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Thermochimica Acta 411 (2004) 73–79

thermochimica acta

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Kinetics of free-surface decomposition of magnesium and barium sulfates analyzed thermogravimetrically by the third-law method

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Received 25 March 2003; received in revised form 4 July 2003; accepted 25 July 2003

Abstract

The application of the third-law method to the determination of the E parameters in cases of free-surface decomposition of $MgSO_4$ and $BaSO_4$ in vacuum and investigation of the effect of oxygen in reactor atmosphere on the rate of $MgSO_4$ decomposition allowed to support the dissociative evaporation mechanism of decomposition of these sulfates with releasing of atomic oxygen as one of the primary products. The experimental values of the E parameter for $MgSO_4$ and $BaSO_4$ are equal to 335.7 ± 1.7 and $411 \pm 4\,\mathrm{kJ\,mol^{-1}}$. The serious difference in decomposition temperatures in vacuum (about 1000 and 1400 K) and the E parameters for these two sulfates is connected with the difference in transfer of condensation energy of oxides to the reactants. In cases of $MgSO_4$ and $BaSO_4$, the values of τ parameter are 0.42 and 0. Dependence of the τ parameter on the ratio of the equivalent pressure to the saturation pressure of corresponding metal oxide has been revealed from a comparison of τ parameters reported in the literature for eight different reactants. This correlation is of prime consideration for understanding of the mechanism of consumption of the condensation energy by the reactant.

Keywords: $BaSO_4$ decomposition; $MgSO_4$ decomposition; Kinetics; Mechanism; Third-law method

1. Introduction

Thermal decomposition of metal sulfates is one of industrial processes for obtaining sulfur dioxide and different metal oxides. Therefore, the investigation of kinetics and mechanism of this reaction is of obvious practical and theoretical interest. Most of the investigations of the sulfate decomposition were carried out before 1980s [1–3]. This can be seen from a comparison of data reported in monographs [2,3]. Decomposition of $MgSO_4$ and $BaSO_4$, which is the object of this work, was studied in [4–7]. Preliminary conclusions about the mechanism of $MgSO_4$ and $BaSO_4$ decomposition has been made also in recent publications [8,9]. The most common interpretation of sulfate decomposition reaction includes a two-step process [1–6]:

$$MgSO_4 \rightarrow MgO\,(s) + SO_3 \qquad (1)$$

$$SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2 \qquad (2)$$

Mohazzabi and Searcy [7] used a mass spectrometer to determine if SO_3 was present in the product, and, on this ground, came to conclusion that the decomposition process should be described as

$$BaSO_4 \rightarrow BaO\,(s) + SO_2 + \tfrac{1}{2}O_2 \qquad (3)$$

On the basis of thermodynamic analysis of the literature data, L'vov and Novichikhin [8] and L'vov [9] have proposed the dissociative evaporation scheme of $BaSO_4$ and $MgSO_4$ decomposition up to gaseous oxides, SO_2 and atomic oxygen:

$$BaSO_4 \rightarrow BaO\,(g) + SO_2 + O \qquad (4)$$

$$MgSO_4 \rightarrow MgO\,(g) \downarrow + SO_2 + O \qquad (5)$$

with the simultaneous condensation of low-volatility oxide MgO.

The purpose of this work consists in further investigation of kinetics of proposed reactions (4) and (5) with application of two new techniques based on the third-law method of determination of the E parameter and on the retardation effect of the excess of primary product in reactor atmosphere on the rate of decomposition. These techniques were described

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doi:10.1016/j.tca.2003.07.012

in detail elsewhere [10–14]. Therefore, only some final relationships describing dependence of the retardation effect on the partial pressure of gaseous product and equations necessary for the experimental determination of the E parameter by the third-law method will be presented below.

2. Theoretical

The main concept in the physical approach [9] applied in this work to the interpretation of kinetics consists of the belief that the decomposition of reactants into primary gaseous species proceeds under equilibrium conditions but the origin and composition of these primary products might differ from those at equilibrium. In the case of sulfates, this difference consists in the decomposition of MSO_4 into atomic oxygen and low-volatility gaseous molecules of MO, which subsequently condense with the formation of solid MO.

