

Kinetics and mechanism of free-surface decomposition of Group IIA and IIB hydroxides analyzed thermogravimetrically by the third-law method

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Abstract

The third-law method was applied to systematic investigation of free-surface decomposition kinetics of Group IIA and IIB hydroxides. The E parameters of the Arrhenius equation (in kJ mol^{-1}) are as follows: 124.8 (Be), 166.4 (Mg), 172.9 (Ca), 181.7 (Sr), 173.4 (Ba), 122.0 (Zn) and 124.7 (Cd). In accord with the physical approach, the obtained values of the E parameter are interpreted as the specific enthalpies of primary gasification reaction with consideration for the partial transfer of condensation energy of low-volatility oxide to the reactant. The τ parameters responsible for consumption of condensation energy by the reactants for all hydroxides except of $\text{Ba}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ are higher than 0.50. The maximum value (0.74) was found for $\text{Be}(\text{OH})_2$. Together with the available values of τ parameter for eight other reactants, they are in good correlation with the supersaturating degrees and/or condensation energies of the low-volatile products at the decomposition temperatures. This makes it possible a priori evaluation of the τ parameter on the basis of the thermodynamic characteristics of the low-volatile product.

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1. Introduction

The dehydration of hydroxides is attractive potential reactant system for fundamental mechanistic studies and one of the industrial processes for production of metal oxides. The kinetics and the mechanism of thermal decomposition of hydroxides (mainly, $\text{Mg}(\text{OH})_2$) have been a subject of a large number of studies, covered partially in [1,2]. In spite of the simplicity of this reaction, there is no general agreement on the mechanism of decomposition and the appropriate kinetic model. The kinetic parameters, particularly the values of the E parameter of the Arrhenius equation measured by different workers are substantially different. As illustration, the literature data on decomposition kinetics of $\text{Mg}(\text{OH})_2$ over last 50 years [3–14] are presented in Table 1. A list of earlier publications (from 1882 to 1947) has been reported in [3]. As can be seen, the values of the E parameter vary in the range from 53 to 372 kJ mol^{-1} . Even in the one

and the same work, these values may differ by a factor of 1.5–2 for different samples and different calculation models [3,5,9,10].

The primary purpose of this work was to measure thermogravimetrically the decomposition kinetics of Group IIA (Be, Mg, Ca, Sr and Ba) and IIB (Zn and Cd) hydroxides and determine the E parameters using the most reliable (as discussed below) third-law method. Then, these values were supposed to compare with the enthalpies of corresponding reactions. In accord with the physical approach to the interpretation of decomposition process [15], these reactions reduce to dissociative evaporation of reactant, followed by condensation of the low-volatile product (metal oxide). As a final result of this comparison, the values of the τ parameter that define the consumption of condensation energy by the reactant will be evaluated. As was revealed recently [16], these values vary for different reactants and are in correlation with the supersaturating degree of low-volatile product at decomposition temperature. Based on our previous study of $\text{Mg}(\text{OH})_2$ decomposition [13], it might be assumed that for some of Group II hydroxides the values of τ parameter should be higher than 0.50 (this value was

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Table 1
Decomposition kinetics for Mg(OH)₂ (the literature data)

Author	Year	Medium	<i>T</i> (K)	Point number	<i>E</i> (kJ mol ⁻¹)	Measurement technique	Calculation method
Gregg and Razouk [3]	1949	Vacuum	578–638	3–5	53–115 ^a	Isothermal	Arrhenius plots
Zhabrova and Gordeeva [4]	1960	Vacuum	543–643	6	121	Isothermal	Arrhenius plots
Anderson and Horlock [5]	1962	Vacuum	520–575	6	79–116 ^a	Isothermal	Arrhenius plots
Turner et al. [6]	1963	Air	653–745	6	215–238 ^a	Non-isothermal	Arrhenius plots
Turner et al. [6]	1963	Air	653–745	6	210	Isothermal	Arrhenius plots
Weber and Roy [7]	1965	1 bar H ₂ O	630–730		190	Non-isothermal	Arrhenius plots
Sharp and Brindley [8]	1966	Vacuum			84–96 ^b	Isothermal	Arrhenius plots
Gordon and Kingery [9]	1967	Vacuum	573–647	7	121–180 ^c	Isothermal	Arrhenius plots
Girgis [10]	1972	Air	650–675	3	192–269 ^b	Non-isothermal	Arrhenius plots
Girgis [10]	1972	Air	626–651	4	171–296 ^b	Isothermal	Arrhenius plots
Criado and Morales [11]	1976	Vacuum	600–680	9	88	Non-isothermal	Arrhenius plots
Mu and Perlmutter [12]	1981	N ₂ flow	558–653		372	Non-isothermal	Arrhenius plots
L'vov et al. [13]	1998	Vacuum	600	2	173 ^d	Isothermal	Third-law

^a For different samples.

^b For different calculation models.

