ELSEVIER

Thermochimica Acta 303 (1997) 161-170

thermochimica
acta

Mechanism of thermal decomposition of alkaline-earth carbonates

Boris V. L'vov*

Department of Analytical Chemistry, St. Petersburg State Technical University, St. Petersburg 195251, Russian Federation

Received 19 December 1996; accepted 24 June 1997

Abstract

A comparison of the kinetic characteristics of $MgCO_3$, $CaMg(CO_3)_2$, $CaCO_3$, $SrCO_3$ and $BaCO_3$ decomposition in vacuum available in the literature, with the data calculated for three possible paths of the process has shown the one involving intermediate hydroxide formation to be most probable. This mechanism includes interaction of the carbonate with water vapor as the main, rate-limiting stage, followed by decomposition of the gaseous Ba hydroxide or condensing Mg, Ca and Sr hydroxides to the oxides and water. Some specific features of the process have been interpreted, in particular, the formation of a metastable calcium modification in decomposition of $CaCO_3$ and $CaMg(CO_3)_2$, as well as the anomalously high activation energies observed in non-isothermal decomposition of $CaCO_3$ in the presence of CO_2. © 1997 Published by Elsevier Science B.V.

Keywords: Activation energies; Carbonate decomposition; Intermediate hydroxide formation mechanism; Kinetics calculation; Water vapor effect

---

1. Introduction

The mechanism and kinetics of thermal decomposition of the carbonates of alkaline-earth metals (in particular, calcium carbonate) have been dealt with a large number of studies summed up partially in a review [1] and a monograph [2]. Nevertheless, there are still no quantitatively substantiated models of carbonate decomposition. No explanation has been also given for some unusual features in their decomposition exemplified below:

1. the low value of the activation energy, E_a for the decomposition of $BaCO_3$ (which is less than the enthalpy of the reaction, ΔH_T^o) contrasting with those for the other alkaline-earth carbonates, for which $E_a > \Delta H_T^o$[2,3];
2. formation of a metastable modification of calcium oxide in decomposition of $CaCO_3$ and $CaMg(CO_3)_2$ [2,4,5];
3. anomalous scatter among the parameters of the Arrhenius equation (E_a and A) available in the literature for decomposition of $CaCO_3$, particularly in the presence of CO_2 [6,7];
4. a 10^3–10^4-fold difference between the partial pressures of CO_2 observed in the decomposition of $CaCO_3$, $CaMg(CO_3)_2$ and $BaCO_3$ in the Knudsen mode (the effusion cell) and under Langmuir conditions (from an open surface), or, in other words, low evaporation coefficients for these compounds in vacuum [3,5].

The present work is an attempt in studying the mechanism of thermal decomposition of the carbonate

---

*Corresponding author. Tel.: 00 7 812 528 0281; fax: 00 7 812 528 0281; e-mail: lvov@achem.hop.stu.neva.ru

PII S0040-6031(97)00261-X

of alkaline-earth metals, which makes use of an untraditional approach based on the concepts of decomposition and interaction among solids in the gas phase. These concepts, first put forward by the present author more than ten years ago, have since been used in interpretation of the mechanism and kinetics of carbothermal oxide reduction [8,9] and, later, to explain the decomposition of nitrates [10–13], azides [14], and of a number of other metal compounds [15].

The method to be employed below consists in comparing experimental data on the kinetic parameters with their values calculated for all conceivable paths of the process. The calculations are based on the classical evaporation model Hertz–Langmuir, extended by the present author to the cases of dissociative evaporation of compounds and their interaction with the ambient gases [16–21].

2. Theoretical

The scheme employed in the calculation of the main kinetic parameters of the decomposition process (the flux of the gaseous product J, the rate constant k, and the parameters of the Arrhenius equation, E_a and A) has been described in a number of our recent publications [14,15,21]. Therefore, we are going to present below only some final relations necessary for the calculations in this work.

2.1. Calculation scheme

In the case of a compound S decomposed in vacuo into gaseous products A and B

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

the flux of product A can be expressed through the partial pressure P_A of this product corresponding to the hypothetical equilibrium of reaction (1) in the form

$$J_A = \frac{MP_A}{(2\pi\bar{M}RT)^{1/2}} \tag{2}$$

where M is the molar mass of the reactant and R the gas constant. Here $\bar{M}$ is the geometric mean of the molar masses of all gaseous particles, i.e.

