thermochimica acta

Thermochimica Acta 315 (1998) 135–143

Mechanism of thermal decomposition of magnesium hydroxide

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Received 17 June 1997; accepted 27 September 1997

Abstract

The kinetic characteristics (the rates of decomposition J and activation energies E_a) of thermal dehydroxylation of $Mg(OH)_2$, reported in a number of available publications, have been analysed with the supposition of dissociative evaporation of $Mg(OH)_2$ in the form of MgO and H_2O molecules. Despite the considerable differences in the measurement conditions, the experimental values of J and E_a have been found to be in agreement with theoretical calculations. The calculations took into account the self-cooling effect, the depressing effect of external water vapor on the decomposition rate, and partial transfer of the energy released in the condensation of MgO(g) to the reactant. The agreement between the calculated and experimental data confirms the proposed mechanism of decomposition. © 1998 Elsevier Science B.V.

Keywords: Decomposition of $Mg(OH)_2$; Dissociative evaporation; Kinetic parameters; Self-cooling effect

1. Introduction

The kinetics and the mechanism of thermal decomposition of hydroxides have been a subject of a large number of studies, covered partially in a monograph [1]. One of the most popular subjects of investigation is the process of $Mg(OH)_2$ dehydroxylation [2–8]

$$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g). \qquad (1)$$

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 activation energies measured [2–8] are substantially different.

The present work is an attempt at analyzing the available experimental data on the kinetics of dehydroxylation of $Mg(OH)_2$, based on an untraditional approach to the process of thermal decomposition of solids, which reduces to dissociative evaporation of the reactant, followed by condensation of the molecules of the non-volatile products. This approach has been successfully used in the interpretation of the decomposition of nitrates [9–12], azides [13], carbonates [14] and a number of other metal compounds [15,16].

Recently, it has been used for the interpretation of the kinetics of thermal dehydration of $Li_2SO_4{\cdot}H_2O$ [17]. In order to fit the calculated to experimental values of the kinetic parameters, the calculations of the enthalpy of the reaction included partial transfer of the energy released in Li_2SO_4(g) condensation to the reactant. It is of interest to use the same calculational scheme in case of $Mg(OH)_2$ decomposition.

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PII S0040-6031(97)00404-8

2. Theoretical

The method to be employed consists in comparing experimental data on the kinetic parameters with their calculated values. The calculations are based on the classical evaporation model of Hertz–Langmuir, extended to the case of dissociative evaporation of compounds [9–17]. The scheme of theoretical calculation of the main kinetic parameters (the flux of the gaseous product J, the rate constant k, the partial pressure P of the product and the parameters of the Arrhenius equation, E_a and A) has been described in a number of previous publications [13–17]. Therefore, we are going to present here only some final relations necessary for the calculations in this work.

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

$$\mathrm{S(s)} \rightarrow \mathrm{A(g)} + \mathrm{B(g)}. \tag{2}$$

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 (2) in the form

$$J_A = \frac{\gamma M P_A}{(2\pi M_A RT)^{1/2}} \tag{3}$$

where M and M_A are the molar masses of the compound and product A, γ the coefficient of conversion from atmospheres to pascals, and R the gas constant.

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

$$\frac{d\alpha}{dt} = 3(1-\alpha)^{2/3}k \tag{4}$$

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), respectively, we obtain on, rearrangement of Eq. (4), a simple expression

$$J = \rho r_0 k \tag{5}$$

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 [17] as

$$P_A^e = \left[\frac{M_A}{M_B}\right]^{1/4} \exp\frac{\Delta_r S_T^o}{2R} \exp\left[-\frac{\Delta_r H_T^o}{2RT}\right] \tag{6}$$

Here $\Delta_r H_T^o$ and $\Delta_r S_T^o$ are, respectively, the changes of the enthalpy and entropy in process (2).