The equilibrium character of decomposition reactions has received recently [10] a strong confirmation. The mean ratio of the initial temperature of decomposition, T_{in}, to the E parameter for 100 different substances ($3.6 \pm 0.4\,\mathrm{kJ\,mol^{-1}}$) taken from the literature practically coincides with the value ($3.6 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$) predicted from equilibrium thermodynamics. The great advantage of the physical approach relative to the standard (chemical one) consists of the possibility for the quantitative description of the decomposition process using the laws of chemical thermodynamics. This possibility will be used in this work for the theoretical calculation and experimental determination of the E parameter.

2.1. Decomposition rate

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

$$\mathrm{S\,(s)} \rightarrow a\mathrm{A\,(g)}\downarrow + b\mathrm{B\,(g)} + c\mathrm{C\,(g)} \tag{6}$$

the flux of each product, which ultimately determines the rate of decomposition, can be expressed through the so-called equivalent partial pressure P_{eq} (atm) of this product corresponding to the hypothetical equilibrium of reaction (6) in the form:

$$J = \frac{\gamma M P_{eq}}{(2\pi MRT)^{1/2}} \tag{7}$$

where M is the molar mass of product. Here $\gamma = 101325\,\mathrm{Pa\,atm^{-1}}$ is the conversion factor from atmospheres to 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 situation corresponding to the *equimolar* evaporation mode, the partial pressure P_A can be expressed [9] as

$$\begin{aligned} P_A^e &= a\left(\frac{K_P}{F}\right)^{1/\nu}\left(\frac{M_A}{M_B}\right)^{b/2\nu}\left(\frac{M_A}{M_C}\right)^{c/2\nu} \\ &= \frac{a}{F^{1/\nu}}\left(\frac{M_A}{M_B}\right)^{b/2\nu}\left(\frac{M_A}{M_C}\right)^{c/2\nu} \\ &\quad\times \exp\frac{\Delta_r S_T^\circ}{\nu R}\exp\left(-\frac{\Delta_r H_T^\circ}{\nu RT}\right) \end{aligned} \tag{8}$$

where

$$F \equiv a^a \times b^b \times c^c \tag{9}$$

$$\nu = a + b + c \tag{10}$$

and

$$K_P = P_A^a \times P_B^b \times P_C^c \tag{11}$$

Here $\Delta_r H_T^\circ$ and $\Delta_r S_T^\circ$ are, respectively, the changes of the enthalpy and entropy in reaction (6).

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

$$\begin{aligned} P_A^i &= \frac{K_P^{1/(a+c)}}{P'^{\,b/(a+c)}_B}\left(\frac{M_A}{M_C}\right)^{c/2(a+c)} = \frac{1}{P'^{\,b/(a+c)}_B}\left(\frac{M_A}{M_C}\right)^{c/2(a+c)} \\ &\quad\times \exp\frac{\Delta_r S_T^\circ}{(a+c)R}\exp\left(-\frac{\Delta_r H_T^\circ}{(a+c)RT}\right) \end{aligned} \tag{12}$$

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 (6) an additional term $\tau a \Delta_c H_T^\circ(\mathrm{A})$, where the coefficient τ corresponds to the fraction of the condensation energy transferred to the reactant. Thus, we can write

$$\begin{aligned} \Delta_r H_T^\circ &= a\Delta_f H_T^\circ(\mathrm{A}) + b\Delta_f H_T^\circ(\mathrm{B}) + c\Delta_f H_T^\circ(\mathrm{C}) \\ &\quad - \Delta_f H_T^\circ(\mathrm{S}) + \tau a \Delta_c H_T^\circ(\mathrm{A}) \end{aligned} \tag{13}$$

For equal temperatures of the solid phases, one may expect equipartition of energy between the two phases, i.e. $\tau = 0.50$. For some of the substances investigated up to now, the condition $\tau = 0.50$ is found to be valid. At the same time for $MgCO_3$, $SrCO_3$ and $BaCO_3$, τ is equal to 0.47, 0.42 and 0.10 [13].

