\Delta_{\rm r}H^\circ_T$ values is within 4–5 kJ mol^{-1}.

2.4. 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

$$\Delta_{\rm r}H^\circ_T = T(\Delta_{\rm r}S^\circ_T - R\ln K_P) \qquad (12)$$

where as before $\Delta_{\rm r}S^\circ_T$ is the entropy change and K_P is the equilibrium constant for the reaction (1). Taking into account Eqs. (6), (9) and (10), Eq. (12) in the case of decomposition of carbonates can be reduced to the equation

$$E^{\rm e} = T\left(\tfrac{1}{2}\Delta_{\rm r}S^\circ_T - R\ln P_{\rm eq}\right) \qquad (13)$$

for the equimolar mode and to the equation

$$E^{\rm i} = T[\Delta_{\rm r}S^\circ_T - R\ln(P_{\rm eq}P'_{\rm CO_2})] \qquad (14)$$

for the isobaric mode, where $P'_{\rm CO_2}$ is the external pressure of CO_2.

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 (2) rewritten as

$$P_{\rm eq} = \frac{(2\pi MRT)^{1/2}J}{\gamma M} \qquad (15)$$

Table 2
Thermodynamic functions for $CaCO_3$ decomposition [17]

Function[a]	T (K)				
	800	900	1000	1100	1200
S°_T (CaO (g))	254.0	258.4	262.3	265.8	269.1
S°_T (CaO (s))	86.0	92.2	97.8	102.9	107.6
S°_T (CO_2)	257.4	263.5	269.2	274.4	279.3
S°_T ($CaCO_3$)	193.2	207.3	220.2	232.2	243.5
$\Delta_{\rm r}S^\circ_T$	**318.2 ± 0.8**	**314.6 ± 0.8**	**311.3 ± 0.8**	**308.0 ± 0.8**	**304.9 ± 0.8**
$\Delta_{\rm f}H^\circ_T$ (CaO (g))	70.7	74.4	78.1	81.9	85.7
$\Delta_{\rm f}H^\circ_T$ (CaO (s))	–600.3	−595.0	−589.7	−584.4	−579.0
$\Delta_{\rm c}H^\circ_T$ (CaO)	−671.0	−669.5	−667.8	−666.3	−664.7
$\Delta_{\rm f}H^\circ_T$ (CO_2)	−361.0	−355.7	−350.4	−344.9	−339.3
$\Delta_{\rm f}H^\circ_T$ ($CaCO_3$)	−1133.9	−1121.9	−1109.6	−1097.0	−1084.1
$\Delta_{\rm r}H^\circ_T$[b]	**508.1 ± 4**	**505.9 ± 4**	**503.4 ± 4**	**500.9 ± 4**	**498.2 ± 4**

[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 $\tau = 0.50$ [8].

Table 3
Thermodynamic functions for $SrCO_3$ decomposition [17]

Function[a]	T (K)		
	1000	1100	1200
S°_T (SrO (g))	273.1	276.6	279.9
S°_T (SrO (s))	117.2	122.7	127.7
S°_T (CO_2)	269.2	274.4	279.3
S°_T ($SrCO_3$)	223.4	235.7	247.6_{1198}[b]
$\Delta_r S^\circ_T$	**318.9** $\pm$ **2**	**315.3** $\pm$ **2**	$\mathbf{311.6_{1198}}$ $\pm$ **2**[b]
$\Delta_f H^\circ_T$ (SrO (g))	22.0	25.7	29.5
$\Delta_f H^\circ_T$ (SrO (s))	-543.0	-537.3	-531.6
$\Delta_c H^\circ_T$ (SrO)	565.0	563.0	561.1
$\Delta_f H^\circ_T$ (CO_2)	-350.4	-344.9	-339.3
$\Delta_f H^\circ_T$ ($SrCO_3$)	-1130.8	-1117.8	-1104.2_{1198}[b]
$\Delta_r H^\circ_T$[c]	**565.1** $\pm$ **5**	**562.1** $\pm$ **5**	$\mathbf{558.7_{1198}}$ $\pm$ **5**[b]

[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] These values correspond to solid α-$SrCO_3$ at 1198 K ($\alpha \rightarrow \beta$ phase transition point).
[c] At $\tau = 0.42$ [16].