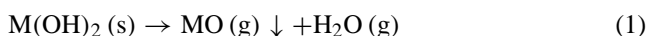
^c For different samples and different calculation models.

^d Absolute rates for decomposition of single crystals were taken from [5,9].

accepted earlier [15] as the most probable value for all reactants).

2. Theoretical

The main concept in the physical approach [15] applied in this work to the interpretation of kinetics consists of the belief that the decomposition of reactants into primary gaseous species proceeds in agreement with equilibrium laws but the origin and composition of these primary products might differ from those at equilibrium. In the case of hydroxides, this difference consists in the decomposition of M(OH)₂ into H₂O and low-volatility gaseous molecules of MO, which subsequently condense with the formation of solid oxide:



The equilibrium character of decomposition reactions has received recently [17] a strong confirmation. The mean ratio of the initial temperature of decomposition, *T*_{in}, to the *E* parameter for 100 different substances (3.6 ± 0.4 kJ mol⁻¹) taken from the literature practically coincides with the value (3.6 ± 0.2 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 in vacuum into gaseous products A and B with simultaneous condensation of low-volatility species A, that is



the flux of each product, *J*, which ultimately determines the rate of decomposition, can be expressed through the so-called equivalent partial pressure *P*_{eq} (in bar) of this product corresponding to the hypothetical equilibrium of reaction (2) in the form

$$J = \frac{\gamma M P_{\text{eq}}}{(2\pi MRT)^{1/2}} \quad (3)$$

where *M* is the molar mass of gaseous product. Here γ = 10⁵ Pa bar⁻¹ is the conversion factor from bars (used to calculate partial pressures in chemical thermodynamics) pascals. This relationship is usually called the Hertz–Langmuir equation.

2.2. Equilibrium pressure of product for dissociative evaporation

In the absence of reaction products in the reactor atmosphere, the partial pressure *P*_A can be expressed [15] as

$$P_A = a \left(\frac{K_P}{F} \right)^{1/\nu} \left(\frac{M_A}{M_B} \right)^{b/2\nu} \\ = \frac{a}{F^{1/\nu}} \left(\frac{M_A}{M_B} \right)^{b/2\nu} \exp \frac{\Delta_r S_T^\circ}{\nu R} \exp \left(- \frac{\Delta_r H_T^\circ}{\nu RT} \right) \quad (4)$$

where

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

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

and

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

where Δ_r*H*_T[°] and Δ_r*S*_T[°] are, respectively, the changes of the enthalpy and entropy in reaction (2).

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 calculations of the

enthalpy of decomposition reaction (2) an additional term $\tau a \Delta_c H_T^\circ$ (A), where the coefficient τ corresponds to the fraction of the condensation energy consumed by the reactant. Thus, we can write

$$\Delta_r H_T^\circ = a \Delta_f H_T^\circ (\text{A}) + b \Delta_f H_T^\circ (\text{B}) - \Delta_f H_T^\circ (\text{S}) + \tau a \Delta_c H_T^\circ (\text{A}) \quad (8)$$

As one of the basic assumptions underlying the physical approach, it was supposed [15] that the energy evolved in the process of condensation is equally divided between the reactant and product phases, i.e. $\tau = 0.50$. For some of the substances investigated up to now (e.g. CaCO_3 [18]), the condition $\tau = 0.50$ is found to be valid. However, as became evident later, for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [19] and $\text{Mg}(\text{OH})_2$ [13] τ is higher than 0.50, and for MgCO_3 , SrCO_3 and BaCO_3 [18] τ is smaller than 0.50. As was revealed recently [16], this parameter varies for different reactants and is in correlation with the supersaturating degree of low-volatile product at decomposition temperature.

Under high vacuum conditions (the equimolar mode of vaporization), the value of the E parameter of the Arrhenius equation is related with the enthalpy of reaction (2) by the obvious relationship [15]

$$\Delta_r H_T^\circ = \nu E \quad (9)$$

Taking into account Eqs. (6), (8) and (9), we obtain for hydroxides under investigation ($a = b = 1$):

$$\tau = \frac{2E - \Delta_f H_T^\circ (\text{A}) - \Delta_f H_T^\circ (\text{B}) + \Delta_f H_T^\circ (\text{S})}{\Delta_c H_T^\circ (\text{A})} \quad (10)$$

The magnitudes of thermodynamic functions (the entropy and enthalpy) for the components of decomposition reactions at different temperatures are listed in Tables 2 and 3 [20,21]. A possible error (S.D.) in calculations of $\Delta_r H_T^\circ$ and $\Delta_r S_T^\circ$ values is within 6 kJ mol^{-1} and $2 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively.