$$\bar{M} \equiv M_A^{a/\nu} \times M_B^{b/\nu} \tag{3}$$

where

$$\nu \equiv a + b \tag{4}$$

The flux of gaseous products J is connected with the rate constant k. For spherical particles, the fraction decomposed is described by the contracting volume model

$$\frac{d\alpha}{dt} = 3(1-\alpha)^{2/3}k \tag{5}$$

Taking into account some obvious relationships: $\alpha \equiv 1 - m/m_0$, $m = (4/3)\pi r^3\rho$ and $J = -(dm/dt)(4\pi r^2)^{-1}$, where m, r and ρ are the mass, radius and density of reactant spherical particle(s), we obtain on rearrangement of Eq. (5) a simple and elegant expression

$$J = \rho\, r_0\, k \tag{6}$$

2.2. Potential reactions

We shall consider below three conceivable paths of carbonate decomposition for subsequent comparison of calculated kinetic parameters with experiment, namely, condensation decomposition:

$$\mathrm{MCO_3(s)} \rightarrow \mathrm{CO_2(g)} + \mathrm{MO(s)} \tag{7}$$

dissociative evaporation:

$$\mathrm{MCO_3(s)} \rightarrow \mathrm{CO_2(g)} + \mathrm{MO(g)} \tag{8}$$

and intermediate hydroxide formation:

$$\mathrm{MCO_3(s)} + \mathrm{H_2O(g)} \rightarrow \mathrm{CO_2(g)} + \mathrm{M(OH)_2(g)} \tag{9}$$

Reaction (7) identifies the universally accepted mechanism of decomposition and reactions (8) and (9) correspond to the first stages in the two schemes of the gasification mechanism. The subsequent stages of the process in the last two schemes are described by reactions

$$\mathrm{MO(g)} \rightarrow \mathrm{MO(s)} \tag{10}$$

and

$$\mathrm{M(OH)_2(g)} \rightarrow \mathrm{MO(s)} + \mathrm{H_2O(g)} \tag{11}$$

The CO_2 partial pressure can be expressed for each of reactions (7)–(9) through the equilibrium constant K_p of the corresponding reaction in the following way

$$P_{CO_2} = K_p(7) \tag{12}$$

$$P_{CO_2} = [K_p(8)]^{1/2} \tag{13}$$

and

$$P_{CO_2} = [K_p(9)] \times P_{H_2O}]^{1/2} \tag{14}$$

2.3. Activation energies

Substituting into Eq. (2) the expressions for P_{CO_2} from Eqs. (12)–(14) and recalling the well-known equation of the third law of thermodynamics

$$K_p = \exp\frac{\Delta S^o_T}{R}\exp\left[-\frac{\Delta H^o_T}{RT}\right] \tag{15}$$

where ΔH^o_T and ΔS^o_T are, respectively, the changes in enthalpy and entropy in reactions (7)–(9), we find from a comparison of the relations thus obtained with the Arrhenius equation:

$$E_a = \Delta H^o_T(7) \tag{16}$$

$$E_a = \Delta H^o_T(8)/2 \tag{17}$$

and assuming P_{H_2O} constant,

$$E_a = \Delta H^o_T(9)/2 \tag{18}$$

Here $\Delta H^o_T(7)$, $\Delta H^o_T(8)$ and $\Delta H^o_T(9)$ are, respectively, the changes in enthalpy in reactions (7)–(9).

3. Results and discussion

3.1. Experimental kinetic data

Despite a wealth of publications in this field, the possibilities of choosing reliable experimental data which would characterize the decomposition kinetics of carbonates are fairly limited. Preference should be given to a series of studies [3–5] performed in the mid-70s by Searcy and colleagues, devoted to the decomposition of $CaCO_3$, $CaMg(CO_3)_2$ and $BaCO_3$, as well as the publications of Pavlyuchenko et al. [22–24], who studied decomposition of $MgCO_3$ and $SrCO_3$. In all these cases, measurements were carried out under continuous pumping of the furnace to 10^{-7}–10^{-8} atm. Samples of natural crystals of known size were used in the experiments of Searcy et al. [3–5] and powders of $MgCO_3$ and $SrCO_3$, in the experiments of Pavlychenko et al. [22–24]. The mass change was measured by the torsion–Langmuir technique in isothermal conditions of sample decomposition. Besides the activation energies, the papers quote the absolute values of one of the mutually related kinetic parameters (P_{CO_2}, J or k). Table 1 sums up these data for the carbonates of all the above metals at the mean temperatures of the measurements, $\bar{T}$. Additional P and J kinetic parameters (not given in Refs. [3–5,22–24] were calculated by us using Eqs. (2)–(6) and taking into account the physico–chemical properties of carbonates specified in Table 2. The mean radius of $MgCO_3$ particles necessary for the calculation of J value by Eq. (6) equals to $\sim 1 \times 10^{-4}$ m [24]. In the case of $SrCO_3$ powder, the radius was estimated from the specific area (s) measurements [22] by the B.E.T. method. For $s = 5.5 \times 10^3 \mathrm{m^2 kg^{-1}}$ and $\rho = 3700 \mathrm{kg\ m^{-3}}$, we have $r_0 = 3/(\rho s) \cong 1.5 \times 10^{-7}$m.

