

Review

Mechanism and kinetics of thermal decomposition of carbonates

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Abstract

A physical approach to the interpretation of the mechanisms and kinetics of thermal decomposition of solids has been applied to the investigation of decomposition mechanisms of Ag, Cd, Zn, Mg, CaMg, Ca, Sr and Ba carbonates. The method consists in comparing experimental literature data on the kinetic parameters with their theoretical values calculated on the basis of the physical approach. Two parameters were used: the E parameter and the initial temperature of decomposition, T_{in} , defined as the temperature of decomposition which corresponds to the fixed partial pressure, P_{in} , of CO_2 evolved. The results of examination of the available data supported the general mechanism of decomposition which includes as a primary stage the congruent dissociative evaporation of reactants. For all the carbonates, except of $BaCO_3$, the transfer to the reactant one-half of the energy released in the course of the condensation of low-volatility product has been taken into account in the calculations. The effect of self-cooling on the results of experimental determination of both parameters has been examined, and several important conclusions has been deduced. In particular, in the decomposition of $CaCO_3$ in the presence of CO_2 (10^{-6} – 10^{-4} bar), the self-cooling effect is responsible for the lack of expected hyperbolic dependence of decomposition rate on CO_2 pressure and the appearance of the Topley–Smith effect. Several quantitative criteria of the validity of measured E values has been proposed. On this basis, the values of E parameters reported in the literature were critically analysed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The mechanism and kinetics of thermal decomposition of carbonates (in particular, calcium carbonate) have been dealt with a large number of studies summed up partially in a review [1] and monographs [2,3]. 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. Anomalous scatter among the kinetic parameters of the Arrhenius equation (E and A) available in the literature for decomposition of $CaCO_3$, particularly measured by non-isothermal methods in the presence of CO_2 [4,5].
2. A 10^4 – 10^5 -fold difference 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 vaporization coefficients, α_v , for these compounds in vacuum [6,7]. This is in contradiction with a widespread statement of their partly reversible decompositions.

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3. Discrepancy in the dependence of decomposition rates of CaCO_3 on CO_2 background pressures observed by different authors. In contrast to the observation of hyperbolic rate law ($\propto 1/P_{\text{CO}_2}$) in [8–10], Darroudi and Searcy [11] observed close to linear decrease of the decomposition rate with the background pressure of CO_2 .

The objective of this work is in presenting an interpretation for the above and related aspects by applying a physical approach to explanation of the thermal decomposition mechanism, which is based on a scheme involving dissociative evaporation of the reactant with simultaneous condensation of the low-volatile product. This approach advanced by Hertz and Langmuir and developed by the author has been successfully employed earlier in the interpretation of the mechanism and kinetics of thermal decomposition of metal oxides [12–14], nitrates [15–17], azides [18], $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [19], $\text{Mg}(\text{OH})_2$ [20], GaN [21], oxalates [22] and of a number of other inorganic compounds [23].

Our earlier attempt [24] to interpret the decomposition mechanism of alkaline-earth carbonates as a result of the carbonate interaction with residual water vapor in the reactor was not successful. The good agreement between calculated and experimental values of the E parameter was accompanied by 10^3 – 10^4 differences of the calculated rates of decompositions from experimental data. Two important factors have not been taken into account in that work [24]: the effect of self-cooling on measured values of the E parameter and the partial transfer of the energy released in the condensation of low-volatility product (MO) to the reactant.

2. Theoretical model

The scheme employed in the theoretical calculation of the main kinetic parameters of the decomposition process (the flux of the gaseous product J , the rate constant k , the product partial pressure P and the parameters of the Arrhenius equation, E and A) has been described in a number of our recent publications [19–22], especially, in a review [23]. Therefore, we are going to present below only some final relations necessary for the calculations in this work.

2.1. Decomposition in vacuum

In the case of a compound S decomposed into gaseous products A and B , i.e.



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

$$J = \frac{\gamma N_A P_A}{(2\pi M_A RT)^{1/2}} \quad (2)$$

where N_A is the Avogadro number and M_A the molar mass of product A . Here $\gamma = 101\,325 \text{ Pa atm}^{-1}$ is the conversion factor from atmospheres to pascals. This relationship derived as shown here by Langmuir [25] is usually called the Hertz–Langmuir equation.

In the case of evaporation of spherical particles, the rate constant is as follows [24]:

$$k = \frac{JM_r}{N_A \rho r_0} \quad (3)$$

where ρ and M_r are the density and molar mass of the reactant.

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 [26] as

$$P_A^e = a \left(\frac{K_p}{F} \right)^{1/v} \left(\frac{M_A}{M_B} \right)^{b/2v} \\ = \frac{a}{F^{1/v}} \left(\frac{M_A}{M_B} \right)^{b/2v} \exp \frac{\Delta S_T^\circ}{vR} \exp \left(-\frac{\Delta_r H_T^\circ}{vRT} \right) \quad (4)$$

where

$$F \equiv a^a \times b^b \quad (5)$$

$$v = a + b \quad (6)$$

and

$$K_p = P_A^a \times P_B^b \quad (7)$$

Here $\Delta_r H_T^0$ and ΔS_T^0 are, respectively, the changes of the enthalpy and entropy in reaction (1).

If the partial pressure P'_B of one of the gaseous components (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

$$P_A^i = \frac{K_P^{1/a}}{(P'_B)^{b/a}} = \frac{1}{(P'_B)^{b/a}} \exp \frac{\Delta S_T^0}{aR} \exp \left(-\frac{\Delta_r H_T^0}{aRT} \right) \quad (8)$$

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, $\tau a \Delta_c H_T^0$ (A), where the coefficient τ corresponds to the fraction of the condensation energy transferred to the reactant. Thus, we can write

$$\Delta_r H_T^0 = a \Delta_f H_T^0(A) + b \Delta_f H_T^0(B) - \Delta_r H_T^0(S) + \tau a \Delta_c H_T^0(A) \quad (9)$$

The most plausible of all conceivable mechanisms for the energy transfer appears to be thermal accommodation [27] or, in other words, direct transfer of the energy at the reaction interface by collisions of the low-volatility molecules with the reactant and the product surface. For equal temperatures of the solid phases, 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.

2.3. Theoretical calculation of Arrhenius parameters

Eqs. (2)–(9) can be used for the calculation of the main parameters determining the kinetics of sublimation/decomposition processes: the evaporation rate J , the initial temperature T_{in} , and two traditional Arrhenius parameters, entering the Arrhenius equation:

$$k = A \exp \left(-\frac{E}{RT} \right) \quad (10)$$

As can be seen from Eqs. (4) and (8), the E parameter for reaction (1) should be different for the

equimolar and isobaric modes of decomposition, i.e.,

$$E^e = \frac{\Delta_r H_T^0}{v} = \frac{\Delta_r H_T^0}{a+b} \quad (11)$$

for the equimolar mode and

$$E^i = \frac{\Delta_r H_T^0}{v-b} = \frac{\Delta_r H_T^0}{a} \quad (12)$$

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.