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

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

$$\Delta_r H_T^\circ = T(\Delta_r S_T^\circ - R \ln K_P) \quad (11)$$

where as before $\Delta_r S_T^\circ$ is the entropy change and K_P is the equilibrium constant for the reaction (2). Taking into account Eqs. (4), (6), (7) and (9), Eq. (11) in the case of decomposition of hydroxides in vacuum can be reduced to the equation

$$E = T \left(\frac{\Delta_r S_T^\circ}{2} - R \ln P_{\text{eq}} \right) \quad (12)$$

The equivalent pressure of the gaseous product (B) is related to the total absolute rate of decomposition, J (in $\text{kg m}^{-2} \text{ s}^{-1}$),

Table 2
Thermodynamic functions [20] for Group IIA species and H_2O

Function ^a	State of aggregation	T (K)			
		400	500	600	700
$\Delta_f H_T^\circ$ (Be(OH) ₂)	s	−898.2	−889.3		
S_T° (Be(OH) ₂)	s	67.0	86.7		
$\Delta_f H_T^\circ$ (BeO)	s	−606.4	−602.7		
S_T° (BeO)	s	22.5	30.6		
$\Delta_f H_T^\circ$ (BeO)	g	137.0	140.1		
S_T° (BeO)	g	206.3	213.2		
$\Delta_f H_T^\circ$ (Mg(OH) ₂)	s	−906.1	−895.9		
S_T° (Mg(OH) ₂)	s		109.5	128.0	
$\Delta_f H_T^\circ$ (MgO)	s	−593.0	−588.3		
S_T° (MgO)	s		48.6	57.1	
$\Delta_f H_T^\circ$ (MgO)	g		39.2	43.1	
S_T° (MgO)	g		230.9	238.0	
$\Delta_f H_T^\circ$ (Ca(OH) ₂)	s	−966.6	−956.2		
S_T° (Ca(OH) ₂)	s		132.5	151.4	
$\Delta_f H_T^\circ$ (CaO)	s	−625.7	−620.7		
S_T° (CaO)	s		62.0	71.1	
$\Delta_f H_T^\circ$ (CaO)	g		49.9	53.4	
S_T° (CaO)	g		237.1	243.6	
$\Delta_f H_T^\circ$ (Sr(OH) ₂)	s	−945.1	−934.2	−922.7	
S_T° (Sr(OH) ₂)	s		144.8	164.6	182.3
$\Delta_f H_T^\circ$ (SrO)	s	−580.8	−575.6	−570.4	
S_T° (SrO)	s		80.2	89.6	97.7
$\Delta_f H_T^\circ$ (SrO)	g		7.2	3.7	0.0
S_T° (SrO)	g		247.7	254.3	259.9
$\Delta_f H_T^\circ$ (Ba(OH) ₂)	s		−904.6	−894.9 ^b	
S_T° (Ba(OH) ₂)	s		192.0	207.0 ^b	
$\Delta_f H_T^\circ$ (BaO)	s		−532.7	−527.3	
S_T° (BaO)	s		107.2	115.5	
$\Delta_f H_T^\circ$ (BaO)	g		−117.2	−113.6	
S_T° (BaO)	g		259.6	265.1	
$\Delta_f H_T^\circ$ (H ₂ O)	g	−238.3	−234.9	−231.3	−227.6
S_T° (H ₂ O)	g	198.7	206.4	212.9	218.6

^a All $\Delta_f H_T^\circ$ values are in kJ mol^{-1} and all S_T° values are in $\text{J mol}^{-1} \text{ K}^{-1}$.

^b At 681.5 K (the melting point).

by the Hertz–Langmuir Eq. (3) rewritten as

$$P_{\text{eq}} = \frac{(2\pi MRT)^{1/2} J}{\gamma M} \quad (13)$$

As can be seen from the analysis of results reported in [20] for several tens of substances, the data calculated by the third-law method are in general the order of magnitude more precise than those calculated by the second-law method. This is connected with the systematic errors in the determination

Table 3
Thermodynamic functions [21] for Zn and Cd species and H_2O

Species	State of aggregation	$\Delta_f H_{298}^\circ$ (kJ mol^{-1})	S_{298}° ($\text{J mol}^{-1} \text{ K}^{-1}$)
Zn(OH) ₂	s	−645.4	77.0
ZnO	s	−350.6	43.6
ZnO	g	104.8	224.7
Cd(OH) ₂	s	−561.5	93.0
CdO	s	−259.0	54.8
CdO	g	81.1	233.0
H ₂ O	g	−241.8	188.7

of the true temperature of reactant (mainly, because of the self-cooling effect). Instead of a proportional dependence of the error in $\Delta_r H_T^\circ$ determination on the error of T in the case of the third-law method, the error in $\Delta_r H_T^\circ$ determination is proportional to the error in the slope of the plot in the case of the second-law and Arrhenius plots methods [17]. For illustration, at $T_{\min} = 900$ K and $T_{\max} = 1000$ K, the error in 10 K ($T_{\max} = 990$ K) results in the error in $\Delta_r H_T^\circ$ calculation about 9% instead of only 1% in case of the third-law method applied at T_{\max} .