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

$$P_A^i = \frac{1}{P'_B} \exp\frac{\Delta_r S_T^o}{R} \exp\left[-\frac{\Delta_r H_T^o}{RT}\right] \tag{7}$$

Substituting Eqs. (6) and (7) into Eq. (3), we obtain:

$$J_A^e = \frac{\gamma M}{(2\pi \bar{M} RT)^{1/2}} \exp\frac{\Delta_r S_T^o}{2R} \exp\left[-\frac{\Delta_r H_T^o}{2RT}\right] \tag{8}$$

for the equimolar mode and

$$J_A^i = \frac{\gamma M}{P'_B (2\pi M_A RT)^{1/2}} \exp\frac{\Delta_r S_T^o}{R} \exp\left[-\frac{\Delta_r H_T^o}{RT}\right] \tag{9}$$

for the isobaric one. Here $\bar{M}$ is the geometric mean of the molar masses of both gaseous particles, i.e.

$$\bar{M} \equiv (M_A \times M_B)^{1/2} \tag{10}$$

As can be seen from Eqs. (8) and (9), the calculated activation energies for reaction (2) should be different for the equimolar and isobaric modes of decomposition, i.e.

$$E_a^e = \Delta_r H_T^o / \nu \tag{11}$$

for the equimolar mode and

$$E_a^i = \Delta_r H_T^o \tag{12}$$

for the isobaric one.

In order to take into account partial transfer of the energy released in the condensation of non-volatile product A to the reactant, we introduced as before [17], into calculations of the enthalpy of the decomposition reaction (2) an additional term $\tau \Delta_c H_T^o$, where the coefficient τ corresponds to the fraction of the condensation energy $\Delta_c H_T^o$ transferred to the reactant.

Table 1
Thermodynamic functions [18] used in the calculations

Species	State of aggregation	$\Delta_f H^o_{600}$/(kJ mol^{-1})	S^o_{600}/(J mol^{-1} K^{-1})
H_2O	g	−218.5±0.1	212.9±0.1
MgO	g	52.4±15	238.0±0.1
MgO	s	−579.0±0.3	57.1±0.2
$Mg(OH)_2$	s	−895.9±0.3	128.0±0.6

Thus, we can write

$$\Delta_r H^o_T = \Delta_f H^o_T(A) + \Delta_f H^o_T(B) - \Delta_f H^o_T(S) + \tau \Delta_c H^o_T(A) \quad (13)$$

Table 1 lists the initial values of the thermodynamic functions for all components of implied reaction

$$Mg(OH)_2(s) \rightarrow MgO(g) + H_2O(g) \quad (14)$$

and Table 2, all the other parameters necessary for subsequent calculations.

3. Results and discussion

3.1. Comparison of the experimental and calculated data

As a basis for comparison with theoretical calculations, we used the results obtained by the authors of Refs. [2–5]. The isothermal version of TG in vacuum ($n \times 10^{-8}$ atm) was used in all these studies. In addition, measurements in the presence of water vapor were carried out in Refs. [2,4]. Single crystals of natural brucite [3,5] and powdered samples of $Mg(OH)_2$, obtained by precipitation from aqueous solution [2–5], were used.

The measurement conditions and the main kinetic parameters (J and E_a) obtained in these works are summarized in Tables 3 and 4. The decomposition rates J for powders were calculated, using Eq. (5), from the rate constant k and the mean radius r_0 of the particles. In its turn, the r_0 values were evaluated from the specific surface area(s) measurements [2,4] by the BET method using equation

$$r_0 = 3/(\rho s) \quad (15)$$

The theoretical values of J were calculated from Eqs. (8) and (9), taking into account the enthalpy and entropy of reaction (14), the partial pressure of H_2O vapor as listed in Table 3, and the coefficient τ=0.61. The choice of the τ coefficient equal to 0.61 corresponds to the best agreement of experimental and calculated data, in the cases of decomposition of single crystals in vacuum and powders in the presence