By combining Eqs. (4), (8) and (10) with Eqs. (2) and (3), it is easy to obtain the relationships for the calculation of the A parameter. For example, in the case of decomposition of spherical particles in vacuum (the equimolar mode) in accordance with process (1), by combination of Eqs. (2)–(4) and (10), we obtain

$$A^e = \frac{\gamma M_r}{\rho r_0 (2\pi M_A RT)^{1/2} F^{1/v}} \frac{a}{\left(\frac{M_A}{M_B} \right)^{b/2v}} \exp \frac{\Delta S_T^0}{vR} \\ = \frac{\gamma M_r}{\rho r_0 (2\pi \bar{M} RT)^{1/2} F^{1/v}} \exp \frac{\Delta S_T^0}{vR} \quad (13)$$

where \bar{M} is the geometrical mean between M_A and M_B , i.e., $\bar{M} = (M_A \times M_B)^{1/2}$. In the case of decomposition of spherical particles in the presence of excess of the gaseous component B (the isobaric mode), by combination of Eqs. (2), (3), (8) and (10), we obtain

$$A^i = \frac{\gamma M_r}{\rho r_0 (2\pi M_A RT)^{1/2}} \frac{1}{(P'_B)^{b/a}} \exp \frac{\Delta S_T^0}{aR} \quad (14)$$

As can be seen from theoretical modelling of the evaporation processes above, by combination of the different equations it is possible to obtain the final formulae for the calculation of the A parameter under different experimental conditions. These equations take into account many parameters describing the properties of solid reactant and primary products (thermodynamic functions, molar mass, density), the sample distribution (a monolayer or spherical particles of known radius), experimental conditions (temperature), and the evaporation modes (equimolar or isobaric) including, in the last case, the value of the excess pressure of the gaseous product. As a result, the A values may vary within very wide limits. For example, for a simple reaction of the type $S(s) \rightarrow A(g)$

+ $bB(g)$, the ratio of the A parameters for the isobaric and equimolar modes of evaporation equals

$$\frac{A^i}{A^e} \cong \frac{1}{(P'_B)^b} \exp \frac{b \Delta S_T^0}{(b+1)R} \quad (15)$$

Substituting into Eq. (15) rather typical values for these parameters: $\Delta S_T^0/(b+1) = 150 \text{ J mol}^{-1} \text{ K}^{-1}$ (see below) and $P'_B = 10^{-5} \text{ bar}$, we obtain $A^i/A^e \cong 3 \times 10^6$ for $b = 0.5$, $A^i/A^e \cong 7 \times 10^{12}$ for $b = 1$ and $A^i/A^e \cong 2 \times 10^{19}$ for $b = 1.5$. Therefore, the isobaric mode of decomposition, compared to the equimolar mode, results in much higher values of the A parameter.

As shown above, this approach allows calculation of both parameters of the Arrhenius equation (E and A). This means that the absolute rates of the dissociative evaporation can be theoretically calculated. Attempts to solve this problem in the framework of the traditional (chemical) approach using for this purpose the ideas of transition-state theory (with another name ‘theory of absolute reaction rates’) were unsuccessful. These attempts (e.g. [28]) have not progressed beyond very approximate estimations of the pre-exponential or frequency factor (in the range 10^{14} – 10^{16} s^{-1}) though, actually, the A values are far beyond these limits and in many cases becomes larger than 10^{20} s^{-1} or lower than 10^{10} s^{-1} [29]. The value of the activation energy in these calculations was usually kept in the shadows.

2.4. Theoretical calculation of initial temperature of decomposition in vacuum

Taking logarithms and solving Eq. (4) for the temperature contained in the enthalpy factor, we obtain the following relationship for the calculation of the initial temperature of decomposition:

$$T_{\text{in}} = \frac{\Delta_r H_T^0}{\Delta S_T^0 + vR[\ln q - \ln F/v + (b/2v)\ln(M_A/M_B) - \ln P_{\text{in}}]} \quad (16)$$

where P_{in} is the partial pressure of product A corresponding to the initial temperature.

Neglecting the first three insignificant items in the square brackets of Eq. (16) and taking into account Eq. (11), we come to the important relationship

$$\frac{T_{\text{in}}}{E} \cong \frac{1}{\Delta S_T^0/v - R \ln P_{\text{in}}} \quad (17)$$

Taking into account that for sublimation or dissociative evaporation of one mole of solid (metal or compound) at the temperature of the initial decomposition, the average value of $\Delta S_T^0/v = 150 \pm 30 \text{ J mol}^{-1} \text{ K}^{-1}$ [12–16,18–22,26] and that the initial temperature corresponds approximately to $P_{\text{in}} = 10^{-7} \text{ bar}$ [14], we obtain $T_{\text{in}}/E \cong 3.5 \pm 0.4 \text{ K mol kJ}^{-1}$. The proportional dependence of the initial/appearance temperature on the E parameter was pointed out on purely empirical grounds in electrothermal atomic absorption spectrometry in the 1970s [30–32]. However, only in the framework of the physical approach has it received a rigorous theoretical explanation.

The relationship (17) can be considered as a generalization of the well-known Trouton’s rule relating the boiling temperature (T_b) and the molar enthalpy of vaporization (ΔH_T^0) of liquids (see, e.g. [33]). At the boiling point when $P = 1 \text{ bar}$, the average value of $\Delta S_T^0/v$ (for a majority of liquids) is about $86 \pm 20 \text{ J mol}^{-1} \text{ K}^{-1}$ [33] and, as a result, $T_b/\Delta H_T^0$ ranges from 9.4 to $15.2 \text{ K mol kJ}^{-1}$.

3. Results and discussion

3.1. Preliminary comments

The method to be employed below consists in comparing experimental data on the kinetic parameters with their theoretical values calculated on the basis of the physical approach outlined above. Two parameters will be used: the E parameter and the initial temperature of decomposition, T_{in} , defined as the temperature of decomposition which corresponds to the fixed partial pressure, P_{in} , of CO_2 evolved. These parameters completely describe the kinetics of steady-state decomposition (in equimolar mode) at any temperature. The choice of metal carbonates for analysis in this study was defined by the availability in the literature of proper experimental data on the decomposition kinetics and reliable thermodynamic functions for reactants and products for the corresponding theoretical calculations. On this basis, carbonates of Ag, Cd, Zn, Mg, CaMg, Ca, Sr and Ba have been chosen. Table 1 presents the results of a correlation between experimental [6,7,11,34–48] and theoretical data. We will give below some comments on the origin of these data.