3.2. Calculated kinetic data

The activation energies and decomposition rates were calculated for a mean temperature $\bar{T}$ with the use of the thermodynamic functions [25,26] presented in Table 3. In view of the fact that the three kinetic parameters (P, J and k) characterizing the decomposi-

Table 1
Experimental kinetic parameters for the thermal decomposition of carbonates in vacuum[a]

Carbonate	$\bar{T}$ (K)	E_a (kJ mol^{-1})	P_{CO_2} (atm)	J (kg m^{-2} s^{-1})	k (s^{-1})	Reference
$MgCO_3$	779	192	1×10^{-8}	2×10^{-6}	$\underline{8 \times 10^{-5}}$	24
$CaMg(CO_3)_2$	862	195	$\underline{1 \times 10^{-7}}$	3×10^{-5}		5
$CaCO_3$	974	205	2×10^{-7}	$\underline{5 \times 10^{-5}}$		4
$SrCO_3$	983	233	2×10^{-8}	4×10^{-6}	$\underline{7 \times 10^{-3}}$	23
$BaCO_3$	1185	226	$\underline{8 \times 10^{-8}}$	3×10^{-5}		3

[a] The underlined data were taken from the given references.

Table 2
Some physico–chemical parameters of carbonates

Carbonate	ρ (kg m^{-3})	M (kg mol^{-1})	$\bar{M}$ (kg mol^{-1})
$MgCO_3$	296	0.084	0.042
$CaMg(CO_3)_2$	2804	0.184	0.046
$CaCO_3$	2710	0.100	0.050
$SrCO_3$	3700	0.148	0.068
$BaCO_3$	4430	0.197	0.082

Table 3
Thermodynamic functions [25,26] used in the calculations

Species	State of aggregation	$\Delta_f H^o_{900}$ (kJ mol^{-1})	S^o_{900} (J mol^{-1} K^{-1})
BaO	g	−95.0 ± 8.5	274.3
BaO	s	−505.0 ± 5.0	129.4
$Ba(OH)_2$	g	−544.1 ± 20	417.9
$BaCO_3$	s	−1122.9 ± 5.0	231.4
CO	g	−86.7 ± 0.2	231.0
CO_2	g	−355.7 ± 0.1	263.5
CaO	g	74.4 ± 15	258.4
CaO	s	−595.0 ± 0.9	92.2
$Ca(OH)_2$	g	−530.1 ± 20	392.1
$CaCO_3$	s	−1121.9 ± 1.0	207.3
$CaMg(CO_3)_2$	s	−2156.8 ± 1.7[a]	384.7[b]
H_2	g	26.1	162.9
H_2O	g	−207.0 ± 0.04	228.4
MgO	g	66.7 ± 15	257.0
MgO	s	−564.3 ± 0.3	76.9
$Mg(OH)_2$	g	−475.6 ± 20	369.7
$MgCO_3$	s	−1013.0 ± 3.0	177.4
SrO	g	18.3 ± 15	269.1
SrO	s	−548.6 ± 1.0	111.4
$Sr(OH)_2$	g	−511.4 ± 20	409.9
$SrCO_3$	s	−1130.8 ± 2.0	210.5

[a] $\Delta_f H^o_{900} = \Delta_f H^o_0 + (H^o_{900} - H^o_0)_{CaCO_3} + (H^o_{900} - H^o_0)_{MgCO_3}$.
[b] $S^o_{900} = S^o_{900}(CaCO_3) + S^o_{900}(MgCO_3)$.

tion rate are interrelated, the comparison of the calculations with experiment was carried out by the magnitude of the CO_2 pressure. The values of P_{CO_2} were determined using Eqs. (12)–(15) and the activation energies, from Eqs. (16)–(18). A correction $(-0.5R\bar{T})$ for the effect of the $(2\pi\bar{M}RT)^{1/2}$ factor on the variation of decomposition rate with temperature [17–20] was introduced into the calculated values of E_a.

In calculations for reaction (9), the partial pressure of water vapor was assumed in all cases to be constant and equal to 10^{-7} atm, in order to take into account that in the decomposition stage the total pressure in the system increased from 10^{-8} atm to 10^{-7} atm [4]. The sources of the water vapor could be the residual air in the system, water adsorbed by the walls, and water contained in samples of natural carbonate crystals. An order-of-magnitude over-evaluation of P_{H_2O} may result in a three-fold over-estimation of the calculated values of P_{CO_2}. The results of the calculations made for three conceivable paths of the decomposition process are presented in Tables 4–6.

3.3. Comparison of the calculated and experimental data

For conveniency in the subsequent discussion, we compare in Table 7 the data calculated for the various mechanisms of carbonate decomposition with experiment. We readily see that the calculations are in considerable conflict with experiment both for the universally accepted mechanism of condensation decomposition and for dissociative evaporation in all cases, with the exception of $BaCO_3$. In the case of dissociative evaporation of $BaCO_3$, the calculated value of P_{CO_2} agrees with experiment, however, at the same time the calculated activation energy E_a exceeds the experimental value by 105 kJ mol^{-1}.