The magnitudes of thermodynamic functions (the entropy and enthalpy) for the components of decomposition reactions and for the reactions as a whole (marked by bold) at different temperatures are listed in Tables 1 and 2. A possible error (S.D.) in these calculations of $\Delta_r H_T^\circ$ values is within $6\,\mathrm{kJ\,mol^{-1}}$.

Table 1
Thermodynamic functions for $MgSO_4$ decomposition [15]

Function[a]	Temperature (K)		
	1000	1100	1200
S_T° (MgO_g)	262.7	268.0	272.8
S_T° (MgO_s)	82.2	87.1	91.6
S_T° (SO_2)	305.5	310.7	315.6
S_T° (O_2)	243.5	246.8	249.9
S_T° (O)	186.7	188.7	190.5
S_T° ($MgSO_4$)	241.1	255.8	269.6
$\Delta_r S_T^\circ$	**513.8 ± 3**	**511.6 ± 3**	**509.3 ± 3**
$\Delta_r S_T^\circ/\nu$	**171.3 ± 1**	**170.5 ± 1**	**169.8 ± 1**
$\Delta_f H_T^\circ$ (MgO_g)	72.1	77.6	83.2
$\Delta_f H_T^\circ$ (MgO_s)	−559.2	−554.1	−548.9
$\Delta_c H_T^\circ$ (MgO)	−631.3	−631.7	−632.1
$\Delta_f H_T^\circ$ (SO_2)	−249.4	−243.9	−238.4
$\Delta_f H_T^\circ$ (O_2)	31.4	34.9	38.4
$\Delta_f H_T^\circ$ (O)	268.4	270.5	272.5
$\Delta_f H_T^\circ$ ($MgSO_4$)	−1171.5	−1156.1	−1140.2
$\Delta_r H_T^\circ$ [b]	**997.5 ± 6**	**995.0 ± 6**	**992.0 ± 6**
$\Delta_r H_T^\circ/\nu$ [b]	**332.5 ± 2**	**331.7 ± 2**	**330.7 ± 2**

[a] All S_T° values are in $J\,mol^{-1}\,K^{-1}$ and all ΔH_T° values are in $kJ\,mol^{-1}$. The uncertainties indicated here and in the text correspond to the S.D.

[b] At $\tau = 0.42$ (see Section 4.1 on choosing this magnitude).

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:

$$\Delta_r H_T^\circ = T(\Delta_r S_T^\circ - R \ln K_P) \tag{14}$$

where as before $\Delta_r S_T^\circ$ is the entropy change and K_P the equilibrium constant for the reaction (6). Taking into account Eqs. (8), (10), (11) and (14) in the case of decomposition of sulfates in vacuum (the equimolar mode) can be reduced to the equation:

$$E^e = T(\tfrac{1}{3}(\Delta_r S_T^\circ) - R \ln P_{eq}) \tag{15}$$

Table 2
Thermodynamic functions for $BaSO_4$ decomposition [15]