Table 2
Parameters used in the calculations of decomposition rates

Parameter	Symbol	Value
Molar mass of $Mg(OH)_2$	M	0.058 kg mol^{-1}
Molar mass of MgO	M	0.040 kg mol^{-1}
Mean molar mass of gaseous products	$\bar{M}$	0.027 kg mol^{-1}
Density of $Mg(OH)_2$	ρ	2400 kg m^{-3}
Enthalpy of reaction (14) at τ=0	$\Delta_r H^o_{600}$	729.8 kJ mol^{-1}
Entropy of reaction (14)	$\Delta_r S^o_{600}$	322.9 J mol^{-1} K^{-1}
Condensation heat of MgO(g)	$\Delta_c H^o_{600}$	−631.4 kJ mol^{-1}
Gas constant	R	8.3145 J mol^{-1} K^{-1}
Stefan–Boltzmann constant	σ	5.6705×10^{-8} W m^{-2} K^{-4}
Emittance of MgO [19]	ε	0.62
Pressure conversion factor	γ	101325 Pa atm^{-1}

Table 3
Decomposition rates of $Mg(OH)_2$

Sample	$\bar{r}_0$/m	Atmosphere	T/K	J/(kg m^{-2} s^{-1})		Reference
				experiment	calculation	
Single crystal		vacuum	600	7.0×10^{-5}	5.0×10^{-5}	Fig. 12 [5]
Single crystal		vacuum	600	1.4×10^{-4} [a]	5.0×10^{-5}	Fig. 5 [3]
Powder	1.5×10^{-6}	vacuum	600	1.9×10^{-6}	5.0×10^{-5}	Fig. 10 [5]
Powder	4.2×10^{-8}	vacuum	600	1.3×10^{-8}	5.0×10^{-5}	Fig. 5 [3]
Powder	2.1×10^{-8}	vacuum	593	1.0×10^{-8}	3.3×10^{-5}	Table 3 [2]
Powder	4.2×10^{-8}	$P_{H_2O} = 3.8 \times 10^{-4}$ atm	553	7.7×10^{-11}	2.6×10^{-11}	Fig. 1a [4]
Powder	4.2×10^{-8}	$P_{H_2O} = 3.8 \times 10^{-4}$ atm	573	8.9×10^{-10}	3.8×10^{-10}	Fig. 1a [4]
Powder	2.1×10^{-8}	$P_{H_2O} = 4.9 \times 10^{-3}$ atm	593	2.8×10^{-9}	9.4×10^{-10}	Table 3 [2]

[a] Two or more times overevaluated because the edge area of crystal used in the calculation of this value was as a minimum two times less than the total area of crystal.

Table 4
Activation energies for the decomposition of $Mg(OH)_2$

Sample	Atmosphere	T/K	E_a/(kJ mol^{-1})		Ref.
			experiment	calculation	
Powder	vacuum	543–643	100	173	[2]
Powder	vacuum	520–575	115	173	[3]
Powder	vacuum	514–600	121	173	[5]
Single crystal	vacuum	550–663	126	173	[5]
Polycrystalline sheets	vacuum	no data	159; 180	173	[5]
Powder	$P_{H_2O} = 3.8 \times 10^{-4}$ atm	553–573	322 [a]	346	[4]
Powder	$P_{N_2} = 1$ atm	558–653	372	346	[8]

[a] Estimated from the J values at 553 and 573 K (see Table 3).

of H_2O vapor. The discrepancy between experimental and calculated J values, in these cases, is not higher than a factor of 3, in spite of the fact that the absolute values of J vary within six orders of magnitude.

At the same time, the calculated J values for powders in vacuum appear to be 2–3 orders of magnitude higher than the experimental J values. A significant disagreement is also observed between the experimental and calculated values of activation energy in the case of powder decomposition in vacuum, though again, the compared results for powder decomposition in the presence of H_2O vapor are in good agreement (Table 4). We attribute these discrepancies to the specific features of temperature distribution in powders decomposed in vacuum, a fact not taken into account in our calculations. Consider this point in more detail.