The situation is different with the mechanism of intermediate hydroxide formation. We recall that gaseous hydroxides of alkaline-earth elements are the

Table 4
Calculated kinetic parameters for the decomposition of carbonates in accordance with reaction (7)

Carbonate	$\bar{T}$ (K)	ΔH^o_{900} (kJ mol^{-1})	ΔS^o_{900} (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})	P_{CO_2} (atm)
$MgCO_3$	779	93.0	163.0	90	2×10^{2}
$CaMg(CO_3)_2$	862	143.1	155.7	139	3×10^{-1}
$CaCO_3$	974	171.2	148.4	167	4×10^{-2}
$SrCO_3$	983	238.7	164.4	235	8×10^{-5}
$BaCO_3$	1185	262.2	161.5	257	8×10^{-4}

Table 5
Calculated kinetic parameters for the decomposition of carbonates in accordance with reaction (8)

Carbonate	$\bar{T}$ (K)	ΔH°_{900} (kJ mol^{-1})	ΔS°_{900} (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})	P_{CO_2} (atm)
$MgCO_3$	779	724.0	343.1	359	5×10^{-16}
$CaMg(CO_3)_2$	862	793.3	328.9	393	4×10^{-16}
$CaCO_3$	974	840.6	314.6	416	5×10^{-15}
$SrCO_3$	983	805.6	322.1	299	1×10^{-13}
$BaCO_3$	1185	672.2	306.4	331	2×10^{-7}

Table 6
Calculated kinetic parameters for the decomposition of carbonates in accordance with reaction (9)

Carbonate	$\bar{T}$ (K)	ΔH°_{900} (kJ mol^{-1})	ΔS°_{900} (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})	P_{CO_2} [a] (atm)
$MgCO_3$	779	388.7	227.4	191	3×10^{-11}
$CaMg(CO_3)_2$	862	426.9	223.7	210	3×10^{-11}
$CaCO_3$	974	443.1	219.9	218	2×10^{-10}
$SrCO_3$	983	482.9	234.5	237	2×10^{-11}
$BaCO_3$	1185	430.1	212.6	210	6×10^{-8}

[a] At $P_{H_2O} = 1 \times 10^{-7}$ atm.

stable species in the low-temperature decomposition of the salts of these metals. In particular, they were reliably detected above 400 K by Prell et al. [27] in a mass-spectrometric investigation of the products of decomposition of the hydrated nitrates of Mg, Ca, Sr, and Ba. As follows from Table 7, the values of E_a are in a very good agreement for all carbonates, and for $BaCO_3$ this agreement extends to P_{CO_2} as well. For other metals, the calculated values of P_{CO_2} lie below the experiment by three orders of magnitude. While this disagreement is smaller than that observed for the same carbonates in other decomposition mechanisms, nevertheless, it requires additional discussion. Errors in the original values of thermodynamic functions (Table 3) cannot bring about the more than four-fold change in the value of P_{CO_2}. Therefore, the observed disagreement by three orders of magnitude has apparently another origin.

One of possible reasons for the discrepancy is connected with specific features in the behaviour of gaseous calcium, strontium and magnesium hydroxides at the decomposition temperature. As seen from Table 8, the saturated vapor pressure of $Ba(OH)_2$ at the mean decomposition temperature of $BaCO_3$ is higher than the partial pressure of the decomposition products, whereas the saturated pressure of $Ca(OH)_2$, $Sr(OH)_2$ and $Mg(OH)_2$ is lower than the partial pressure of the products of $CaCO_3$, $SrCO_3$ and $MgCO_3$ decomposition. In these conditions, the $Ca(OH)_2$, $Sr(OH)_2$ and $Mg(OH)_2$ vapours should condense with formation of solid $Ca(OH)_2$, $Sr(OH)_2$ and $Mg(OH)_2$, with their subsequent decomposition to the oxide and H_2O. Since condensation of $M(OH)_2$ molecules involves liberation of a larger amount of energy, part of this energy could possibly go into excitation of the H_2O molecules released in the decomposition of the solid $M(OH)_2$. This process can be presented schematically as

$$M(OH)_2(g) \rightarrow M(OH)_2(s) \rightarrow MO(s) + H_2O^* \tag{19}$$

When activated, H_2O molecules transfer to one of the numerous excited vibrational–rotational levels of the ground electronic state of H_2O with energies ranging from 19 to 210 kJ mol^{-1} [28]. The molecules activated in this way turn out to be more effective in interaction with a carbonate compared to inactivated H_2O molecules, thus compensating for their insufficiently high concentration.

The above difference between the hydroxides of Ca, Sr and Mg on the one hand, and the Ba hydroxide, on the other, namely the appearance of an additional stage of condensation of the $Ca(OH)_2$, $Sr(OH)_2$ and $Mg(OH)_2$ vapours, provides an explanation for the formation of a metastable modification of the oxide in the decomposition of $CaCO_3$ and $CaMg(CO_3)_2$ [4,5]