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. The reacting materials were high purity powders obtained by precipitation from aqueous solutions in this laboratory and some commercial reagents (Ca and Mg hydroxides). Composition of all materials was checked beforehand by the dynamic TG and DSC with a STA 449 instrument. The powder sample (20–40 mg) 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).

In experiments on determination of the E parameter, the sample chamber was evacuated to a residual pressure about $n \times 10^{-8}$ bar with the use of rotation and oil-diffusion pumps. All measurements have been conducted at continuous pumping under isothermal conditions. The heating rate of the sample from the room temperature to intermediate one (20 K lower than the desired temperature) was 3–5 K min^{-1} and from intermediate to the desired temperature was 1 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 powders during this period were taken into account. A decrease of the surface area, as was checked experimentally [22], was proportional to $(1 - \alpha)^{2/3}$ where α is the decomposition degree. This dependence can be interpreted as a combined result of the reduction of number and size of particles in the process of decomposition. 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 30 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 [22]. 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 [16,18,22], does not depend on the temperature, residual pressure of gas in the reactor, grain size and mass of a powder sample.

4. Results and discussion

4.1. Kinetics and mechanism of dehydration

The experimental conditions and results of determination of the E parameter by the third-law method are presented in Table 4. The final (averaged) values of the E parameter and the calculated values of specific enthalpies for the fully equilibrium reactions (corresponding to the formation of equilibrium primary products) are collected in Table 5. This table contains also the values of T/E ratio and τ parameter calculated by Eq. (10).

The following conclusions can be deduced from the analysis of these data.

1. For the first time, the kinetic decomposition parameters are obtained for hydroxides of all Group IIA and IIB metals by the use of the most reliable third-law method. The standard deviation for repetitive measurements in all cases is equal or below 2 kJ mol^{-1} . This magnitude includes a small systematic increase of the E values with temperature due to the self-cooling effect.
2. The average magnitude of T/E ratio ($3.3 \pm 0.1 \text{ K mol kJ}^{-1}$) is in agreement with the theoretically predicted value for $P_{\text{eq}} = 2 \times 10^{-8}$ bar [17]. This is an additional proof of validity of the data received.
3. The values of the E parameter for all hydroxides are 30–150 kJ mol^{-1} higher than the enthalpies of fully equilibrium reactions (corresponding to the formation of equilibrium primary products). In accord with this general difference, the dehydration of $\text{Cd}(\text{OH})_2$ is actually the endothermic process instead of exothermic one as it should be for the equilibrium reaction.
4. In the framework of the physical approach, the obtained values of the E parameter are interpreted as the specific enthalpies of primary gasification reaction with consideration for the partial transfer of condensation energy of low-volatility oxide to the reactant. The values of τ factor indicated in Table 5 correspond to the condition (9).
5. The τ parameters for all hydroxides (except of $\text{Ba}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$) are higher than 0.50. The maximum value ($\tau = 0.74$) was found for $\text{Be}(\text{OH})_2$. The peculiarities of variation of τ parameter for different hydroxides will be discussed in Section 4.3.

Table 4

Experimental conditions and results of calculation of the E parameter for hydroxide dehydration by the third-law method