Table 1
Kinetic parameters for thermal decomposition of carbonates

Carbonate	T_{in} (K)		α_v		E^c (kJ mol ⁻¹)		E^i (kJ mol ⁻¹)		P'_{CO_2} (Torr) ^a
	Theory ^b	Experiment	Corrected	Theory	Experiment	Theory	Experiment	Theory	
Ag ₂ CO ₃	371	420 [34]	387	4×10^{-5}		102	96 [34]	143	
CdCO ₃	442	513 [35]	469	2×10^{-3}		135	151 [35]	270	272 [35]
									268 [36]
ZnCO ₃	497	523 [37]	508	4×10^{-8}		151	159 [37], 161 [38]	302	251 [39]
									280 [39]
									100
MgCO ₃	689	714 [40]	705	8×10^{-9}		204	192 [40], 150 [41]	408	450 [42]
CaMg(CO ₃) ₂	809	824 [6]	820	5×10^{-6}	1×10^{-4} [6]	234	195 [6], 221 [43]	468	
CaCO ₃	895	934 [11]	928	5×10^{-5}	2×10^{-5}	253	220 [11], 209 [11]	506	
					[11,44]		205 [44], 222 [45]		
SrCO ₃	908	888 [46]	887	5×10^{-3}		261	290 [46], 222 [47]	522	
BaCO ₃	1205 ^c	1215 [47]	1214	2×10^{-4}	2×10^{-4} [7]	319 ^c	283 [47], 264 [48]	639 ^c	643 [48]
							226 [7]		3.5

^a 1 Torr = 133.322 Pa.

^b At $P_{CO_2} = 3 \times 10^{-7}$ bar.

^c At $\tau = 0$.

3.2. 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 was given to a series of studies under isothermal conditions performed in the mid-1970s by Searcy and colleagues, devoted to the decomposition of CaCO₃ [6,11], CaMg(CO₃)₂ [6] and BaCO₃ [7], as well as to the publications of Pavlyuchenko [37], who studied decomposition of CdCO₃ [35], ZnCO₃, MgCO₃ [40] and SrCO₃ [46]. In case of Ag₂CO₃, we used the only available data from a publication by Spencer and Topley in 1929 [34]. Some data were taken from the works by Hüttig et al. [38] (ZnCO₃), Britton et al. (MgCO₃ [41] and CaMg(CO₃)₂ [43]), Judd and Pope [47] (SrCO₃ and BaCO₃) and from a recent publication by Maciejewski [45] (CaCO₃).

In all these works (except [45]), measurements were carried out under continuous pumping of the furnace to 10^{-7} – 10^{-8} bar (the equimolar mode). For CdCO₃, ZnCO₃, MgCO₃ and BaCO₃, the experimental values of E parameter in the presence of CO₂ (the isobaric mode) were also included. Samples of natural crystals of known size were used in the experiments of Searcy and his colleagues and powders, in the experiments of all other workers. The mass change were measured continuously with a quartz microbalance [34–48] or

by the torsion–Langmuir technique [6,7]. The manometric technique with an ion-gauge was used only in [11]. When runs to be made in CO₂, the diffusion pump was turned off and CO₂ was held at a steady-state level by adjusting a leak value.

3.3. Theoretical kinetic data

Theoretical values of E and T_{in} parameters in Table 1 were calculated with the use of thermodynamic functions tabulated in [49,50]. Table 2 presents the values of enthalpy and entropy changes for the deduced decomposition reactions. Eqs. (11) and (12) were used for the calculation of E^c and E^i parameters and Eq. (17) was used for the calculation of T_{in} parameter. In the calculations of the enthalpy of decomposition reactions for all the carbonates except of BaCO₃, we took into account the transfer of one-half of the condensation energy to the reactant ($\tau = 0.5$). For BaCO₃, the best correlation between experiment and theory corresponds to the condition $\tau = 0$. This means that, for reasons unknown to us, any energy transfer to the reactant in the process of condensation of low-volatility molecules of BaO is absent. The values of $\Delta S_T^0/v$ (see the last column in Table 2) are in agreement with the regularity $\Delta S_T^0/v = 150 \pm 30 \text{ J mol}^{-1} \text{ K}^{-1}$ (Section 2.4) valid for different classes of solids.

In the calculations of the initial temperatures of decomposition, we assumed that this temperature

Table 2

Enthalpy and entropy changes for the deduced decomposition reactions of carbonates [49,50]

Reaction ^a	ν	τ	ΔH_T^0 (kJ mol ⁻¹)	ΔS_T^0 (J mol ⁻¹ K ⁻¹)	$\Delta S_T^0/\nu$ (J mol ⁻¹ K ⁻¹)
Ag ₂ CO ₃ → 2Ag(g) ↓ + 0.5O ₂ + CO ₂	3.5	0.5	358.0 ₂₉₈	494.6 ₂₉₈	141.3
CdCO ₃ → CdO(g) ↓ + CO ₂	2	0.5	270.1 ₂₉₈	356.2 ₂₉₈	178.1
ZnCO ₃ → ZnO(g) ↓ + CO ₂	2	0.5	302.1 ₂₉₈	355.9 ₂₉₈	178.0
MgCO ₃ → MgO(g) ↓ + CO ₂	2	0.5	408.5 ₉₀₀	343.1 ₉₀₀	171.6
0.5CaMg(CO ₃) ₂ → 0.5CaO(g) ↓ + 0.5MgO(g) ↓ + CO ₂	2	0.5	468.2 ₉₀₀	328.9 ₉₀₀	164.5
CaCO ₃ → CaO(g) ↓ + CO ₂	2	0.5	505.9 ₉₀₀	314.6 ₉₀₀	157.3
SrCO ₃ → SrO(g) ↓ + CO ₂	2	0.5	522.2 ₉₀₀	322.1 ₉₀₀	161.1
BaCO ₃ → BaO(g) + CO ₂	2	0	638.7 ₁₂₀₀	275.2 ₁₂₀₀	137.6

^a An arrow (↓) implies taking into account the condensation energy transfer to the reactant.

corresponds to the initial pressure of evolved CO₂, $P_{in} = 3 \times 10^{-7}$ bar. In our estimates, this magnitude is close within a factor of 3 to the true values of P_{in} in different works. Because of different techniques, instrumentation and experimental conditions used in different studies, this parameter is subject to variation in the range from 10^{-7} to 10^{-6} bar.

3.4. Correlation between experimental and theoretical values of T_{in}

Most studies of the decompositions of powders and single crystals in thermal analysis tacitly assume that the temperature of the sample is equal to that of the furnace, and that the self-cooling due to some heat being expended in the endothermic decomposition can be neglected. However, as early as 1931, Smith and Topley [51] showed that the temperature of a single crystal in vacuum was lower than that in the furnace by 4–8 K. It is rather obvious that, for powders, the self-cooling effect should be much greater.