Table 7
Correlation between the calculated and experimental data

Decomposition mechanism	$(E_a)_{calc} - (E_a)_{exp}$ (kJ mol^{-1})					$(P_{CO_2})_{calc}/(P_{CO_2})_{exp}$				
	$MgCO_3$	$CaMg(CO_3)_2$	$CaCO_3$	$SrCO_3$	$BaCO_3$	$MgCO_3$	$CaMg(CO_3)_2$	$CaCO_3$	$SrCO_3$	$BaCO_3$
Condensation decomposition (7)	−102	−56	−38	2	31	2×10^{10}	3×10^{6}	2×10^{5}	5×10^{3}	1×10^{4}
Dissociative evaporation (8)	167	198	211	166	105	5×10^{-8}	4×10^{-9}	3×10^{-8}	7×10^{-6}	3
Intermediate hydroxide formation (9)	−1	15	13	4	−16	3×10^{-3}	3×10^{-4}	1×10^{-3}	1×10^{-3}	1

Table 8
Melting point and volatility of hydroxides [25,26]

Hydroxide	T_m (K)	$\bar{T}$ (K)	$P^o_{M(OH)_2}$ (atm)	ΔH_T^{cond} (kJ mol^{-1})
$Mg(OH)_2$	—	779	8×10^{-15}	-373_{298}
$Ca(OH)_2$	1023	974	2×10^{-10}	-367_{1000}
$Sr(OH)_2$	808	983	5×10^{-10}	-331_{1000}
$Ba(OH)_2$	681	1185	2×10^{-5}	-267_{1200}

and for its absence in the decomposition of $BaCO_3$ [3].

In accordance with the mechanism of intermediate hydroxide formation this 'metastable modification' should be simply a crystalline $Ca(OH)_2$ structure or some structure transitional from $Ca(OH)_2$ to CaO. This conclusion was supported by the results obtained by Beruto et al. [29] a few years later after the publication of their first work [4]. This metastable phase turned out to be a really poor crystalline $Ca(OH)_2$. In the authors [29] opinion, it was formed by the reaction of active CaO with water vapor in the atmosphere at room temperature before the X-ray measurements could be performed.

3.4. *Effect of external CO_2, H_2O and H_2 partial pressure*

Based on the mechanism of intermediate hydroxide formation, it becomes possible to interpret the effect of excess CO_2, H_2O and H_2 content in the furnace atmosphere on decomposition rate, activation energy and initial decomposition temperature.

3.4.1. *Effect of CO_2 partial pressure*

The equilibrium constant of reaction (9) can be written

$$K_p(9) = \frac{P_{M(OH)_2} \times P_{CO_2}}{P_{H_2O}} \tag{20}$$

Whence for the hydroxide partial pressure, which determines the carbonate decomposition rate in the presence of excess CO_2, we can write

$$P_{M(OH)_2} = K_p(9)\frac{P_{H_2O}}{P_{CO_2}} \tag{21}$$

Consider first the case of the partial pressure of H_2O remaining constant. Eqs. (2) and (21) show immediately that the decomposition rate J is a hyperbolic function of P_{CO_2}, i.e.

$$J \propto \frac{1}{P_{CO_2}} \tag{22}$$

The correctness of this relation is supported by the results of a comprehensive investigation of $CaCO_3$ decomposition in CO_2 atmosphere by Hyatt et al. [30]. The above authors used 'dry' $N_2 + CO_2$ mixtures, with the CO_2 content varying from 0 to 100%. A constant total flow of gases was maintained at a rate of 90 cm^3 min^{-1}. Large crystals of calcite were cleaved to produce plates about 1 mm in thickness and 10–15 mm in width and length. For each isothermal experimental run, one of the plates was placed in a platinum-screen basket and was suspended from the balance. The experiments were carried out at temperatures of 800, 850, 900 and 950°C. The data presented in [30] provide support for the hyperbolic relation (22).

The experiments of Zemtsova et al. [22] on the decomposition of $SrCO_3$ in vacuum and in atmosphere of CO_2 give a further proof of the validity of Eq. (21) and Eq. (22). Zemtsova et al. [22] found that the mean decomposition temperature for $SrCO_3$ increased from 983 K in vacuum up to 1583 K in 1 atm of CO_2. If we calculate the value of $P_{Sr(OH)_2}$ at 1583 K using Eq. (21) and the parameters from Table 6, we will obtain the same 2×10^{-11} atm, as that in vacuum at 983 K.

One of recent studies in this field was described by Criado et al. [31]. Non-isothermal experiments were performed at a heating rate of 12 K min^{-1} and CO_2 pressure of 1.3, 2.7, 12 and 20 kPa. Analytical grade $CaCO_3$ and 99.9% CO_2 were used. Sample mass was about 25 mg. The results of these experiments presented in Table 9 clearly support the constancy of the product $P_{CO_2}k$ within fifteen-fold range of variation of P_{CO_2}.