3.2. *Temperature distribution in powders decomposed in vacuum*

Most studies of the decomposition of powders in vacuum 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 decomposition can be neglected. At the same time, Smith and Topley [20] and, later, Cooper and Garner [21] and Anous et al. [22] showed that the temperature of a single crystal decomposing in vacuum was lower than that of the furnace by 4–8 K. One may suggest that the self-cooling effect should be still stronger for powders.

Simulation of the temperature distribution, inside a powder sample, can be reduced to modelling the vertical temperature 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 a multilayered sample, from the central, 0th or 1st layer, to the *n*th outermost layer.

Disregarding heat conduction through point contacts among the grains and through residual gas present in the furnace, and assuming a steady-state decomposition, one can write for any *i*th layer the following equality between the amount of the heat expended for the decomposition and radiation and that received in the form of radiation from the adjacent layers

$$AT_i^{-1/2}\exp\frac{B}{T_i} + CT_i^4 = \frac{C}{2}\left(T_{i-1}^4 + T_{i+1}^4\right) \qquad (16)$$

where

$$A \equiv \frac{\gamma\Delta_r H_T^{\mathrm{o}} \exp\left(\Delta_r S_T^{\mathrm{o}}/2R\right)}{\left(2\pi\bar{M}R\right)^{1/2}} \qquad (17)$$

$$B \equiv -\frac{\Delta_r H_T^{\mathrm{o}}}{2R} \qquad (18)$$

and

$$C \equiv \varepsilon\sigma \qquad (19)$$

Here ε is the emittance of the grain surface and σ the Stefan–Boltzmann constant.

Eq. (16) can be conveniently recast in the form

$$T_{i+1}^4 = \frac{2A}{C}T_i^{-1/2}\exp\frac{B}{T_i} + 2T_i^4 - T_{i-1}^4 \qquad (20)$$

For the central (i=0, or i=1), coldest layer, one should write the following additional boundary condition

$$T_{i+1} = T_{i-1} \qquad (21)$$

if the total number of layers is odd (n_t=2n+1), or

$$T_i = T_{i-1} \qquad (22)$$

if it is even (n_t=2n). Thus Eq. (20) takes on the form

$$T_1^4 = \frac{A}{C}T_0^{-1/2}\exp\frac{B}{T_0} + T_0^4 \qquad (23)$$

for the case (21), and

$$T_2^4 = \frac{2A}{C}T_1^{-1/2}\exp\frac{B}{T_1} + T_1^4 \qquad (24)$$

for the case of Eq. (22). Eqs. (23) and (24) permit one to determine the temperature of the layer adjacent to the coldest layer, if the temperature of the latter is prescribed arbitrarily (T_0 or T_1). The temperatures of the other layers can be calculated from Eq. (20), with due account of the fact that the temperature of the (n+1)th layer should coincide with that of the furnace. To do this, one should vary properly T_0 to T_1 while keeping the other conditions constant. Computer is indispensable in such calculations.