L'vov et al. [20,52] 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. Simulation of the temperature distribution, inside a powder sample, can be reduced to modelling 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 cen-

tral, 0th or 1st layer, to the n th outermost layer. All the calculations were performed with the laboratory-developed computer program described in [52].

As an illustration of the value of self-cooling effect for the decomposition of single crystals of carbonates in vacuum (10^{-7} bar), Fig. 1 presents the results of calculations of the temperature of the sample (reactant), T_s , related to the temperature of the furnace, T_f . It can be seen that the T_s/T_f ratio depends not only on the absolute rate of decomposition (or the partial pressure of evolved CO₂). The effect is increased with reducing of the decomposition temperature. For example, the P_{CO_2} values, corresponding to $T_s/T_f = 0.95$, equal to about 3×10^{-4} bar for BaCO₃, 5×10^{-5} bar for CaCO₃ and 5×10^{-6} bar for CdCO₃. It is easy to understand. Heating of the sample via the radiation from the furnace (in accord with the Stefan–Boltzman Law), is dramatically reduced with a temperature decrease.

The corrected T_{in} values given in Table 1 were calculated in the same manner. They correspond to the true temperatures of single crystals of carbonate in the process of their decomposition in furnaces at the initial temperatures of experiments. It should be mentioned that the emittance parameter ε in the calculations was assumed to be equal to its maximum value ($\varepsilon = 1$) and therefore the corrected values of temperature correspond to their maximum allowable values. As can be expected, the effect of self-cooling is more pronounced at low temperatures. The T_s/T_f ratio is about 0.92 for Ag and Cd carbonates, 0.95 for ZnCO₃ and higher than 0.994 for CaMg, Ca, Sr and Ba carbonates.

The correlation between theoretical and experimental (corrected) values of the initial decomposition

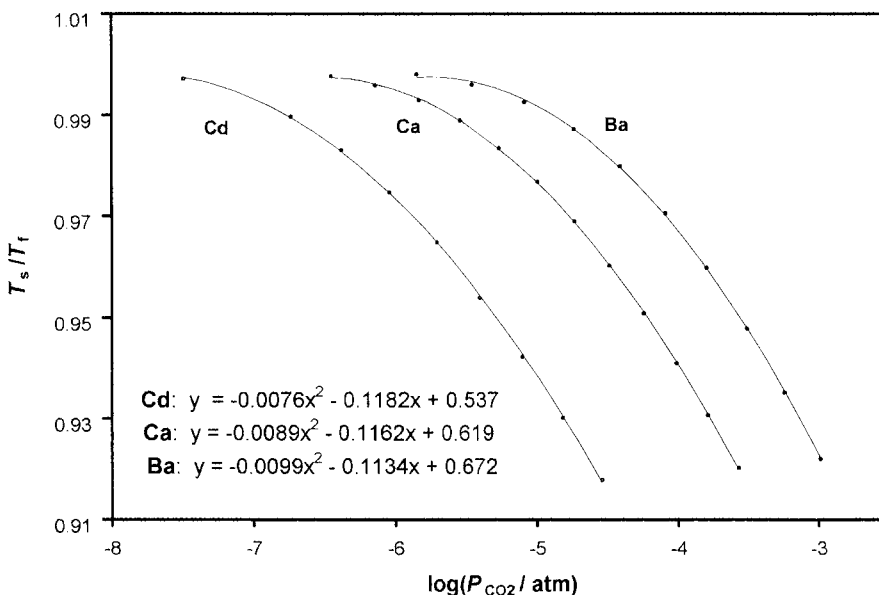


Fig. 1. The self-cooling effect for the decomposition of CdCO_3 , CaCO_3 and BaCO_3 in vacuum.

temperatures is presented in Fig. 2. The agreement is excellent though, we should admit, is rather accidental, if we take into account the discrepancies between initial temperatures listed for the same carbonate (e.g.

CaCO_3) by different authors. As can be seen from the correlation equation (see Fig. 2), a mean systematic overestimation of experimental (corrected) values over theoretical values is about 25 K.

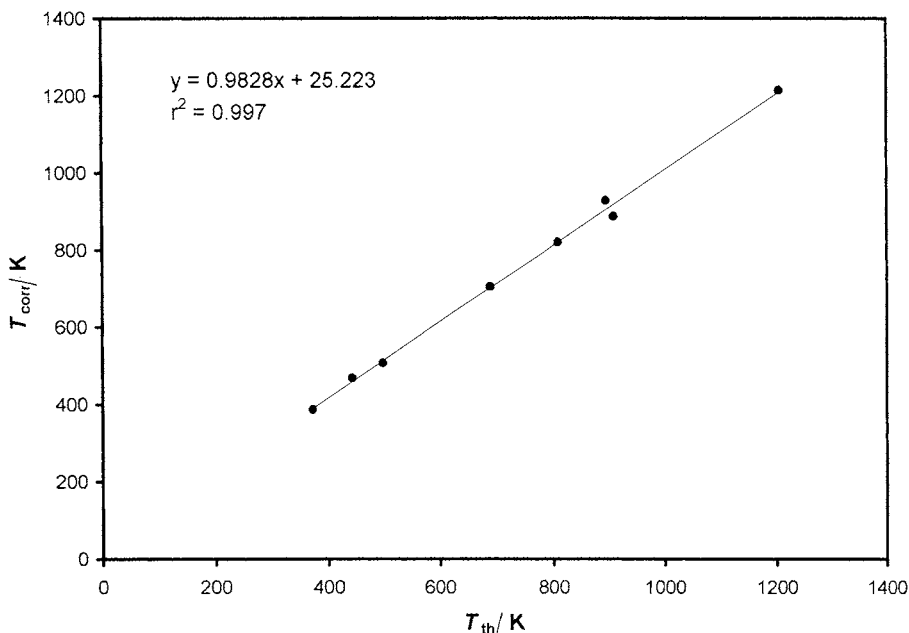


Fig. 2. Correlation of theoretical and experimental (corrected) values of the initial temperatures of decompositions presented in Table 1.

For $\text{CaMg}(\text{CO}_3)_2$, CaCO_3 and BaCO_3 , the values of α_v were included in Table 1. They correspond to the ratio of decomposition rates (or, what is the same, to the ratio of equivalent pressures of CO_2) for the equilibrium and deduced schemes of decompositions. Experimental values of α_v were measured by the torsion–effusion and torsion–Langmuir methods. The agreement for CaCO_3 and BaCO_3 is excellent. Twenty times difference between theory and experiment in α_v for $\text{CaMg}(\text{CO}_3)_2$ may be attributed to the underestimation of the decomposition rate in case of effusion experiments [6].