Table 4
Thermodynamic functions for $BaCO_3$ decomposition [17]

Function[a]	T (K)		
	1200	1300	1400
S°_T (BaO (g))	285.0	288.0	290.8
S°_T (BaO (s))	145.9	150.7	155.1
S°_T (CO_2)	279.3	283.8	288.1
S°_T ($BaCO_3$)	289.1	304.2	316.0
$\Delta_r S^\circ_T$	**275.2** $\pm$ **2**	**267.6** $\pm$ **2**	**262.9** $\pm$ **2**
$\Delta_f H^\circ_T$ (BaO (g))	-83.9	-80.2	-76.4
$\Delta_f H^\circ_T$ (BaO (s))	-487.7	-481.8	-475.9
$\Delta_c H^\circ_T$ (BaO)	-403.8	-401.6	-399.5
$\Delta_f H^\circ_T$ (CO_2)	-339.3	-333.6	-327.9
$\Delta_f H^\circ_T$	-1061.9	-1043.1	-1027.1
$\Delta_r H^\circ_T$[b]	**598.3** $\pm$ **5**	**589.1** $\pm$ **5**	**582.9** $\pm$ **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 $\tau = 0.10$ [16].

2.5. Theoretically predicted indications confirming the dissociative evaporation mechanism

From the above theoretical discussion, the following consequences can be deduced:

1. The value of the E parameter for decomposition of carbonates in the presence of CO_2 (isobaric mode) should be invariant with respect to the partial pressure of CO_2, P'_{CO_2}. This is follow from consideration of Eqs. (2) and (7) defined the temperature dependence of the decomposition rate.
2. As follows from the same equations, the decomposition rate, J, is in inverse proportion to $(P'_B)^{b/a}$ or for carbonates (when $a = b = 1$)

$$J \propto \frac{1}{P'_{CO_2}} \tag{16}$$

3. The values of the E parameter for solid decomposition in the presence of gaseous product B (isobaric mode) and in its absence (equimolar mode) should be subjected to the relation

$$E^i = \left(\frac{\nu}{a}\right) E^e \tag{17}$$

and in case of carbonate decomposition (when $a = 1$ and $\nu = 2$), to the relation

$$E^i = 2E^e \tag{18}$$

Of the above consequences, the last one is probably the most important indication of the dissociative evaporation mechanism of solid decomposition. The validity of this condition in the case of dissociative evaporation of metal oxides to free atoms of metal (without any condensation) and oxygen is supported by the results of determination of the E parameter in isobaric and equimolar modes obtained by electrothermal atomic absorption spectrometry

Table 5
Experimental values of the E parameter for dissociative evaporation of metal oxides in the isobaric and equimolar modes [18]

Reaction	T (K)	E (kJ mol^{-1})		E^i/E^e	ν	$(E^i/E^e)/\nu$
		Isobaric	Equimolar			
$(1/2)Li_2O$ (s) → Li (g) + $(1/4)O_2$	1400	472	361	1.30	1.25	1.04
BeO (s) → Be (g) + O	2400	1145	583	1.96	2.00	0.98
MgO (s) → Mg (g) + $(1/2)O_2$	1700	710	504	1.41	1.50	0.94
CaO (s) → Ca (g) + $(1/2)O_2$	1900	714	518	1.38	1.50	0.92
SrO (s) → Sr (g) + $(1/2)O_2$	2000	745	500	1.49	1.50	0.99
BaO (s) → Ba (g) + O	2300	893	468	1.91	2.00	0.96
SnO_2 (s) → Sn (g) + O_2	1400	832	460	1.81	1.50	1.21
PbO (s) → Pb (g) + $(1/2)O_2$	1100	391	240	1.63	1.50	1.09
MnO (s) → Mn (g) + $(1/2)O_2$	1700	627	450	1.39	1.50	0.93
$(1/2)Al_2O_3$ (s) → Al (g) + $(3/4)O_2$	2100	1107	638	1.74	1.75	0.99
$(1/2)Ga_2O_3$ (s) → Ga (g) + $(3/4)O_2$	1500	712	427	1.67	1.75	0.95
$(1/2)In_2O_3$ (s) → In (g) + $(3/4)O_2$	1400	685	361	1.90	1.75	1.09
$(1/2)Bi_2O_3$ (l) → Bi (g) + $(3/4)O_2$	1200	470	245	1.92	1.75	1.10
$(1/2)V_2O_3$ (l) → V (g) + (3/2)O	2300	1389	633	2.19	2.50	0.88
$(1/2)Cr_2O_3$ (s) → Cr (g) + $(3/4)O_2$	2000	1074	502	2.14	1.75	1.22
Average						1.02 ± 0.10

(Table 5). As can be seen from these results, the agreement of E^i/E^e ratio with a number of moles of gaseous products ν is very good. For 15 metal oxides with the ν parameter varied from 1.25 to 2.5, the average value of $(E^i/E^e)/\nu$ is equal to 1.02 ± 0.10.