Function[a]	Temperature (K)			
	1400	1423[b]	1423[b]	1500
S_T° (BaO_g)	290.8	291.4	291.4	293.4
S_T° (BaO_s)	155.1	156.0	156.0	159.2
S_T° (O_2)	255.4	256.0	256.0	258.0
S_T° (O)	193.7	194.0	194.0	195.1
S_T° (SO_2)	324.2	325.1	325.1	328.1
S_T° ($BaSO_4$)	350.5	353.5	360.5	369.5
$\Delta_r S_T^\circ$	**458.2 ± 3**	**457.0 ± 3**	**450.0 ± 3**	**447.1 ± 3**
$\Delta_r S_T^\circ/\nu$	**152.7 ± 1**	**152.3 ± 1**	**150.0 ± 1**	**149.0 ± 1**
$\Delta_f H_T^\circ$ (BaO_g)	−76.4	−75.5	−75.5	−72.7
$\Delta_f H_T^\circ$ (BaO_s)	−475.9	−474.5	−474.5	−469.8
$\Delta_c H_T^\circ$ (BaO)	−399.5	−398.9	−398.9	−397.1
$\Delta_f H_T^\circ$ (O_2)	45.6	46.5	46.5	49.3
$\Delta_f H_T^\circ$ (O)	276.7	277.2	277.2	278.8
$\Delta_f H_T^\circ$ (SO_2)	−227.2	−225.9	−225.9	−221.5
$\Delta_f H_T^\circ$ ($BaSO_4$)	−1264.2	−1260.0	−1250.0	−1236.9
$\Delta_r H_T^\circ$ [c]	**1237.3 ± 6**	**1235.8 ± 6**	**1225.8 ± 6**	**1221.5 ± 6**
$\Delta_r H_T^\circ/\nu$ [c]	**412.4 ± 2**	**411.9 ± 2**	**408.6 ± 2**	**407.2 ± 2**

[a] All S_T° values are in $J\,mol^{-1}\,K^{-1}$ and all ΔH_T° values are in $kJ\,mol^{-1}$. The uncertainties indicated here and in the text correspond to the S.D.

[b] $T = 1423\,K$ corresponds to the point of $\alpha \rightarrow \beta$ phase transformation of $BaSO_4$.

[c] At $\tau = 0$ (see Section 4.1 on choosing this magnitude).

The equivalent pressure of the gaseous product (B or C) is related to the total absolute rate of decomposition, J ($kg\,m^{-2}\,s^{-1}$), by the Hertz–Langmuir equation (7) rewritten as

$$P_{eq} = \frac{(2\pi RT)^{1/2} J}{2\gamma} \left(\frac{\sqrt{M_B} + \sqrt{M_C}}{M_B + M_C} \right) \tag{16}$$

The factor 2 in denominator and additional factor in brackets are installed in this equation to take into account the fact that the J value actually includes the flows of two gaseous products (B and C) with the different molar masses.

As can be seen from the analysis of results reported in [15] 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 mainly connected with the systematic and random errors in the determination of the true temperature of reactant (for example, because of the self-cooling effect). Instead of a proportional dependence of the error in ΔH_T° determination on the error of T in the case of the third-law method, the error in ΔH_T° determination is proportional to the error in the slope of the plot in the case of the second-law and Arrhenius-plots methods [10]. For illustration, at $T_{min} = 900$ and $T_{max} = 1000\,K$, the error in 10 K ($T_{max} = 990\,K$) results in the error in ΔH_T° 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 rhombic crystals of natural barite and high purity powders of anhydrous magnesium and barium sulfates. A powder sample (20 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). The surface area of crystal was evaluated from the known mass and the density of barite ($4500\,kg\,m^{-3}$) taking into account a real shape of the crystal.

In experiments on determination of the *E* parameter, the sample chamber was evacuated to a residual pressure about $n \times 10^{-8}$ atm 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 10 K min^{-1} and from intermediate to the desired temperature was 2 K min^{-1}. At the beginning of each measuring cycle, the system was heated at the temperature chosen, usually during 10 min, to reach a constant rate of the decomposition. The changes of the mass and surface area of crystals and powders during this period were taken into account. A decrease of the surface area, as was checked experimentally, was proportional to $(1-\alpha)^{2/3}$ where α is the decomposition degree. Temperature was measured with Pt–Pt10%Rh thermocouple placed with its junction immediately below the crucible. Temperature variations in the process of mass-change measurements (usually, during 20–30 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 of $MgSO_4$ was estimated using the method proposed in our previous work [12]. 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 [12–14], does not depend on the temperature, residual pressure of gas in the reactor, grain size and mass of a powder sample. This is not the case for $BaSO_4$. Due to the high saturation pressure of BaO vapor, which is comparable with the equivalent pressure (see below), the decomposition of particles in inner parts of powder sample is blocked and decomposition occurs only on the outer surface of the sample. In this case, the correction factor should be omitted. To support this statement, a comparative experiment with $BaSO_4$ crystal has been performed.