Hydrate ^a	Vacuum (atm)	T (K)	m_0 (mg)	S_0 (mm ²)	α_m^b	S_m^c (mm ²)	$\Delta m/\Delta t$ ($\mu\text{g s}^{-1}$)	J_{cor}^d ($\text{kg m}^{-2} \text{s}^{-1}$)	P_{eq} (bar)	$\Delta_r S_T^{\text{oe}}$ ($\text{J mol}^{-1} \text{K}^{-1}$)	E (kJ mol^{-1})
Be(OH) ₂	6×10^{-8}	406.5	20	81.5	0.245	67.6	0.770	4.07×10^{-6}	4.36×10^{-8}	337.7	125.9
Be(OH) ₂	5×10^{-8}	397.0	20	81.5	0.186	71.1	0.535	2.69×10^{-6}	2.85×10^{-8}	338.1	124.5
Be(OH) ₂	5×10^{-8}	396.0	20	81.5	0.204	70.0	0.538	2.75×10^{-6}	2.91×10^{-8}	338.2	124.1
Mg(OH) ₂	8×10^{-8}	510.4	40	77.9	0.026	76.6	0.104	4.82×10^{-7}	5.79×10^{-9}	327.4	164.0
Mg(OH) ₂	9×10^{-8}	535.2	40	77.9	0.033	76.2	0.260	1.22×10^{-6}	1.50×10^{-8}	326.0	167.4
Mg(OH) ₂	9×10^{-8}	536.7	40	77.9	0.059	74.8	0.260	1.24×10^{-6}	1.53×10^{-8}	326.0	167.8
Ca(OH) ₂	5×10^{-8}	602.3	30	69.8	0.083	65.9	0.815	4.42×10^{-6}	5.76×10^{-8}	305.1	175.4
Ca(OH) ₂	6×10^{-8}	572.0	30	70.7	0.0036	70.6	0.315	1.59×10^{-6}	2.02×10^{-8}	306.9	172.0
Ca(OH) ₂	4×10^{-8}	572.8	30	70.7	0.022	69.7	0.377	1.93×10^{-6}	2.45×10^{-8}	306.9	171.4
Sr(OH) ₂	6×10^{-8}	592.3	30	65.4	0.100	60.9	0.101	5.93×10^{-7}	7.67×10^{-9}	303.3	181.8
Sr(OH) ₂	6×10^{-8}	592.3	30	65.4	0.011	64.9	0.113	6.19×10^{-7}	8.01×10^{-9}	303.3	181.6
Ba(OH) ₂	5×10^{-8}	617.9	30	63.6	0.395	45.5	0.362	2.84×10^{-6}	3.75×10^{-8}	279.4	174.2
Ba(OH) ₂	5×10^{-8}	607.5	30	63.6	0.324	49.0	0.315	2.30×10^{-6}	3.01×10^{-8}	280.0	172.5
Zn(OH) ₂	5×10^{-8}	398.1	30	68.1	0.344	51.4	0.648	4.51×10^{-6}	4.78×10^{-8}	336.4	122.8
Zn(OH) ₂	5×10^{-8}	388.4	30	68.1	0.223	57.5	0.453	2.81×10^{-6}	2.94×10^{-8}	336.4	121.3
Cd(OH) ₂	6×10^{-8}	382.0	30	64.5	0.053	62.2	0.070	4.02×10^{-7}	4.18×10^{-9}	328.7	124.1
Cd(OH) ₂	6×10^{-8}	388.9	30	64.5	0.056	62.1	0.098	5.61×10^{-7}	5.88×10^{-9}	328.7	125.2

^a The apparent density of pellets was equal to 461 kg m^{-3} for Be(OH)₂, 1045 kg m^{-3} for Mg(OH)₂, 1120 kg m^{-3} for Ca(OH)₂, 1470 kg m^{-3} for Sr(OH)₂, 1680 kg m^{-3} for Ba(OH)₂, 1238 kg m^{-3} for Zn(OH)₂ and 1567 kg m^{-3} for Cd(OH)₂.

^b The decomposition degree by the time of measurement.

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

^d $J_{\text{cor}} = (\Delta m/\Delta t)/(2.8S_m)$.

^e Interpolated for temperatures used taking into account the values listed in Table 2. No interpolation was used for Zn(OH)₂ and Cd(OH)₂.

4.2. Comparison of our results with the literature data

With the exception of Mg(OH)₂, there are only a few publications on investigation of decomposition kinetics of other hydroxides. In Table 6, we compare our results with available data from the literature. In case of Mg(OH)₂, we used for comparison the results obtained by Gordon and Kingery [9], which, in our opinion, are the most reliable. As can be seen from the analysis of these data, in all cases the literature data are smaller than our results. The difference is maximum for Sr(OH)₂ and Ba(OH)₂ (55 and 110 kJ mol^{-1}) when the non-isothermal technique was used. For the isothermal methods, the difference is in the range of 10–30 kJ mol^{-1} . We attribute this systematic underestimation of the E parameters to the self-cooling effect, which is extremely important as discussed in Section 2.3, for the Arrhenius plots method [27].

A small discrepancy (about 4%) between the value of the E parameter for Mg(OH)₂ found in this work (166 kJ mol^{-1}) and that one (173 kJ mol^{-1}) reported in [13] is due to the difference in temperatures used for determination of the absolute rates of decomposition (535 and 600 K, respectively). As expected from Eq. (12), the self-cooling effect, in contrast to the Arrhenius plots method, should slightly increase the E values. At higher rates of decomposition, the self-cooling and resulted overestimation of the E value is higher.

4.3. Dependence of τ parameter on thermodynamic characteristics of low-volatile product

Recent analysis of variation of τ parameters for eight different reactants (all for alkaline earth metals) made it possible to correlate these values with the supersaturating degree of the low-volatile product (metal oxide) at the moment

Table 5

Enthalpies for hydroxide decomposition up to equilibrium products and the E and τ parameters