3.5. The self-cooling effect and measurements of E parameters

Effect of self-cooling on measured values of the E parameter is much more pronounced than that on the T_{in} parameter. This results from higher mean temperature used for the determination of E parameter. (The initial temperature usually corresponds to the lowest value of the temperature interval). The method of corrections of kinetic parameters and particularly of the E parameter for the self-cooling effect was described earlier [20]. To remind, it consists in the following. The deviation of the measured E parameter from the true value, which corresponds to the assumed spatially uniform sample heating up to the furnace temperature, is determined, first, by the difference between the temperatures of the furnace, T_f , and of the sample surface, T_s , and second, by the effective number of powdered layers n_e involved in decomposition. The last factor corresponds to the effective number of powdered sample layers whose decomposition occurs at the same rate as that of the surface layer. Taking into account these two factors, the

corrected value of the E parameter can be calculated using the relationship [20]

$$E_{\text{cor}} = \frac{(1/T_f' - 1/T_f'')E_{\text{exp}} + R \ln(n_e'/n_e'')}{1/T_s' - 1/T_s''} \quad (18)$$

Here one and two primes refer, respectively, to the lower and higher temperatures used to determine E and the corresponding parameters n_e , and the subscript ‘exp’, to the experimental value of the E parameter.

Eq. (18) can be applied not only to powders but also to single crystals. In this case, $n_e = 1$, and the calculation of corrections takes into account only the temperatures of the furnace and of the sample. In case of powders, for the calculation of n_e factors it is necessary to know the actual number of layers n in the sample. For spherical particles, this can be calculated using the relationship [20]

$$n = \frac{12}{\pi^2} \frac{m}{\rho r_0 d^2} \quad (19)$$

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

The described method was used in this study for the evaluation of the self-cooling effect on the E parameters in the experiments of Searcy et al. with CaCO_3 [44], $\text{CaMg}(\text{CO}_3)_2$ [6] and BaCO_3 [7] and in the experiments with CaCO_3 (in vacuum and nitrogen) described recently by Maciejewski [45]. Table 3 presents the results of this evaluation. Single crystals were used in the experiments of Searcy et al. [6,7,44] and powders in [45]. For the calculation of total number of layers, n , in powdered samples of CaCO_3 , we used the following magnitudes of parameters [53]: $m = 20 \text{ mg} = 2 \times 10^{-5} \text{ kg}$, $\rho = 2710 \text{ kg m}^{-3}$, $r_0 = 7.5 \mu\text{m} =$

Table 3
Correction of measured values of E parameters for the self-cooling effect

Carbonate	T_{min} (K)		T_{max} (K)		P_{air} (bar)	n	n_e		E (kJ mol ⁻¹)		Reference
	Measured	Corrected	Measured	Corrected			T_{min}	T_{max}	Measured	Corrected	
CaCO_3	934	928.38	1013	984.43	1×10^{-7}	1	1	1	205	278.8	[44]
CaCO_3	788	787.68	823	821.82	5×10^{-4}	15	13.12	9.72	222	274.5	[45]
CaCO_3	973	972.03	1046	1040.87	1	15	11.52	5.64	180	277.2	[45]
$\text{CaMg}(\text{CO}_3)_2$	824	819.94	900	873.93	1×10^{-7}	1	1	1	191.6 ^a	260.6	[6]
BaCO_3	1160	1159.83	1210	1209.44	1×10^{-7}	1	1	1	225.9	227.5	[7]

^a Recalculated on the basis of tabulated data reported in [6].

7.5×10^{-6} m and $d = 6.3$ mm = 6.3×10^{-3} m. The calculations were performed with a computer program described in [52].

As can be seen from the results in Table 3, in all cases of CaCO_3 decompositions, the corrected values of E are close to 277 kJ mol $^{-1}$. This is 9% higher than the theoretical value (253 kJ mol $^{-1}$). However, this discrepancy is 2–3 times smaller than that between the theoretical and original data. Moreover, irrespective of the differences in experimental conditions, the corrected values practically coincide. It is interesting that in case of powders (in vacuum and nitrogen), the difference between the temperatures of the furnace and samples is very small ($<0.5\%$ even for the maximum temperatures), so that the final large differences in the E parameters are mainly due to the difference in n_e factors for different (minimum and maximum) temperatures. In case of $\text{CaMg}(\text{CO}_3)_2$, the corrected value of E (260.6 kJ mol $^{-1}$) is also about 10% higher than the theoretical value (234 kJ mol $^{-1}$). This is nearly 2 times smaller than the discrepancy with the original value (191.6 kJ mol $^{-1}$). Only in case of BaCO_3 the correction value is small (1.6 kJ mol $^{-1}$).

This is in accord with the results of calculations presented in Fig. 1.

3.6. Correlation between experimental (uncorrected) and theoretical values of E

Fig. 3 presents the correlation between theoretical and available experimental values of the E parameters for both the equimolar and isobaric modes of decomposition for eight carbonates under investigation (Table 1). As can be seen from the correlation equation (see Fig. 3), the general agreement is quite satisfactory (a mean systematic underestimation of experimental values the E parameter is only about 19 kJ mol $^{-1}$), though the scatter of experimental results from a correlation line is rather high. The mean relative value of the standard deviation is about 11%. This is 4 times larger than that for the T_{in} parameter. Despite this at first sight satisfactory agreement, there are some doubts in the correctness of some experimental results, especially those which are greater than the theoretical values. These doubts are connected with the expectation of the serious decreasing effect of self-cooling on

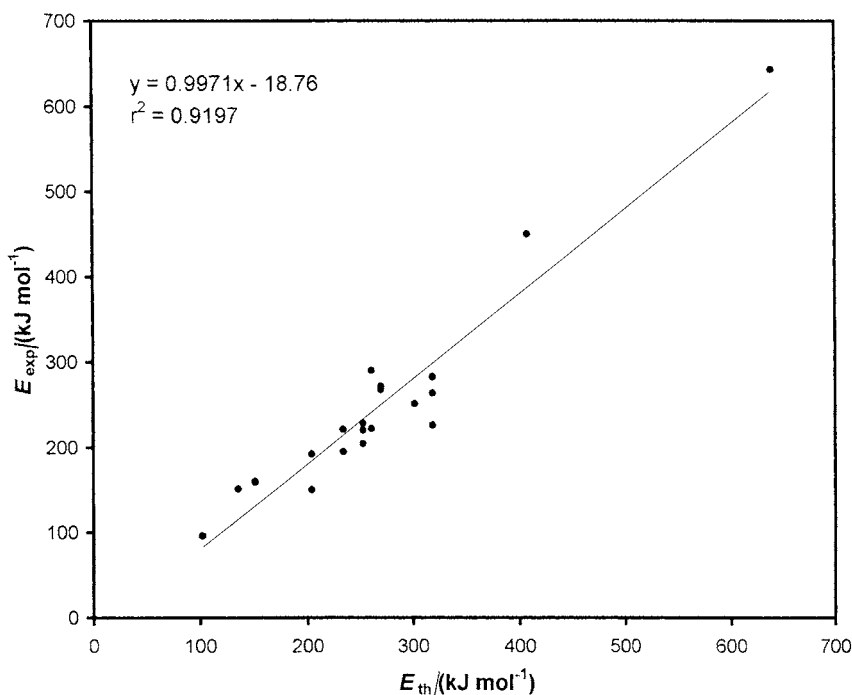


Fig. 3. Correlation of theoretical and experimental values of the E parameters presented in Table 1.

the E values obtained in high vacuum for powder samples (CdCO_3 , ZnCO_3 , MgCO_3 and SrCO_3). Contrary to these expectations, the values of the E parameter for these carbonates in some cases are equal to (or even greater than) the theoretical values. As a result, they partly 'equilibrate' the underestimated values of the E parameter for other carbonates and produce the apparent agreement between theory and experiment.