Therefore, if P_{H_2O} and the excess partial pressure P_{CO_2} in the reaction system remain constant (isobaric mode), the value of $P_{M(OH)_2}$ is determined, by the equation

$$P_{M(OH)_2} = \frac{P_{H_2O}}{P_{CO_2}} \exp\frac{\Delta S^\circ_T}{R} \exp\left[-\frac{\Delta H^\circ_T}{RT}\right] \tag{23}$$

Thus the activation energy is determined by the equation

Table 9
The kinetic parameters of $CaCO_3$ decomposition at different pressures of CO_2 [31]

P_{CO_2} (kPa)	E_a (kJ mol^{-1})	ln (A/min^{-1})	k (min^{-1}) at 1000 K	$P_{CO_2}k$ (kPa min^{-1})
1.33	187	21.2	0.275	0.37
2.67	196	21.6	0.139	0.37
12.0	188	18.8	0.0221	0.27
20.0	195	19.7	0.0234	0.47

$$E_a = \Delta H^\circ_T(9) \tag{24}$$

rather than by Eq. (18) which is valid for the equimolar mode of decomposition. Taking into account the temperature correction $-0.5\ RT$, the value of E_a in the case of $CaCO_3$ is 439 kJ mol^{-1}. As already mentioned, variation of P_{CO_2} should inversely proportionately affect the quantities J and k, while not influencing in any way the value of E_a. The increase of E_a with increasing P_{CO_2}, a phenomenon pointed repeatedly in the literature, has another origin, as this will be shown below.

3.4.2. *Effect of H_2O partial pressure in the absence of CO_2*

We are turning now to a discussion of the effect of water vapor on the decomposition of carbonates. Unfortunately, of the numerous publications dealing with carbonate decomposition, we have been able to locate only one short communication by Hrabe and Svetic [32], which presents the results of an investigation into the influence of water vapor on the decomposition of magnesite. Of the data quoted in Ref. [32], the most reliable appear to be the half-decomposition of 200 mg of $MgCO_3$ at the heating rate of 2 K min^{-1} in air, water vapor, and mixtures of water vapor with CO_2 containing 25, 50, 75 and 100% CO_2. The measured $T_{\alpha=0.5}$ temperatures were found to be, respectively, 857.5, 779, 851, 871, 893 and 935.5 K. The most significant observation was that replacing air with H_2O vapor reduces substantially the decomposition temperature, which is consistent with the mechanism involving intermediate hydroxide formation. Assuming the activation energy of $MgCO_3$ decomposition to be 192 kJ mol (see Table 1), we readily calculate that the rate constants corresponding to the temperatures of 857.5 and 779 K differ by a factor

15.1. In the equimolar decomposition regime, where the fluxes of the decomposition products, CO_2 and $Mg(OH)_2$ are equal, the decomposition rate of $MgCO_3$, as is evident from Eq. (14), is proportional to $(P_{H_2O})^{1/2}$. Therefore, reducing the temperature from 857.5 to 779 K should have brought about an increase of the partial water vapor pressure by $(15.5)^2$=228 times. Regrettably, it is not clear from Ref. [32] what was the value of P_{H_2O} when the 'air' and 'water vapor' ambients were used. It thus appears impossible to make a quantitative comparison of our calculation with the experiment. Nevertheless, assuming the water vapor content in the gas flow from a tank with conventional, undried compressed air to be at a level of 10^{-4} atm and taking the partial pressure P_{H_2O} for the 'water vapor' ambient to be equal to the room-temperature saturated vapor pressure, i.e. 2×10^{-2} atm, we come to a result close to the calculated value.

3.5. *Effect of H_2O partial pressure in the presence of CO_2*

Water vapor in the presence of excess of CO_2 in a reaction system should affect the decomposition rate still stronger than it would in its absence. This is clearly seen from a comparison of Eqs. (21) and (14). We also see from Eq. (21) that simultaneous increase or decrease of the excess content of CO_2 and H_2O should not produce any effect on the decomposition rate of carbonates. Finally, Eq. (21) provides an explanation for the anomalously high values of E_a observed in non-isothermal decomposition of carbonates in an atmosphere containing excess CO_2. We associate them with the continuous growth of the partial vapor pressure of H_2O in the reaction system resulting from the water evolving out of the decomposing carbonate which contains a small amount of the hydroxide of the same metal. For instance, samples of $SrCO_3$ (supplied by Johnson Matthey) studied by Judd and Pope [33] contained up to 5% $Sr(OH)_2$ or about 0.7% H_2O. Samples of $SrCO_3$ prepared under laboratory conditions contained about 0.4% H_2O [22].

Taking this factor into account, consider now the results of the study reported by Caldwell et al. [7], where values of E_a as high as 2142 kJ mol^{-1} were obtained in non-isothermal decomposition of $CaCO_3$ in CO_2. The measurements were carried out on 4 mg samples. The flow rate of CO_2 was 40 cm^3 min^{-1} and the heating rate was 5 K min^{-1}. The temperature interval within which the sample decomposed with α varying from 0.1 to 0.9 was not more than 30 K, for example, from 1100 to 1130 K. Let us assume that the H_2O content in the sample was 0.2%. To this content in a sample 4 mg in mass corresponds to an H_2O vapor volume of about 1×10^{-2}cm^3. If H_2O vapours emerged uniformly into the CO_2 flow for 6 min this would have raised the partial pressure up to $1\times10^{-2}/(40\times6)\cong4\times10^{-5}$ atm. But, if we recall the continuous rise of the decomposition rate with temperature, the content of H_2O by the end of the decomposition process should increase by at least a factor of two, i.e. ca 8×10^{-5} atm. The furnace was purged by 'dry' CO_2 (see Ref. [34]), which most probably contained not more than 10^{-4}% H_2O, i.e. about 10^{-6} atm. Therefore, the H_2O partial pressure in the flow could rise from 10^{-6} to 8×10^{-5} atm, i.e. 80 times, within the measurement interval of 1100–1130 K. To this increase of P_{H_2O} should correspond the same additional increase in the decomposition rate. Thus the increase of the activation energy, ΔE_a, associated with the increase of P_{H_2O}, should be