Hydroxide	T^a (K)	Equilibrium products	$\Delta_r H_T^\circ$ (kJ mol^{-1})	Primary products (physical approach)	E (kJ mol^{-1})	T/E (K mol kJ^{-1})	τ parameter
Be(OH) ₂	395	BeO (s) + H ₂ O	53.6 ± 2	BeO (g)↓ + H ₂ O	124.8 ± 0.9	3.2	0.74
Mg(OH) ₂	540	MgO (s) + H ₂ O	77.4 ± 1	MgO (g)↓ + H ₂ O	166.4 ± 2.1	3.2	0.64
Ca(OH) ₂	570	CaO (s) + H ₂ O	103.9 ± 2	CaO (g)↓ + H ₂ O	172.9 ± 2.1	3.3	0.65
Sr(OH) ₂	610	SrO (s) + H ₂ O	127.0 ± 2	SrO (g)↓ + H ₂ O	181.7 ± 0.1	3.4	0.59
Ba(OH) ₂	600	BaO (s) + H ₂ O	140.6 ± 2	BaO (g)↓ + H ₂ O	173.4 ± 1.2	3.5	0.50
Zn(OH) ₂	385	ZnO (s) + H ₂ O	53.0 ± 2	ZnO (g)↓ + H ₂ O	122.0 ± 0.8	3.2	0.58
Cd(OH) ₂	400	CdO (s) + H ₂ O	-27.0 ± 2	CdO (g)↓ + H ₂ O	124.7 ± 0.6	3.2	0.45

^a Temperature that corresponds to $P_{\text{eq}} \cong 2 \times 10^{-8}$ bar.

Table 6
Comparison of the E parameters measured in this work with the literature data

Hydroxide	E (kJ mol ⁻¹)		Measurement conditions ^a	Reference
	This work	Literature data		
Be(OH) ₂	124.8 ± 0.9	115	TG, iso, vacuo, powders	[23]
Mg(OH) ₂	166.4 ± 2.1	126–134	TG, iso, vacuo, single crystals	[9]
Ca(OH) ₂	172.9 ± 2.1	145–174	TG, iso, vacuo, powders	[24]
Sr(OH) ₂	181.7 ± 0.1	126	TG, non-iso, vacuo, powders	[11]
Ba(OH) ₂	173.4 ± 1.2	63	TG, non-iso, vacuo, powders	[11]
Zn(OH) ₂	122.0 ± 0.8	95	TG, iso, vacuo, powders	[25]
Cd(OH) ₂	124.7 ± 0.6	95–116	TG, iso, vacuo, powders	[26]

^a Iso: isothermal; non-iso: non-isothermal.

of decomposition [16]. This correlation was approximated (with the correlation coefficient $r^2 = 0.894$) by the equation:

$$\tau = 0.138 \ln x + 0.03 \quad (14)$$

where $x \equiv \log(P_{\text{eq}}/P_{\text{sat}})$. Here P_{eq} and P_{sat} are the equivalent and saturation pressures of low-volatile product. The values of τ parameter varied from 0 for BaSO₄ to 0.61 for Mg(OH)₂.

It is possible now to add to this list of reactants a number of new data for six other hydroxides (Table 5) and also for Li₂SO₄·H₂O [27] and BN [28]. The full list of reactants is presented in Table 7. The τ parameter for Mg(OH)₂ was recalculated using the experimental results obtained in this work. Fig. 1 illustrates graphically this correlation for all 16 reactants. As can be seen, the approximation function

$$\tau = 0.134 \ln x + 0.07 \quad (15)$$

has not been changed significantly in comparison with Eq. (14), though the range of supersaturating degree, x , for all 16 reactants was more than doubled (81.3 against 37.5).

This correlation can be improved if to limit the list of reactants by similar compounds. As illustration, Fig. 2 presents

the appropriate results for alkaline earth hydroxides only. In this case, the approximate function

$$\tau = 0.120 \ln x + 0.187 \quad (16)$$

differs from that in Eqs. (14) and (15), but the correlation coefficient ($r^2 = 0.997$) is close to maximum. However, it is conceivable that this excellent correlation is only coincident (for carbonates, for example, the correlation is significantly worse).

The other possible way for description of the correlation between the τ parameter and thermodynamic characteristics of the low-volatile product is presented in Fig. 3. The approximation function takes the form:

$$\tau = 0.423 \ln \left(-\frac{\Delta_c H_T^\circ}{RT} \right) - 1.48 \quad (17)$$

Instead of the supersaturating degree, $x \equiv \log(P_{\text{eq}}/P_{\text{sat}})$, the reduced value of condensation energy, $-\Delta_c H_T^\circ/RT$, is used as a controlling parameter. The correlation coefficient increased in this case from 0.882 up to 0.936.

The correlation revealed should be considered as an important step in the development of the physical approach as a whole. We remind that the τ parameter was introduced into

Table 7
Dependence of τ parameter on the condensation energy and supersaturating degree of the low-volatile product at decomposition temperature