The most plausible reason of overestimation of the E parameters in the experiments with Cd, Zn, Mg and Sr carbonates performed by Pavlyuchenko and his colleagues [35,37,39,40,46] is, in our opinion, in an appropriate mathematical model used for processing of primary experimental data (α , t). They used the very popular Avrami–Erofeev model with the variable n factor derived for sigmoid α -time curves (see, e.g. [2]). This model takes into account nucleation and growth processes which are typical for most of carbonates. However, these stages of decomposition do not give true information about the *steady-state rate* of decomposition at the deceleratory stage, which an accord with the physical approach [23] is

the only parameter suitable for the strict quantitative interpretation. We can assume that the overestimation of the E parameters is the result of application of the Avrami–Erofeev model. To prove this supposition, we have investigated several publications by Pavlyuchenko and his colleagues, and in one of them [54], we have found a comparison of the results obtained from processing of the same data (for the decomposition of CdCO_3) with the Avrami–Erofeev (An) and contracting volume (R3) models. These data are presented in Fig. 4. It can be seen that a slope of the Arrhenius graph for An model is 1.34 times higher than that for the R3 model. We are conscious that this particular fact is not enough for general conclusions, and this problem needs further consideration. Nevertheless, in support of this conjecture one can refer to the results reported for the recent ICTAC kinetics project [45,55]. The discrepancy between E parameters obtained by different workers from kinetic analysis of identical sets of data (in particular, for CaCO_3 decomposition), using different computational procedures, was much worse than might have been expected.

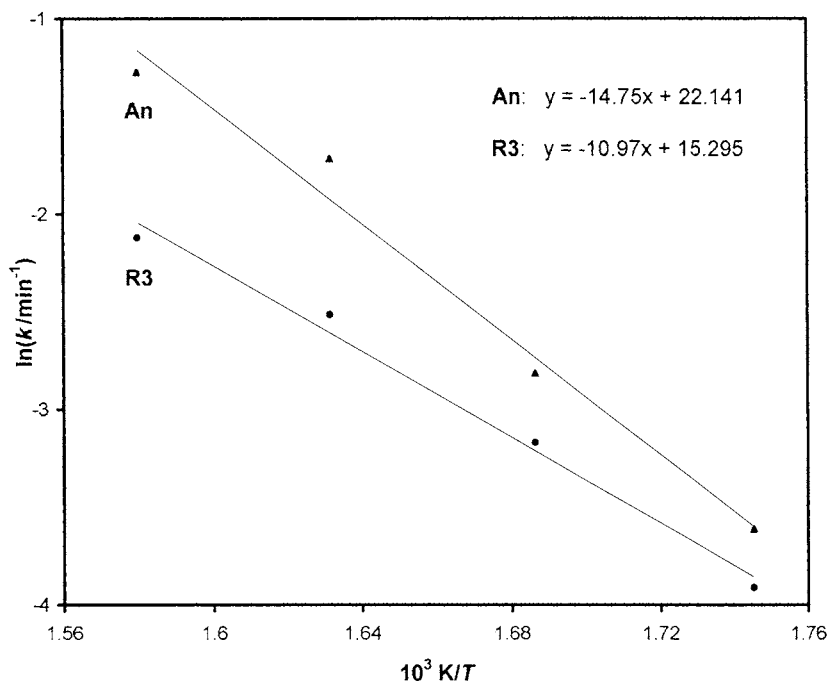


Fig. 4. The Arrhenius graphs for the decomposition of CdCO_3 corresponding to the different mathematical models used in [54] for processing of the same set of primary data.

3.7. Validation criteria for measured E parameters

Of two kinetic parameters (A and E) entering the Arrhenius equation, only the E parameter is usually used for the interpretation of the mechanisms of decompositions. This explains why in a majority of publications, authors report only E values. Variations of the A parameter in very wide limits and, in particular, observing of high values of A in the presence of gaseous products have not found any theoretical explanation in the framework of the traditional ideas. This problem has been solved in the framework of the physical approach to the interpretation of decomposition kinetics. As it was shown above (see Section 2.3), the isobaric mode of decomposition results in much higher values of A compared to that for the equimolar mode.

However, in the absence of gaseous products in the reactor (e.g. in vacuum), the values of A parameter can vary only within narrow limits. It is clear from the analysis of Eq. (13). Let us estimate its average value and the limits of variation in case of the decomposition of carbonates. If we take into account that the radius of a spherical particle for a sample taken as a single crystal or powder can vary from 0.01 to 1 mm, then with a factor of 10 the average radius $r_0 = 1 \times 10^{-4}$ m. The average value of $\Delta S_T^\circ/\nu$ for the carbonate decomposition is $160 \pm 20 \text{ J mol}^{-1} \text{ K}^{-1}$ (see Table 2). The variations (for different carbonates) of other parameters entering Eq. (13) are smaller. We can use for this purpose the averaged magnitudes: $\rho = 3000 \text{ kg m}^{-3}$, $M_r = 0.1 \text{ kg mol}^{-1}$, $\bar{M} = 0.05 \text{ kg mol}^{-1}$ and $T = 700 \text{ K}$. It follows from these results that the $\ln(A)$ (s^{-1}) parameter can vary from 21 to 31 (taking into account the maximum variations of the entropy of reaction and particle size).

From the above reasoning it is clear that any deviation of the $\Delta S_T^\circ/\nu$ or $\ln(A)$ (s^{-1}) parameters from the limits defined should be interpreted as a defect (or

defects) in the experimental or computational stages of kinetic analysis and a warning of a possible error in the determination of the E parameter. At the same time, the agreement of the reaction entropy or A parameter with the limits defined should be considered only as the *necessary, but not the sufficient* condition for the correctness of measured E value. This is connected with a possibility of interference of two or more effects (opposite in sign) which can partly or completely compensate each other.