$$\Delta E_a = \frac{R\ln(8\times10^{-5}/10^{-6})}{1100^{-1}-1130^{-1}} = 1510\,\mathrm{kJ\,mol^{-1}} \tag{25}$$

If we add to this true value E_a=439 kJ mol^{-1} (see Section 3.4.1), the total value $E_a+\Delta E_a$ becomes 1950 kJ mol^{-1}, which is in good agreement with the measurements [7]. In view of the fairly reasonable choice of the H_2O content in 'dry' CO_2 and of the H_2O in the $CaCO_3$ sample, this agreement may be considered as an argument for the correctness of the proposed explanation and of the carbonate decomposition mechanism developed here on the whole.

3.6. *Effect of H_2 partial pressure*

By analogy with reaction (9), the decomposition of alkaline-earth carbonates in a H_2 atmosphere should proceed in accordance with the reaction

$$MCO_3(s) + H_2(g) \rightarrow CO(g) + M(OH)_2(g) \tag{26}$$

As can be seen from Table 10, the decomposition rates for reaction (26) under condition $P_{H_2} = 10^{-7}$ atm are

Table 10
Calculated kinetic parameters for the decomposition of carbonates in accordance with reaction (26)

Carbonate	$\bar{T}$ (K)	ΔH°_{900} (kJ mol^{-1})	ΔS°_{900} (J mol^{-1} K^{-1})	E_a (kJ mol^{-1})	P_{CO} (atm)	
					$P_{H_2} = 10^{-7}$ atm	$P_{H_2} = 10^{-3}$ atm
$MgCO_3$	779	424.6	260.4	209	1×10^{-11}	1×10^{-9}
$CaMg(CO_3)_2$	862	462.8	256.7	228	2×10^{-11}	2×10^{-9}
$CaCO_3$	974	479.0	252.9	235	2×10^{-10}	2×10^{-8}
$SrCO_3$	983	506.6	267.5	249	1×10^{-10}	1×10^{-8}
$BaCO_3$	1185	466.0	254.6	228	8×10^{-8}	8×10^{-6}

in rough agreement with those for reaction (9) (see Table 6), and a rise of P_{H_2} up to 10^{-3} atm should result in a hundred-fold increase of the decomposition rate. The further rise of P_{H_2} should not significantly change the decomposition rate since an increase of P_{CO} in proportion to $(P_{H_2})^{1/2}$ should be compensated with a rise of diffusion limitation for a CO flow in H_2. It is easy to calculate that a hundred-fold increase in the decomposition rate corresponds to the reduction of the decomposition temperature by 150–160 K.

This conclusion is in complete agreement with experiments. As it was found by Reller et al. [35,36], the reaction temperatures for the thermal decomposition of magnesite, dolomite and calcite in a hydrogen atmosphere are lowered by at least 150 K compared with the analogous degradation in inert or oxidizing atmospheres. Besides, at mass-spectrometric measurements of the evolved gases, the authors [35] observed the evolution of carbon monoxide as the main product of the carbonate decomposition in H_2. Therefore, the enhancement of the carbonate decomposition rate in a hydrogen atmosphere is further proof of the intermediate hydroxide formation mechanism.

4. Conclusions

As analysis of available literature data on the kinetics of the thermal decomposition of alkaline-earth carbonates and a comparison of the most reliable of them with the kinetic parameters calculated for three conceivable paths of the process have shown the mechanism involving intermediate hydroxide formation to be the most probable one. It is based on the interaction of the carbonate with water vapor or hydrogen and subsequent decomposition of the gaseous Ba hydroxide or of the condensing Mg, Ca and Sr hydroxides to the oxides and water. Water acts in this process as a catalyst. This mechanism has permitted one to explain some unusual features in the decomposition of the carbonates of alkaline-earth metals.

The author would like to hope that this work will stimulate researchers to a more thorough investigation of the aspects of the mechanism which up to now have been remained unexplored, in particular, of the role of water and hydrogen. It is possible that by choosing the optimum conditions (continuous pumping in the presence of up to 10^{-3}–10^{-2} atm water vapor or hydrogen) the decomposition temperature of carbonates could be reduced by 100–200 K compared to the presently accepted regime of their decomposition in an inert gas atmosphere or in air. In any case, such studies could either confirm or disprove the decomposition mechanism proposed in this work.