Reactant	Low-volatile product	T (K) ^a	$\ln(-\Delta_c H_T^\circ/RT)$	P_{sat} (bar)	$\log(P_{\text{eq}}/P_{\text{sat}})$	τ parameter	Reference
BaSO ₄	BaO	1390	3.54	1.2×10^{-8}	0.2	0	[16]
BN	B	1790	3.63	1.9×10^{-9}	1.0	0	[28]
BaCO ₃	BaO	1080	3.81	5.3×10^{-13}	4.6	0.10	[18]
MgSO ₄	MgO	1000	4.33	2.8×10^{-21}	15.2	0.42	[16]
Ba(OH) ₂	BaO	600	4.42	8.8×10^{-24}	15.4	0.50	This work
SrCO ₃	SrO	910	4.72	6.8×10^{-25}	16.5	0.42	[18]
CaCO ₃	CaO	800	4.61	9.2×10^{-36}	27.0	0.50	[18]
Cd(OH) ₂	CdO	400	4.63	7.9×10^{-36}	27.4	0.45	This work
MgCa(CO ₃) ₂	MgO, CaO	790	4.63	2.6×10^{-36}	27.9	0.50	[22]
MgCO ₃	MgO	675	4.72	3.9×10^{-40}	31.7	0.47	[18]
Sr(OH) ₂	SrO	610	4.73	4.2×10^{-41}	32.7	0.59	This work
Li ₂ SO ₄ ·H ₂ O	Li ₂ SO ₄	320	4.84	9.4×10^{-46}	37.3	0.56	[27]
Mg(OH) ₂	MgO	540	4.95	2.4×10^{-52}	43.9	0.64	This work
Zn(OH) ₂	ZnO	385	4.94	4.7×10^{-53}	44.6	0.58	This work
Ca(OH) ₂	CaO	570	4.96	1.7×10^{-53}	45.1	0.65	This work
Be(OH) ₂	BeO	395	5.42	2.0×10^{-89}	81.3	0.74	This work

^a Temperature that corresponds to $P_{\text{eq}} \cong 2 \times 10^{-8}$ bar.

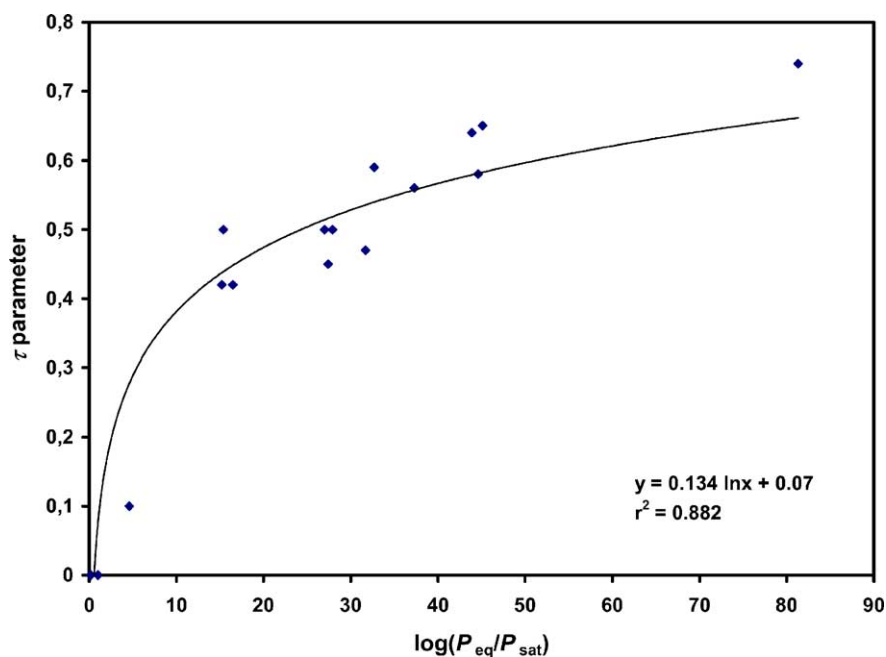


Fig. 1. Dependence of τ parameter on the supersaturating degree of low-volatile product at decomposition temperature (for all reactants, Table 7).

theory of the physical approach as adjusting factor to correlate the value of E parameter with the enthalpy of deduced reaction [19]. That was, on admission of the author himself, “the most weak point of the theory as a whole” [29]. Later [15], it was assumed that in most cases “the condensation energy is approximately equally divided between the reactant and product phases”, so that the τ parameter should be equal to 0.50. However, as it became evident recently, this

is not the case. Now, it has become possible to evaluate this parameter a priori on the basis of the saturation pressure, P_{sat} , or condensation energy, $\Delta_c H_T^\circ$, for the low-volatile product at decomposition temperature and Eqs. (15)–(17). But, some questions remain unanswered. The all-important problems consist in the physical interpretation of this correlation and the mechanism of energy consumption by the reactant.