Besides these two interrelated criteria, there is one more criterion of the validity based on the ratio of the initial temperature of decomposition to the E parameter, T_{in}/E . As shown above (Section 2.4), this ratio is rather constant for different solids. In case of carbonates, when $140 < \Delta S_T^\circ/\nu < 180$ (in $\text{J mol}^{-1} \text{ K}^{-1}$) and $10^{-7} < P_{\text{in}} < 10^{-6}$ (in bar), we obtain from Eq. (17): $3.2 < T_{\text{in}}/E < 3.9$ (in K mol kJ^{-1}).

To illustrate the efficiency of these criteria, we have applied them to some of the data discussed above. Tables 4–6 present the results of such consideration with the use each of the parameters mentioned above. For MgCO_3 and SrCO_3 , $\ln(A)$ (s^{-1}) and T_{in}/E parameters were used, for other carbonates, $\Delta S_T^\circ/\nu$ and T_{in}/E parameters. From examination of these results, the following conclusions can be deduced:

1. The E parameter for SrCO_3 reported in [46] is slightly overestimated. This is supported by the higher value of $\ln(A)$ (s^{-1}) parameter and lower value of T_{in}/E ratio (compared with their theoretical values).
2. The E parameter for MgCO_3 reported in [40] is slightly underestimated, and this is in accord with the smaller value of $\ln(A)$ (s^{-1}) parameter and higher value of T_{in}/E ratio (compared with their theoretical values).
3. The E parameters for $\text{CaMg}(\text{CO}_3)_2$, CaCO_3 and BaCO_3 reported in [6,7,44] are strongly underestimated, and this is in accord with the much

Table 4
Experimental and theoretical values of $\ln(A)$ (s^{-1}) for the decomposition of Sr and Mg carbonates

Carbonate	$\ln(A)$ (s^{-1})		$\Delta \ln(A)$ (s^{-1})	E (kJ mol^{-1})		ΔE (kJ mol^{-1})
	Experiment	Theory		Experiment	Theory	
SrCO_3	26.1 [46]	25.9	0.2	290 [46]	261	29
MgCO_3	20.3 [40]	27.2	-6.9	192 [40]	204	-12

Table 5

Experimental and theoretical values of entropy for the decomposition of alkaline-earth carbonates (in order of decreasing experimental values of $\Delta S_T^0/v$)

Carbonate	$\Delta S_T^0/v$ (J mol ⁻¹ K ⁻¹)		$\Delta(\Delta S_T^0/v)$ (J mol ⁻¹ K ⁻¹)	E (kJ mol ⁻¹)		ΔE (kJ mol ⁻¹)
	Experiment	Theory		Experiment	Theory	
CaMg(CO ₃) ₂	93 ± 6 [6]	164	-71	195 ± 1 [6]	234	-39
CaCO ₃	84 ± 12 [11]	157	-73	209 ± 12 [11]	253	-44
BaCO ₃	54 ± 3 [7]	138	-84	226 ± 7 [7]	319	-93

Table 6

Experimental and theoretical values of T_{in}/E ratio for the decomposition of alkaline-earth carbonates (in order of increasing T_{in}/E ratio)

Carbonate	T_{in} (K)	E (kJ mol ⁻¹)	Reference	T_{in}/E (K mol kJ ⁻¹)		Experiment to theory ratio	E (kJ mol ⁻¹)		ΔE (kJ mol ⁻¹)
				Experiment	Theory		Experiment	Theory	
SrCO ₃	888	290	[46]	3.1	3.5	0.89	290	261	29
MgCO ₃	714	192	[40]	3.7	3.4	1.09	192	204	-12
CaMg(CO ₃) ₂	824	195	[6]	4.2	3.5	1.20	195 ± 1	234	-39
CaCO ₃	934	209	[11]	4.5	3.4	1.32	209 ± 12	253	-44
BaCO ₃	1163	226	[7]	5.1	3.8	1.34	226 ± 7	319	-93

smaller values of $\Delta S_T^0/v$ parameter and higher values of T_{in}/E ratio (compared with their theoretical values).

The use of these criteria allows to exclude from succeeding consideration the wrong data. For example, for the isothermal decomposition of CaCO₃ in vacuum, a set of E and $\ln(A)$ (s⁻¹) parameters calculated by different workers were reported (Table 3, [55]). From a list of $\ln(A)$ (s⁻¹) values (24.78; 25.96; 32.10; 24.91; 32.10; 25.94; 21.3; 36.25; 11.04; 25.66; 13.43; 25.13 and 3.68), more than half of them (32.10; 32.10; 21.3; 36.25; 11.04; 13.43 and 3.68) can be rejected as erroneous because they are outside the limits for variation of this parameter (23–28) in case of CaCO₃. This does not mean that all other data in this list are correct because of the possibility of interference of two or more effects (opposite in sign) which can compensate each other. As examples of such effects, the self-cooling effect, on the one hand, and the inappropriate kinetic model used for the calculations, on the other, may be mentioned. It is worth to note that the same conclusion about the validity of the above set of data can be made, if we compare experimental and theoretical values of the T_{in}/E ratio.

3.8. The Topley–Smith (T–S) effect for the decomposition of CaCO₃

Anomalous variation of the rate of dehydration of crystalline hydrates with increasing water vapor pressure (P_w) was discovered by Topley and Smith 70 years ago [56] in a study of the rate of dehydration of MnC₂O₄·2H₂O. In contrast to the expected monotone decrease of the rate with increasing P_w , the dehydration rate, on reaching a certain critical pressure (10⁻⁵–10⁻⁴ bar), begins to grow, passes through a maximum, and falls off again. In the time elapsed thereafter, the T–S effect was observed in a score of different crystalline hydrates [52]. A recent theoretical study [52] has shown that this anomaly is actually the result of competition between the depressing influence of water vapor during dehydration, on the one hand, and the increasing heat transfer from the furnace to the sample by water vapor, on the other, in the presence of intense self-cooling. The computer model developed [52] accounted for all the main features of the T–S effect, in particular, the enhancement of the effect with increasing decomposition temperature and with decreasing powder grain size. The main argument against this interpretation is the fact that the T–S effect has been observed up to now only for the

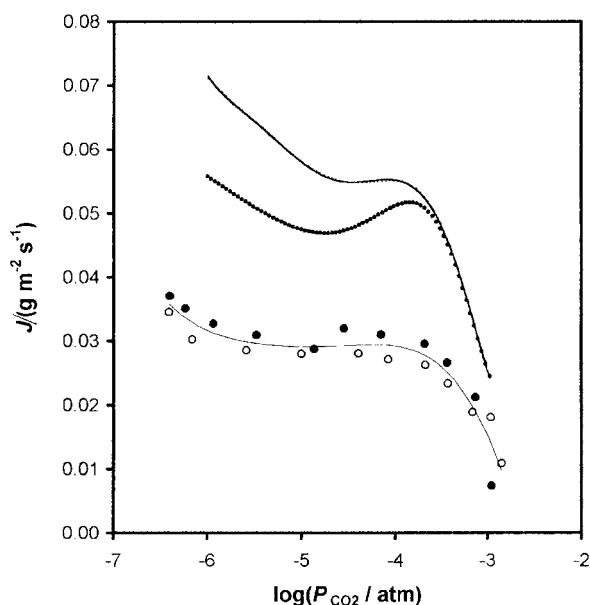


Fig. 5. Effect of CO_2 pressure on the rate of decomposition of CaCO_3 . Two sets of the experimental data (points) are taken from [11]. Theoretical curves were calculated for the different emittance factors: 0.020 (above) and 0.015 (below).

decompositions of crystalline hydrates and, therefore, this effect (as might appear) should be connected with some particular features of dehydration reactions.