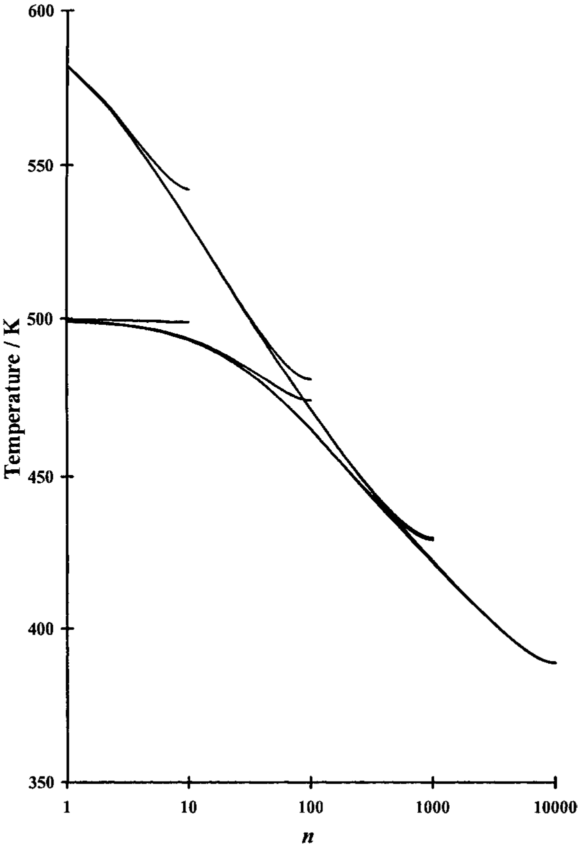

Fig. 1. Calculated temperature distribution for a $Mg(OH)_2$ powdered in vacuum at 500 and 600 K furnace temperature for the following different numbers of layers: 10, 10^2, 10^3 and 10^4.

As an illustration, Fig. 1 displays the temperature distribution for a $Mg(OH)_2$ powdered sample, calculated for different numbers of grain layers and two furnace temperatures, 500 and 600 K. An analysis of temperature distribution curves in Fig. 1 and of the results of calculations permits one to draw the following conclusions:

1. Other conditions being equal, the temperature of the outermost layer of a powdered sample is lower than that of the surface of a single-crystal sample. For instance, for a furnace temperature of 600 K, the temperature of the powder surface layer is 582.0 K, and that of the crystal surface, 593.2 K.
2. The temperature of the outermost powdered sample layer remains practically constant, irrespective of the number of the powder layers (for n>10), and depends only on the furnace temperature.
3. The temperature difference between adjacent layers decreases monotonically with distance from the surface.
4. The temperature of the central layer in the powdered sample depends primarily on the number of layers and remains practically constant for n>1000, irrespective of the furnace temperature. For example, for furnace temperatures of 500 and 600 K, the central-layer temperature is, accordingly, 472.7 and 479.3 K for n=100, 427.2 and 427.8 K for n=1000, and 386.6 K for n=10 000.

Obviously, disregarding this behavior of the temperature distribution within a powdered sample can result in significant errors in evaluating the kinetic parameters. Let us evaluate the contribution of these errors to the measurement data presented in Tables 3 and 4.

3.3. Corrections to kinetic parameters

To facilitate calculation of corrections to the kinetic parameters (J and E_a), we introduce the quantity

$$n_e \equiv \frac{\sum_{i=0}^{n} T_i^{-1/2} \exp(B/T_i)}{T_n^{-1/2} \exp(B/T_n)} \tag{25}$$

corresponding to the effective number of powdered sample layers whose decomposition occurs at the same rate as that of the surface layers. As shown by calculations (calculation of the quantity, n_e, can be conveniently performed simultaneously with that of the temperature distribution in the powder), the magnitude of n_e decreases rapidly with increasing furnace temperature. Remarkably, the value of n_e practically does not depend on the total number of layers n (provided n>100), and is determined only by the furnace temperature. Fig. 2 presents graphically a $n_e = f(T_f)$ relationship calculated for n=1000.

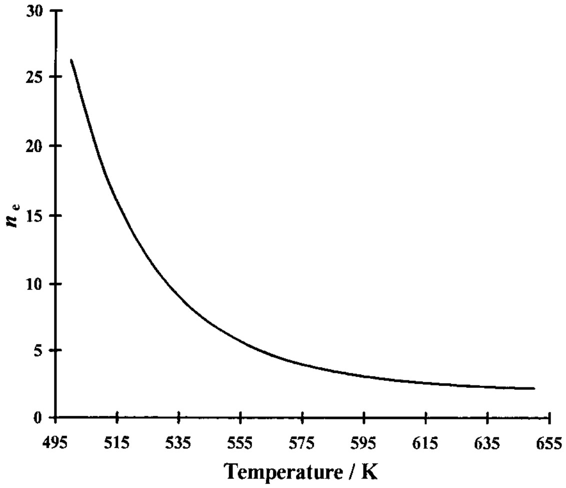

Fig. 2. Dependence of effective number of layers on furnace temperature for the decomposition of $Mg(OH)_2$ powder in vacuum.