Acknowledgements

This work was supported in part by BSW Perkin-Elmer.

References

[1] K.H. Stern and E.L. Weise, High Temperature Properties and Decomposition of Inorganic Salts. Part 2. Carbonates, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.(U.S.), 30 Nov. 1969.
[2] M.E. Brown, D. Dollimore and A.K. Galwey, Reactions in the Solid State, Elsevier, Amsterdam, 1980.
[3] T.K. Basu, A. Searcy, J. Chem. Soc. Faraday Trans. I, 72 (1976) 1889.
[4] D. Beruto, A. Searcy, J. Chem. Soc. Faraday Trans. I, 70 (1974) 2145.
[5] E.K. Powell, A. Searcy, J. Amer. Ceram. Soc., 61 (1978) 216.
[6] J. Zsako, H.E. Arz, J. Therm. Anal., 6 (1974) 651.

[7] K.M. Caldwell, P.K. Gallagher, D.W. Johnson Jr., Thermochim. Acta, 18 (1977) 15.
[8] B.V. L'vov, Izv. Vuzov. Chern. Metallurgiya, No. 1 (1986) 4.
[9] B.V. L'vov and A.V. Ilyukhin, Izv. Vuzov. Chern. Metallurgiya, No. 9 (1988) 10.
[10] B.V. L'vov, Zh. Anal. Khim., 45 (1990) 2144.
[11] B.V. L'vov, Mikrochim. Acta (Wien)II (1991) 299.
[12] B.V. L'vov, A.V. Novichikhin, Spectrochim. Acta Part B, 50 (1995) 1427.
[13] B.V. L'vov, A.V. Novichikhin, Spectrochim. Acta Part B, 50 (1995) 1459.
[14] B.V. L'vov, Thermochim. Acta, 291 (1997) 179.
[15] B.V. L'vov, A.V. Novichikhin, Thermochim. Acta, 290 (1997) 239.
[16] B.V. L'vov, Atomic Absorption Spectral Analysis, Nauka, Moscow, 1966, p. 251 (in Russian).
[17] B.V. L'vov, P.A. Bayunov, G.N. Ryabchuk, Spectrochim. Acta Part B, 36 (1981) 397.
[18] B.V. L'vov, G.N. Ryabchuk, Zh. Anal. Khim., 36 (1981) 2085.
[19] B.V. L'vov, G.H.A. Fernandes, Zh. Anal. Khim., 39 (1984) 221.
[20] B.V. L'vov, G.N. Ryabchuk, G.H.A. Fernandes, Zh. Anal. Khim., 39 (1984) 1206.
[21] B.V. L'vov, Spectrochim. Acta Part B, 52 (1997) 1.
[22] Z.N. Zemtsova, M.M. Pavlychenko and E.A. Prodan, in: M.M. Pavlychenko and E.A. Prodan (Ed.), Heterogeneous Chemical Reactions, Nauka i Tekhnika, Minsk, Russia, 1970 (in Russian).
[23] Z.N. Zemtsova, M.M. Pavlychenko, E.A. Prodan, Izv. AN BSSR, Ser, Khim Nauk, 6 (1970) 16.
[24] M.M. Pavlychenko, E.A. Prodan, F.G. Kramarenko, L.E. Shiplevskaya and L.N. Zhukovskay, in: E.A. Prodan (Ed.), Heterogeneous Chemical Reacions, Nauka i Tekhnika, Minsk, Russia, 1979, p. 53 (in Russian).
[25] V.P. Glushko (Ed.), Thermodynamic Properties of Individual Substances, Handbook in 4 volumes, Nauka, Moscow, 1978–1982 (in Russian).
[26] V.P. Glushko (Ed.), Thermodynamic Constants of Substances. Handbook in 10 volumes, Akad. Nauk SSSR, Moscow, 1962–1982 (in Russian).
[27] L.J. Prell, D.L. Styris, D.A. Redfield, J. Anal. At. Spectrom., 6 (1991) 25.
[28] M.A. El'yashevitch, Atomic and Molecular Spectroscopy, Nauka, Moscow, 1962, p. 699 (in Russian).
[29] D. Beruto, L. Barko, A.W. Searcy, G. Spinolo, J. Amer. Ceram. Soc., 63 (1980) 439.
[30] E.P. Hyatt, I.B. Cutler, M.E. Wardsworth, J. Amer. Ceram. Soc., 41 (1958) 70.
[31] J.M. Criado, M. Gonzalez, J. Malek, A. Ortega, Thermochim. Acta, 254 (1995) 121.
[32] Z. Hrabe, S. Svetik, Thermochim. Acta, 92 (1985) 653.
[33] M.D. Judd, M.I. Pope, J. Therm. Anal., 4 (1972) 31.
[34] P.K. Gallagher, D.W. Johnson Jr., Thermochim. Acta, 17 (1976) 255.
[35] A. Reller, C. Padeste, P. Hug, Nature, 329 (1987) 527.
[36] A. Reller, Thermochim. Acta, 137 (1988) 11.