To prove that T–S effect can be observed in case of other decomposition reactions, we simulated $J = f(P_{\text{CO}_2})$ curve for the decomposition of a single crystal of CaCO_3 at 1000 K in the presence of 10^{-6} – 10^{-3} bar CO_2 . The same computer program was used as before [52]. It was assumed that the heat expended for the decomposition is compensated by the radiation emitted from the heater and through heat transfer by the gas molecules of CO_2 . It was found that under these conditions the T–S effect can be observed if the emittance factor, ε , is smaller than 0.02 (Fig. 5). At higher values of ε , a maximum disappears, and only a small bend of the curve can be observed. In this case, the effect of self-cooling is smaller and therefore the increase of temperature of CaCO_3 with CO_2 pressure is compensated by the retardation effect of CO_2 on the decomposition (in the isobaric mode).

It happened that the effect of 10^{-6} – 10^{-3} bar CO_2 on the decomposition of CaCO_3 at different temperatures (898, 983, 1006 and 1073 K) has been investigated by Darroudl and Searcy [11]. The vacuum chamber with

internal hairpin-shaped heating elements connected in parallel was used. To reduce temperature gradients and contamination of the samples by condensable products of reaction of CO_2 with the tungsten filaments, a platinum cylinder 3 cm in diameter and 10 cm long was placed around the sample. It means that heating of the sample by radiation from the tungsten filament has been performed through the intermediate heating of Pt cylinder. Moreover, the emittance of platinum is rather low. At 1000 K, ε is about 0.10 [57] or 0.08 [58]. We can conclude that as a result of these two factors, the actual magnitude of ε in these experiments was smaller than 0.08. Be it as it may, in some of the figures (at 983, 1006 and 1073 K) in this work, we can clearly observe the effect of bending of, and even the appearance of a maximum on, $J = f(P_{\text{CO}_2})$ curves. As an illustration, we reproduce in Fig. 5 the experimental data obtained at 1006 K. The shape of theoretical and experimental curves is very similar. As expected from our calculations, the maximum (or bending) is observed at about 10^{-4} bar. Moreover, the absolute rates of decompositions differ from theoretical ones not more than by a factor of 2. The agreement is excellent if we take into account the simplifications of the calculation model and experimental errors.

The other important conclusion, which can be deduced from examination of these experimental results [11], is connected with the discrepancy in the dependence of decomposition rates of CaCO_3 on CO_2 background pressures observed by different authors (hyperbolic rate law in [8–10] and close to linear decrease observed by Darroudl and Searcy [11]). This is also connected with the effect of severe self-cooling of samples in high vacuum. Instead of expected two orders decrease of the decomposition rate in the range from 10^{-6} to 10^{-4} bar CO_2 , its value retained practically constant. This is in accord with our direct calculations of self-cooling effect (Section 3.4). Only at CO_2 pressure higher than 10^{-4} bar used in [8–10], the self-cooling effect is significantly reduced and the dependence of decomposition rates approximates to the hyperbolic law.

4. Conclusions

The following conclusions can be made on the basis of this study:

- The effect of self-cooling of reactant is of primary importance in the explanation of many controversial results obtained by different researchers in investigations of the kinetics of carbonate decomposition. In all cases of decompositions in vacuum, it is responsible for the experimental underestimation of the E parameters and overestimation (at temperatures lower than ca. 500 K) of the initial temperatures of decomposition, T_{in} . This effect cannot be avoided for the decomposition of powdered samples at any conditions (even in an atmosphere of foreign gases) because of the serious temperature gradient inwards different at different temperatures. Probably, experiments with single crystals of carbonates in an atmosphere of CO_2 (10^{-3} – 10^{-2} bar) might correspond to the best approximation to the spatially isothermal heating conditions. In the last case, due to the additional heat transfer by CO_2 and higher temperature of decomposition in the isobaric mode, the effect of self-cooling is smaller. For example, at 1000 K and $\varepsilon = 1$, the temperature of a single crystal of CaCO_3 in the presence of 10^{-2} bar of CO_2 should be about 999.98 K instead of 977 K in vacuum.
- In this context, the data on the E parameter obtained by Searcy et al. [6,7,11,44] for the decomposition of CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$ and BaCO_3 in high vacuum, which are considered as a standard of accuracy and a sort of reference values in carbonate decompositions, are also erroneous. The belief expressed by Beruto and Searcy in [44] ('The design of the apparatus used in the present study reduces the heat transfer problem to a negligible source of error in the temperature and decomposition pressure range used') was too optimistic.
- The self-cooling effect in the decomposition of CaCO_3 in the presence of CO_2 (10^{-6} – 10^{-4} bar) is responsible for the lack of expected hyperbolic dependence of decomposition rate on CO_2 pressure and the appearance of the T–S effect [11].
- The effect of overestimation of the E parameters reported by Pavlyuchenko et al. [35,37,39,40,46] for Cd, Zn, Mg and Sr carbonates has been revealed. It is most likely connected with an inappropriate mathematical model (An) used for processing of primary experimental data (α , t).
- Several criteria, which should be considered as the necessary, but not the sufficient condition for the validity of measured E values, have been proposed. These include the fulfilment of the conditions: $140 < \Delta S_T^\circ/\nu < 180$ (in $\text{J mol}^{-1} \text{K}^{-1}$) or $21 < \ln(A) (\text{s}^{-1}) < 31$ or $3.2 < T_{in}/E < 3.9$ (in K mol kJ^{-1}).
- The results of examination of the available literature data (the E and T_{in} parameters) for decomposition of carbonates and their comparison with the theoretical calculations in the framework of the physical approach support the general mechanism of decomposition which includes as a primary stage the congruent dissociative evaporation of reactants. For all the carbonates, except of BaCO_3 , the transfer to the reactant one-half of the energy released in the course of the condensation of low-volatility product has been taken into account. The reason of the exception of BaCO_3 from this rule requires further investigation.

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