Let us now calculate the corrections to the kinetic parameters J and E_a, measured without taking into account the temperature distribution in powdered samples. For both parameters, the deviation from the values, which correspond 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. Taking into account these two factors, the corrected values of the parameters (or, in other words, the values reduced to the assumed conditions of isothermal heating) can be calculated using the relationships

$$J_{cor} = \frac{P(T_f)}{P(T_s)} \frac{n}{n_e} J_{exp} \tag{26}$$

and

$$E_{cor} = \frac{(1/T'_f - 1/T''_f)E_{exp} + R\ln(n'_e/n''_e)}{1/T'_s - 1/T''_s} \tag{27}$$

Here one and two primes refer, respectively, to the lower and higher temperatures used to determine E_a and the corresponding parameters n_e, and the subscript 'exp', to the experimental values of the kinetic parameters. The quantities $P(T_f)$ and $P(T_s)$ denote the H_2O

vapor pressure for reaction (14) at the corresponding temperatures.

Using Eq. (6), we readily come to

$$\frac{P(T_\mathrm{f})}{P(T_\mathrm{s})} = \exp\left[\frac{\Delta_\mathrm{r}H_T^\circ}{2R}\left(\frac{1}{T_\mathrm{s}} - \frac{1}{T_\mathrm{f}}\right)\right] \tag{28}$$

whence one obtains

$$J_\mathrm{cor} = \exp\left[\frac{\Delta_\mathrm{r}H_T^\circ}{2R}\left(\frac{1}{T_\mathrm{s}} - \frac{1}{T_\mathrm{f}}\right)\right]\frac{n}{n_\mathrm{e}}J_\mathrm{exp} \tag{29}$$

Here, a few comments on the use of these equations are in order.

1. Eqs. (27) and (29) can be applied not only to powders but also to single crystals. In this case, $n_\mathrm{e}/n=1$, and the calculation of corrections takes into account only the temperatures of the furnace and of the sample. The temperature difference is calculated from Eq. (23).
2. The correction to the decomposition rate of a powdered sample includes the number of layers n. Assuming the powdered grains to be spherical and to have the same size, the value of n can be found knowing the grain radius r_0, the sample mass m and density ρ, and the diameter d of the balance pan on which the sample is placed. Taking the area, occupied by one grain in a powdered layer, to be a square with side $2r_0$, i.e. $4r_0^2$, we obtain for the total number of layers

$$n_t = \frac{12}{\pi^2}\frac{m}{\rho r_0 d^2} \tag{30}$$

3. The calculation of E_cor includes only the effective number of layers n_e which, as already mentioned, is practically independent of their total number. Therefore Eq. (27) can be used even in the cases where one cannot calculate the value of n. It is essential that $n>100$.

Taking due account of the aforementioned comments, we used Eqs. (27) and (29) to reduce the experimental values of the kinetic parameters (J and E_a) listed in Tables 3 and 4 to the conditions of the assumed isothermal heating of the sample. All this naturally relates to the measurements made in vacuum. In the presence of H_2O vapor and, even more so in a nitrogen atmosphere, heat conduction through gas makes sample heating more effective, so that the effect of self-cooling on the results of measurements may be neglected. (This assumption requires, however, additional quantitative validation.)

Table 5 presents the effective number of layers calculated for the conditions of Refs. [2–5], and Table 6 lists the original and corrected values of both kinetic parameters, J and E_a. In all cases, the corrected experimental values of J agree well with the theoretical values of 3.3×10^{-5} atm at 593 K and 5.0×10^{-5} atm at 600 K. The corrected value of E_a for the case of decomposition of a single crystal practically coincides with the theoretical value. For powdered samples, the corrected experimental values (198–205 kJ mol^{-1}) are somewhat in excess of the theoretical value of 173 kJ mol^{-1}. This can be attributed to an overevaluation of the self-cooling effect because the heat conduction through residual H_2O vapor present in the system (up to 10^{-7} atm) is neglected.