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 calcite crystals about 3 mm × 2 mm × 0.5 mm in size (maximum values) and about 7–8 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 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, all measurement have been performed in atmosphere of argon with the addition of 0.1 atm CO_2 for $CaCO_3$ and $SrCO_3$ and 0.001 atm CO_2 for $BaCO_3$. Pressure was measured, respectively, with a membrane manometer and thermal-conduction manometer. All measurements have been conducted 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, during 10–20 min) did not exceed ±0.2 K. A single measurement of the decomposition rate took entirely about 2–3 h.

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 (10^{-8} to 10^{-4} atm), grain size and mass of a powder sample.

4. Results and discussion

In addition to the results of our own experiments, some data on $CaCO_3$ and $SrCO_3$ decomposition reported in the literature will be used in this paper for the determination of the E parameter by the third-law method. The data of the present work will be considered first.

Table 6
Experimental conditions and results of calculation of the E parameter for carbonate decomposition in CO_2 by the third-law method

Carbonate	Sample	P'_{CO_2} (atm)	T (K)	m_0 (mg)	S_0 (mm^2)	α_m[a]	S_m[b] (mm^2)	$\Delta m/\Delta t$[c] ($\mu g\,s^{-1}$)	J_{corr}[c] ($kg\,m^{-2}\,s^{-1}$)	P_{eq} (atm)	$(\Delta_r S^\circ_T)$[d] ($J\,mol^{-1}\,K^{-1}$)	E ($kJ\,mol^{-1}$)
$CaCO_3$	Crystal	0.10	1100.3	8.3	16.52	0.196	14.3	1.145	8.00×10^{-5}	9.05×10^{-7}	308.0	487.3
$CaCO_3$	Crystal	0.10	1071.0	8.3	16.52	0.076	15.7	0.187	1.20×10^{-5}	1.30×10^{-7}	308.9	492.5
$CaCO_3$	Crystal	0.10	1070.9	7.4	14.73	0.140	13.3	0.221	1.66×10^{-5}	1.80×10^{-7}	308.9	489.3
$CaCO_3$	Powder	0.10	1070.8	20.0	57.3	0.200	49.33	2.133	1.55×10^{-5}	1.72×10^{-7}	308.9	489.9
$CaCO_3$	Powder	0.10	1070.4	20.0	57.3	0.124	52.45	2.51	1.71×10^{-5}	1.90×10^{-7}	308.9	488.9
$SrCO_3$	Powder	0.10	1131.2	20.0	56.41	0.01	56.05	0.069	4.40×10^{-7}	5.00×10^{-9}	313.9	556.5
$SrCO_3$	Powder	0.10	1151.1	20.0	56.41	0.007	56.16	0.036	2.30×10^{-7}	2.70×10^{-9}	313.4	571.6
$BaCO_3$	Powder	0.001	1249.1	40.0	61.78	0.025	60.73	0.120	7.10×10^{-7}	8.40×10^{-9}	271.4	603.9
$BaCO_3$	Powder	0.001	1249.2	40.0	61.78	0.119	56.78	0.093	5.90×10^{-7}	7.10×10^{-9}	271.4	605.7

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

[b] The surface area by the time of measurement calculated by the equation $S_m = S_0\ (1 - \alpha_m)^{2/3}$.

[c] $J_{cor} = (\Delta m/\Delta t)/S_m$ for crystals and $J_{cor} = (\Delta m/\Delta t)/2.8\ S_m$ for powders.

[d] Interpolated for the temperatures used taking into account the values listed in Tables 2–4.

4.1. *This work*

The experimental conditions and results of determination are presented in Table 6. For all the carbonates, the powders were used as samples. In case of $CaCO_3$, single crystals of natural calcite were used in addition to powders. The purpose of these experiments was to check the validity of the evaluation of absolute decomposition rate for powders as described in Section 3 under atmospheric pressure of argon. The average values of the E parameter for decomposition of single crystals (489.7 ± 2.6) and powders (489.4 ± 0.7) practically coincide. This means that the correction factor (2.8) used for the calculation of absolute rates of powder decomposition in vacuum [16,17] can be equally used for corresponding calculations at atmospheric pressure of ambient gas (argon). The averaged values of the E parameter for decomposition of $SrCO_3$ and $BaCO_3$ in the presence of CO_2 are equal, respectively, to 564 ± 10 and $605 \pm 1\,kJ\,mol^{-1}$.