The experiments on the retardation effect of oxygen on the decomposition of $MgSO_4$ were carried out in two different gases: nitrogen and air at atmospheric pressure. In this case, only relative losses of mass over 100 min were measured under isothermal conditions. The purpose of these experiments was to prove the absence of any significant retardation effect of O_2 on the decomposition rate (in comparison with that in nitrogen).

4. Results and discussion

4.1. Interpretation of decomposition kinetics on the basis of vacuum experiments

Experimental conditions and results of determination of the *E* parameter for $MgSO_4$ and $BaSO_4$ decomposition in vacuum by the third-law method are presented in Table 3. As expected, the reproducibility of determinations of the *E* parameter is very high. If one compares the kinetic parameters for these two sulfates, serious differences in the decomposition temperatures and the *E* parameters stand out. The decomposition temperature for $BaSO_4$ is about 400 K higher and the *E* parameter is 80 kJ mol^{-1} higher than these parameters for $MgSO_4$. This is difficult to understand because the enthalpies for dissociative evaporation for both sulfates (without taking into account the condensation energy transfer to the reactant or at $\tau = 0$) are approximately equal: 1263 and 1237 kJ mol^{-1} (see Tables 1 and 2). The only explanation of this difference in the framework of a physical approach is to propose that the value of τ parameter for these sulfates is different. In case of $BaSO_4$, its value should be equal to zero ($\tau = 0$). Then the theoretical values of the *E* parameter at 1397 and 1427 K (412.4 and 408.6 kJ mol^{-1}) are the most close to experiment (415.8 and 407.6 kJ mol^{-1}). The discrepancy is lower than 1%. Any increase of the τ parameter may only enlarge the discrepancy. At first glance, this explanation may seem to be strange because solid BaO is the real product of $BaSO_4$ decomposition. However, if we compare the saturation pressure of BaO vapor at 1397 K (1.4×10^{-8} atm) with the equivalent pressure (2.7×10^{-8} atm), it can be seen that these values are very close. Under this condition, the transfer of the condensation energy to the reactant, as might be expected, is inefficient.

In case of $MgSO_4$, the difference between the equivalent pressure and the saturation pressure of MgO vapor at

Table 3
Experimental conditions and results of determination of the *E* parameter for sulfate decomposition in vacuum by the third-law method

Sulfate	Sample	T (K)	m_0 (mg)	S_0 (mm^2)	α_m[a]	S_m[b] (mm^2)	$\Delta m/\Delta t$[c] (µg s^{-1})	J_{corr}[c] (kg m^{-2} s^{-1})	P_{eq} (atm)	$(\Delta_r S^{\circ}_T/\nu)$ (J mol^{-1} K^{-1})	E (kJ mol^{-1})
$MgSO_4$	Powder	1005.8	20.0	61.78	0.0464	59.86	0.117	6.98×10^{-7}	3.75×10^{-9}	171.3	334.5
$MgSO_4$	Powder	1005.5	20.0	61.78	0.0225	60.85	0.089	5.22×10^{-7}	2.80×10^{-9}	171.3	336.9
$BaSO_4$	Powder	1396.9	20.0	57.30	0.1513	51.37	0.216	4.20×10^{-6}	2.66×10^{-8}	152.7	415.9
$BaSO_4$	Powder	1396.3	20.0	57.30	0.0948	53.62	0.227	4.23×10^{-6}	2.68×10^{-8}	152.7	415.6
$BaSO_4$	Crystal	1426.6	20.2	18.66	0.0359	18.21	0.232	1.27×10^{-5}	8.12×10^{-8}	150.0	407.6

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

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

[c] $J_{cor} = (\Delta m/\Delta t)/2.8S_m$ for $MgSO_4$ and $J_{cor} = (\Delta m/\Delta t)/S_m$ for $BaSO_4$.