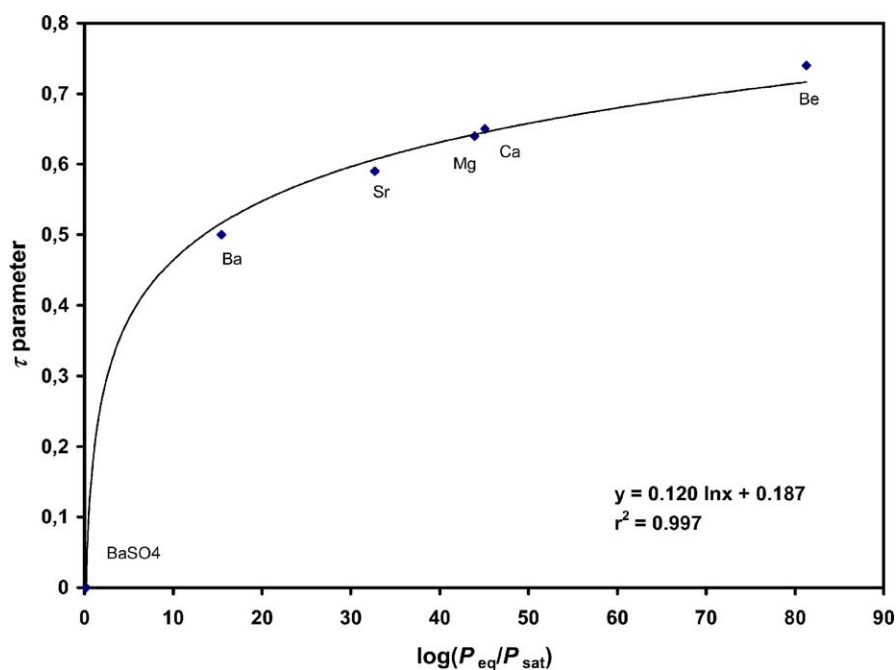


Fig. 2. Dependence of τ parameter on the supersaturating degree of metal oxide at decomposition temperature (for alkaline earth hydroxides and BaSO_4 , Table 7).

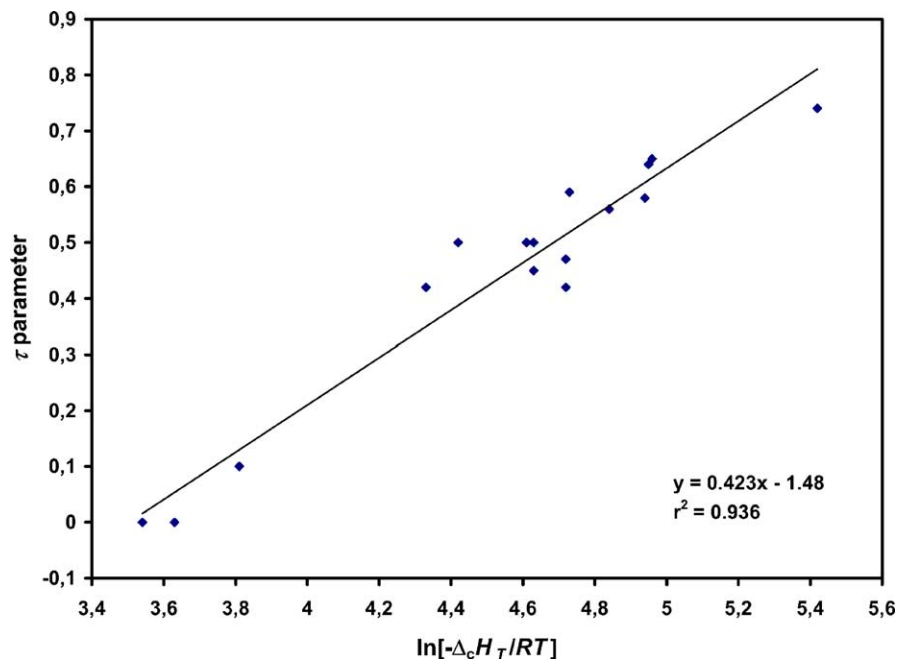


Fig. 3. Dependence of τ parameter on the condensation energy of low-volatile product at decomposition temperature (for all reactants, Table 7).

5. Conclusions

The third-law method was applied to the systematic investigation of free-surface decomposition kinetics of Group IIA and IIB hydroxides. The much lower dependence on the self-cooling effect and the order of magnitude higher precision of this method compared to the Arrhenius plots method permitted for the first time over the long story of these investigations to obtain reliable (precise and accurate) data on the E parameters. For all hydroxides, these values are much higher than the enthalpies of equilibrium reactions (corresponding to the formation of equilibrium primary products). In accord with the physical approach, the obtained values of the E parameter are interpreted as the specific enthalpies of primary gasification reaction with consideration for the partial transfer of condensation energy of low-volatility oxide to the reactant.

The τ parameters responsible for consumption of condensation energy by the reactants for all hydroxides (except of $\text{Ba}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$) are higher than 0.50. The maximum value ($\tau = 0.74$) was found for $\text{Be}(\text{OH})_2$. Together with the available values of τ parameter for eight other reactants, they are in good correlation with some thermodynamic characteristics of the low-volatile products. This makes it possible a priori evaluation of the τ parameter. Further investigations are necessary to find the physical interpretation for this correlation.

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