Taking into account the measurement errors of the original kinetic parameters and the assumptions made in calculations of the self-cooling effect, the agreement between the experimental and theoretical values for both kinetic parameters, relating to the decomposition of $Mg(OH)_2$ in vacuum, appears quite satisfactory. In addition, the likewise satisfactory agreement between theory and experiment observed in the case of $Mg(OH)_2$ decomposition in the presence of H_2O vapor and nitrogen (see Tables 3 and 4), we

Table 5
Number of layers in the experiments with powders

Sample mass/kg	Particle radius/m	Total number of grains	Diameter of balance pan/m	Total number of layers	n	Reference
$\approx5\times10^{-5}$ [a]	2.1×10^{-8}	5.4×10^{14}	$\approx1\times10^{-2}$ [a]	12000	6000	[2]
5×10^{-5}	4.2×10^{-8}	6.7×10^{13}	1×10^{-2}	6000	3000	[3]
2×10^{-5}	1.5×10^{-6}	5.9×10^{8}	1.5×10^{-2}	30	15	[5]

[a] Our estimation.

Table 6
Original and corrected values of decomposition rates and activation energies in the experiments with $Mg(OH)_2$ powders and single crystals (n=1) in vacuum

n	Temperature/K		n_e	n_e/n	$P(T_s)/P(T_f)$	J/(kg m^{-2} s^{-1})		E_a/(kJ mol^{-1})		Ref.
	Furnace	Sample				Original	Corrected	Original	Corrected	
6000	643	604.4	1.79	3.0×10^{-4}						[2]
6000	593	577.7	2.83	4.7×10^{-4}	0.396	1.0×10^{-8}	5.6×10^{-5}	100	201	[2]
6000	543	539.1	7.30	1.2×10^{-3}						[2]
3000	600	582.1	2.59	8.6×10^{-4}	0.346	1.3×10^{-8}	4.6×10^{-5}			[3]
3000	575	565.1	3.72	1.2×10^{-3}				115	205	[3]
3000	520	518.2	13.76	4.6×10^{-3}						[3]
15	600	582.2	2.57	0.17	0.348	1.9×10^{-6}	3.3×10^{-5}	121	198	[5]
15	514	513.0	10.92	0.73						[5]
1	663	628.1	1.00	1						[5]
1	600	593.5	1.00	1	0.685	7.0×10^{-5}	10×10^{-5}	126	172	[5]
1	550	549.6	1.00	1						[5]

may consider the proposed mechanism of decomposition of $Mg(OH)_2$ as well-substantiated.

4. Conclusions

The interpretation of the dehydroxylation kinetics of $Mg(OH)_2$ has been based on the same calculation scheme as that of the dehydration of $Li_2SO_4 \cdot H_2O$ [17], with the magnitude of the coefficient τ turning out to be practically the same for both cases, namely 0.60 for $Li_2SO_4 \cdot H_2O$ and 0.61 for $Mg(OH)_2$. This coincidence argues at least for the decomposition mechanisms of both compounds being identical. In our opinion, it reduces to dissociative evaporation of reactants, with subsequent condensation of the non-volatile products, Li_2SO_4 or MgO.

A comparison of the original with theoretical values of the kinetic parameters (J and E_a) has revealed a significant discrepancy of the results obtained in vacuum, particularly on powdered samples, with theory. We attribute this discrepancy to the self-cooling effect. Theoretical analysis has confirmed this conjecture of ours, and the corresponding correction scheme has permitted calculation of the deviations of experimental from expected results. The calculation scheme, for taking into account the self-cooling effect, can be used to study the decomposition kinetics in vacuum of other compounds as well. Apart from this, it offers a possibility of quantitative interpretation of the Topley–Smith effect [23].

Acknowledgements

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

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