Table 4
Kinetics of isothermal decomposition of $MgSO_4$ in atmosphere of nitrogen and air at 1202 K

Atmosphere	Consecutive run of the relative loss of mass per each 10 min (%)										Overall loss over 100 min (%)[a]
Nitrogen	0.71	0.87	0.88	0.91	0.92	0.93	0.94	0.96	0.97	0.97	9.06
Nitrogen	0.83	0.88	0.88	0.93	0.94	0.95	0.96	0.98	0.98	1.02	9.35
Air	0.84	0.90	0.89	0.89	0.89	0.88	0.90	0.91	0.90	0.97	8.97
Air	0.78	0.87	0.89	0.86	0.90	0.90	0.89	0.89	0.91	0.88	8.69

[a] Averaged loss ratio: nitrogen/air = (9.06 + 9.35)/(8.97 + 8.69) = 1.042.

1000 K reaches 15 orders of magnitude, so that efficiency of transfer of the condensation energy to $MgSO_4$ is expected to be high. The best correlation between experimental (335.7 ± 1.7 kJ mol^{-1}) and theoretical (332.5 ± 2 kJ mol^{-1}) values of the E parameter is observed at $\tau = 0.42$. This magnitude is lower than the value 0.50 observed for $CaCO_3$ [11] and $MgCa(CO_3)_2$ [12] but higher than the value of τ (0.10) for decomposition of $BaCO_3$ [13]. Therefore, it must not be ruled out that the composition of primary products of decomposition differs from that in reaction (5). In particular, it can be proposed that all or a part of oxygen in the process of $MgSO_4$ decomposition is released as O_2 and the value of τ parameter is actually lower than 0.42. For example, the E parameter for the reaction

$$MgSO_4 \rightarrow MgO\,(s) \downarrow + SO_2 + \tfrac{1}{2}O_2 \qquad (17)$$

under condition of $\tau = 0.28$ should be equal to 333.3 ± 2 kJ mol^{-1}. This value is also in agreement with the experimental (335.7 ± 1.7 kJ mol^{-1}) value. Therefore, additional experiments are necessary to prove the absence of molecular oxygen in primary products of $MgSO_4$ decomposition.

4.2. *Decomposition of $MgSO_4$ in nitrogen and air*

To check this statement, we measured the decomposition rate of $MgSO_4$ in two gases: nitrogen and air at 1202 K and 1 atm pressure (see Table 4). The only difference between these gases is the presence in air of about 21% O_2. If the decomposition proceeds in accord with reaction (17), the presence of O_2 should seriously reduce the rate of decomposition. As follows from Eqs. (8)–(12), the ratio of the equilibrium pressures in nitrogen and air, which corresponds to the ratio of decomposition rates, in case of $MgSO_4$ decomposition is equal to

$$\frac{P_A^e}{P_A^i} \cong 1.20\frac{(P'_B)^{0.25}}{K_P^{0.1}} \qquad (18)$$

If we install into Eq. (18) $P'_B = 0.21$ and $K_P = 1.707 \times 10^{-13}$ atm$^{2.5}$ valid for reaction (17) at $T = 1202$ K, we obtain the value $P_A^e/P_A^i \cong 15.4$. As can be seen from Table 4, the actual ratio of the decomposition rates is equal to 1.04. The absence of any significant retardation effect of O_2 on the rate of $MgSO_4$ decomposition means that the release of oxygen in the process of decomposition occurs in the form of O atoms in accord with reaction (5). A residual difference (4%) in the decomposition rates can be related with higher value of the coefficient of diffusion of gaseous species (SO_2) in nitrogen compared to that in air [16].