4.2. *The literature data*

The results of calculation of the E parameter by the third-law method using the literature data [9–12] on the absolute rate for $CaCO_3$ decomposition are presented in Table 7. (For completeness, the results obtained in this work for single crystals are included.) As can be seen from analysis of these data, the partial pressure of CO_2 varies in the range of 5 orders of magnitude: from 3.6×10^{-6} to 0.6 atm. Despite of this, the E parameter remains practically constant. The average value is equal to $495 \pm 6\,kJ\,mol^{-1}$ (14 points) with the exception of only two results. One of them ($468.3\,kJ\,mol^{-1}$) is underestimated because of the probable catalytic effect of H_2O vapor (in ambient air) on the rate of decomposition; the other result ($515.4\,kJ\,mol^{-1}$) is obviously overestimated because of the self-cooling effect under conditions of decomposition in vacuum (10^{-3} atm) at rather high temperature (1073 K).

Table 7
Values of the E parameter for $CaCO_3$ decomposition in the presence of CO_2 calculated from the literature data and our experiments by the third-law method

Atmosphere	P'_{CO_2} (atm)	T (K)	P_{eq} (atm)	$\Delta_r S^\circ_T$ ($J\,mol^{-1}\,K^{-1}$)	E ($kJ\,mol^{-1}$)	Reference
N_2 (dry)	2.0×10^{-1}	1123	4.75×10^{-7}	307.2	496.0	[9]
N_2 (dry)	6.0×10^{-1}	1173	9.70×10^{-7}	305.8	498.7	[9]
N_2 (dry)	5.4×10^{-1}	1223	5.00×10^{-6}	304.2	502.4	[9]
Air	2.4×10^{-1}	1123	8.55×10^{-6}	307.2	468.3[a]	[10]
Vacuum	1.0×10^{-4}	898	5.10×10^{-8}	314.6	493.8	[11]
Vacuum	1.0×10^{-3}	983	8.00×10^{-8}	311.9	496.6	[11]
Vacuum	1.0×10^{-3}	1006	1.08×10^{-7}	311.3	505.1	[11]
Vacuum	1.0×10^{-3}	1073	1.11×10^{-6}	308.9	515.4[b]	[11]
He (8 mbar)	3.6×10^{-6}	857	2.23×10^{-8}	316.1	485.7	[12]
He (8 mbar)	1.5×10^{-5}	897	5.60×10^{-8}	314.6	489.8	[12]
He (8 mbar)	4.0×10^{-5}	935	1.49×10^{-7}	313.4	494.0	[12]
He (8 mbar)	5.8×10^{-5}	954	2.46×10^{-7}	312.8	496.5	[12]
He (8 mbar)	7.8×10^{-5}	974	4.86×10^{-7}	312.2	498.4	[12]
Ar	1.0×10^{-1}	1100.3	9.05×10^{-7}	308.0	487.3	This work
Ar	1.0×10^{-1}	1071.0	1.30×10^{-7}	308.9	492.5	This work
Ar	1.0×10^{-1}	1070.9	1.80×10^{-7}	308.9	489.3	This work
Average		1020 ± 110			495 ± 6[c]	

[a] Underestimated because of the possible catalytic effect of H_2O impurity in air.
[b] Overestimated because of the strong self-cooling effect in vacuum.
[c] The E values in '*a*' and '*b*' cases are excluded from calculation.

Table 8
Values of the E parameter for $SrCO_3$ decomposition in the presence of CO_2 calculated from the literature data [19] and our experiments (last two lines) by the third-law method

Atmosphere	P'_{CO_2} (atm)	T (K)	k (s^{-1}) [19]	J ($kg\,m^{-2}\,s^{-1}$)	P_{eq} (atm)	$\Delta_r S^\circ_T$ ($J\,mol^{-1}\,K^{-1}$)	E ($kJ\,mol^{-1}$)
Vacuum	3.9×10^{-5}	1003	1.38×10^{-4}	5.92×10^{-7}	6.38×10^{-9}	318.9	561.9
Vacuum	2.2×10^{-4}	1053	1.05×10^{-4}	4.51×10^{-7}	4.98×10^{-9}	317.0	574.9
Vacuum	1.3×10^{-3}	1133	9.50×10^{-4}	4.08×10^{-6}	4.67×10^{-8}	314.5	577.9
Argon	1.0×10^{-1}	1131.2		4.40×10^{-7}	5.00×10^{-9}	314.6	556.5
Argon	1.0×10^{-1}	1151.1		2.30×10^{-7}	2.70×10^{-9}	313.9	571.6
Average		1090 ± 60					569 ± 9