4.3. *The literature data on decomposition kinetics of $MgSO_4$ and $BaSO_4$*

The literature data on the E parameter for decomposition of $MgSO_4$ and $BaSO_4$ are presented in Table 5. (For completeness, the results obtained in this work are included.) The results reported in work [4] seem to be the least reliable. The decomposition temperature was about 100 K higher than in other works [5,6] and only three points were used for plotting the Arrhenius graph. The value obtained for pure $MgSO_4$ (661.1 kJ mol^{-1}) is unrealistically high. In case of

Table 5
Experimental conditions and kinetic characteristics for the decomposition of Mg and Ba sulfates (overall data)

Reactant	Sample	Atmosphere	Temperature (K)	Point number	Method	E (kJ mol^{-1})	Reference
$MgSO_4$	Powder	N_2 flow	1293–1333	3	Arrhenius plots	661.1, 369.4[a]	[4]
$MgSO_4$	Powder	Air	1164–1245	5	Arrhenius plots	343.1 ± 10	[5]
$MgSO_4$	Powder	Air	1193–1353	7	Arrhenius plots	311.7 ± 13	[6]
$MgSO_4$	Powder	Vacuum	1006	2	Third-law	335.7 ± 1.7	This work
$BaSO_4$	Crystal	Vacuum	1422–1540	42	Second-law	383.5 ± 8.4[b]	[7]
$BaSO_4$	Crystal	Vacuum	1450	1	Third-law	409.7[c]	[7]
$BaSO_4$	Powder	Vacuum	1397	2	Third-law	415.8 ± 0.2	This work
$BaSO_4$	Crystal	Vacuum	1427	1	Third-law	407.6	This work

[a] For pure $MgSO_4$ and $MgSO_4 + 5\%\ Fe_2O_3$, respectively.

[b] The "apparent enthalpy of activation" for reaction (3): 575.3 ± 12.6 kJ (mol $BaSO_4$)$^{-1}$ [7] is related to 1 mol of gaseous products.

[c] Calculated in this work on the basis of data reported in [7]: $P_{eq} = 1.15 \times 10^{-7}$ atm at $T = 1450$ K ($\Delta_r S^\circ_{1450}/\nu = 149.7$ J mol^{-1} K^{-1}).

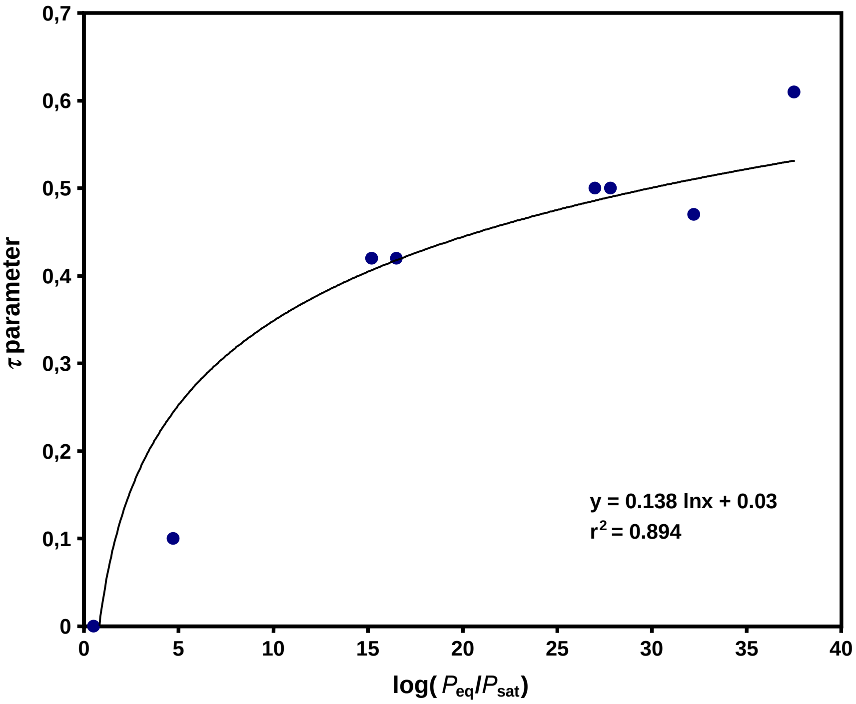

Fig. 1. Dependence of τ parameter on the ratio of the equivalent pressure of metal oxide to its saturation pressure at decomposition temperature.

mixture of $MgSO_4$ with 5% Fe_2O_3, the value of the *E* parameter (369.4 kJ mol^{-1}) is more reasonable. Of two other works [5,6], the result reported in [5] is probably more reliable because of lower temperatures used in experiment. This result is in a good agreement with our data (only 2% higher).

The value of the *E* parameter for $BaSO_4$ decomposition calculated by the second-law method [7] is probably underestimated because of the self-cooling effect. This is obvious from a comparison of the results calculated by the third-law and second-law methods. The similar discrepancy has been observed in cases of determination of the *E* parameter for calcite [11], dolomite [12] and witherite ($BaCO_3$) [13]. At the same time, the value calculated by the third-law method (409.7 kJ mol^{-1}) is in excellent agreement with the theoretical value (408.1 ± 2 kJ mol^{-1}) at 1450 K (see Table 2) and with our results: 407.6 and 415.7 kJ mol^{-1} at 1427 and 1397 K, respectively.

Table 6

Dependence of τ parameter on the ratio of the equivalent pressure of metal oxide to its saturation pressure at decomposition temperature

Reactant	*T* (K)	$\log(P_{eq}/P_{sat})$	τ parameter	Reference
$BaSO_4$	1400	0.5	0	This work
$BaCO_3$	1077	4.7	0.10	[13]
$MgSO_4$	1000	15.2	0.42	This work
$SrCO_3$	908	16.5	0.42	[13]
$CaCO_3$	800	27.0	0.50	[13]
$MgCa(CO_3)_2$	812	27.8	0.50	[13]
$MgCO_3$	670	32.2	0.47	[13]
$Mg(OH)_2$	600	37.5	0.61	[17]

4.4. *Dependence of τ parameter on condensation conditions of low-volatile product*

The availability of the reliable values of τ parameters obtained recently in cases of decomposition of different reactants for alkaline earth metals made it possible to correlate these values with the conditions of condensation of low-volatility oxides for these metals. Of several possible parameters, we used the ratio of the equivalent pressure to the saturation pressure of corresponding metal oxide (P_{eq}/P_{sat}) as a criterion responsible for this correlation. As can be seen from the data presented in Table 6 and especially from Fig. 1, there is a rather monotonous increase of τ parameter with log (P_{eq}/P_{sat}). This correlation is not only of practical importance but is of prime consideration for understanding of the mechanism of consumption of the condensation energy by the reactant. This problem calls for further experimental and theoretical investigation.

5. Conclusions

The application of the third-law method to the determination of the *E* parameters in cases of free-surface decomposition of $MgSO_4$ and $BaSO_4$ in vacuum and investigation of the effect of oxygen in reactor atmosphere on the rate of $MgSO_4$ decomposition allowed to support the dissociative evaporation mechanism of decomposition of these sulfates with releasing of atomic oxygen as one of the primary products. The experimental (averaged) and theoretical values of the *E* parameter, which can be recommended as the most

Table 7
The ultimate experimental[a] and theoretical values of the E parameter

Decomposition reaction	T (K)	τ	E (kJ mol^{-1})	
			Experiment	Theory
$MgSO_4 \rightarrow MgO (g) \downarrow + SO_2 + O$	1200	0.42	330 ± 16	331 ± 2
$BaSO_4 \rightarrow BaO (g) \downarrow + SO_2 + O$	1425	0	411 ± 4	409 ± 2

[a] The most reliable data from the literature [5–7] and this work are averaged.

reliable data, are presented in Table 7. The serious difference in decomposition temperatures and the E parameters for these two sulfates is connected with the difference in transfer of condensation energy of oxides to the reactants. In cases of $MgSO_4$ and $BaSO_4$, the values of τ parameter are 0.42 and 0.

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