Table 9
Experimental values of the E parameter for carbonate decomposition in the isobaric (this work) and equimolar [8,16] modes

Reaction	T (K)		E ($\mathrm{kJ\,mol^{-1}}$)		E^i/E^e
	Isobaric	Equimolar	Isobaric	Equimolar	
$CaCO_3 \rightarrow CaO\ (g)_\downarrow + CO_2$	1020	820 [8]	495 ± 6	254 ± 6 [8]	1.95
$SrCO_3 \rightarrow SrO\ (g)_\downarrow + CO_2$	1090	908 [16]	569 ± 9	285.5 ± 1.3 [16]	1.99
$BaCO_3 \rightarrow BaO\ (g)_\downarrow + CO_2$	1249	1077 [16]	605 ± 1	302.1 ± 1.5 [16]	2.00
Average					1.98 ± 0.03

Decomposition of $SrCO_3$ in CO_2 was investigated by Zemtsova et al. [19]. We used some of the reported data (the rate constant of the Arrhenius equation, k, temperature and partial pressure of CO_2) for the calculation of the E parameter by the third-law method (Table 8). The absolute rate of decomposition, J, necessary for the calculation of the E parameter was estimated by the formula [20]:

$$J = kr_0\rho \tag{19}$$

where r_0 and ρ are the mean radius and density of particles of $SrCO_3$, respectively. Taking into account that $r_0 = 1.2 \times 10^{-6}\,\mathrm{m}$ (by estimation of the authors [19]) and $r = 3700\,\mathrm{kg\,m^{-3}}$, we received J and P_{eq} values. Using Eq. (11) and the entropy changes from Table 3, we calculated the values of the E parameter. The average value of the literature and our data ($569 \pm 9\,\mathrm{kJ\,mol^{-1}}$) is in excellent agreement with the theoretical value ($562 \pm 5\,\mathrm{kJ\,mol^{-1}}$) at 1100 K.

The only available literature data for $BaCO_3$ decomposition in CO_2 is the E parameter measured under isothermal conditions by the Arrhenius plots method [21]. The found value ($643\,\mathrm{kJ\,mol^{-1}}$ [21]), in contrast to the literature data for calcite (Table 1), is in satisfactory agreement with our result ($605\,\mathrm{kJ\,mol^{-1}}$).

5. Conclusions

When the experimental results obtained in this work are compared with the theoretical predictions (Section 2.5), it becomes apparent that they are in excellent agreement. Firstly, the values of the E parameters for decomposition of $CaCO_3$ (Table 7) and $SrCO_3$ (Table 8) in the presence of CO_2 are invariant with respect to the partial pressure of CO_2. Secondly, the decomposition rate, J, is in inverse proportion to P'_{CO_2}. This conclusion is supported by the direct measurements for $CaCO_3$ reported in [7,9,10]. (A linear decrease of J with P'_{CO_2} observed by Darroudi and Searcy [11] was connected with the effect of severe self-cooling of samples in high vacuum. This effect was quantitatively analyzed in [13].) Thirdly, the values of the E parameter for decomposition $CaCO_3$, $SrCO_3$ and $BaCO_3$ in the presence and in the absence of CO_2 (Table 9) are subjected to the theoretically predicted relation $E^i = 2E^e$. The averaged value E^i/E^e is equal to 1.98 ± 0.03 instead of 2.00. The observed underestimation for $CaCO_3$ partly results from different decomposition temperatures in cases of the isobaric and equimolar modes. The enthalpy for all reactions decreases with temperature (see Tables 2–4). As a result, the theoretical ratio E^i/E^e for $CaCO_3$ at 1020 and 820 K for the isobaric and equimolar modes, respectively, should be equal to 1.98 instead of 2.00. The experimental value (1.95) is in a better agreement with this magnitude.

We consider the agreement of experimental results with theoretical predictions as a very strong proof of validity of the primary dissociative evaporation mechanism for carbonate decomposition and the physical approach to the interpretation of kinetics of solid decomposition on the whole. The failure of all the previous investigations into the effect of CO_2 on kinetics of carbonate decomposition may be attributed mainly to shortages of the Arrhenius plots method, especially in combination with the non-isothermal measurement technique and, in case of calcite, to the strong catalytic effect of H_2O vapor on the decomposition rate [20].

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