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KINETICS AND MECHANISM OF DEHYDRATION OF KAOLINITE, MUSCOVITE AND TALC ANALYZED THERMOGRAVIMETRICALLY BY THE THIRD-LAW METHOD

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The third-law method has been applied to determine the enthalpies, $\Delta_r H_T^0$, for dehydration reactions of kaolinite, muscovite and talc. The $\Delta_r H_T^0$values measured in the equimolar (in high vacuum) and isobaric (in the presence of water vapour) modes (980±15, 3710±39 and 2793±34 kJ mol^{-1}, for kaolinite, muscovite and talc, respectively) practically coincide if to take into account the strong self-cooling effect in vacuum. This fact strongly supports the mechanism of dissociative evaporation of these compounds in accordance with the reactions (primary stages): $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O(s){\rightarrow}Al_2O_3(g){\downarrow}+2SiO_2(g){\downarrow}+2H_2O(g)$; $K_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2H_2O(s){\rightarrow}$ ${\rightarrow}K_2O(g){\downarrow}+3Al_2O_3(g){\downarrow}+6SiO_2(g){\downarrow}+2H_2O(g)$ and $3MgO{\cdot}4SiO_2{\cdot}H_2O(s){\rightarrow}3MgO(g){\downarrow}+4SiO_2(g){\downarrow}+H_2O(g)$. The values of the *E* parameter deduced from these data for equimolar and isobaric modes of dehydration are as follows: 196 and 327 kJ mol^{-1} for kaolinite, 309 and 371 kJ mol^{-1} for muscovite and 349 and 399 kJ mol^{-1} for talc. These values are in agreement with quite a few early results reported in the literature in 1960s.

Keywords: *dehydration kinetics, dissociative evaporation, kaolinite, muscovite, talc, third-law method*

Introduction

Layer silicates, including clays, which occur in geological deposits, are of considerable importance as source materials for many technological uses. Studies of thermal dehydration of such materials have been undertaken to determine the mechanisms of changes, which occur during firing [1, 2]. Such knowledge may be then exploited in the design of individual processes, the use of cheaper source minerals and development of new products. Besides, it is of considerable scientific interest. Of three compounds chosen in this work for investigation, kaolinite, muscovite and talc, the first one is studied more than two others. Nevertheless, even for kaolinite, the major features of this process remain an enigma. In particular, there are serious disagreements between the values of the *E* parameter of the Arrhenius equation reported in different works [3–10]. In the absence of water vapour in the reactor, the values of the *E* parameter range from 159 [3], 172 [8] and 182 kJ mol^{-1} [4] to 213 [7] and 233 kJ mol^{-1} [10]. Still higher discrepancies in the *E* parameters are observed in the presence of water vapour. Weber and Roy [6] reported a value of 490 kJ mol^{-1} at $P_{H_2O}\cong 1$ bar. Brindley *et al.* [7] found a value of 352 kJ mol^{-1} at P_{H_2O}=6 mbar and of 469 kJ mol^{-1} at P_{H_2O}=60 mbar. Anthony and Garn [9] observed an increase of the *E* parameter from 261 to 1060 kJ mol^{-1} at P_{H_2O} increase from 0.4 to 3.2 bar. In contradiction to a significant increase of the *E* parameter observed in these papers, some workers reported that the *E* parameter decreases in the presence of water vapour. In particular, Toussaint *et al.* [5] measured a value of 105 kJ mol^{-1} at P_{H_2O}=6 mbar and Nahdi *et al.* [10] have found recently a value of 188 kJ mol^{-1} at P_{H_2O}=5 mbar.

These discrepancies in values of the *E* parameter are caused, in our opinion, by the shortages of the methods, which used for determination of this parameter. No wonder that under these circumstances no single reasonable explanation has been found up to now for the dehydration mechanism and the effect of water vapour on the decomposition rate. The primary purpose of this paper is to measure the reaction enthalpies and related values of the *E* parameter for dehydration of kaolinite, muscovite and talc in the absence and in the presence of water vapour by the most precise and reliable third-law method, which has been successfully used already for investigation of many other decomposition reactions [11, 12]. The values obtained will be used for the interpretation of the dehydration mechanism and the related effect of water vapour.

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Theoretical

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

$$\Delta_r H_T^0 = T(\Delta_r S_T^0 - \mathrm{R}\ln K_P) \qquad (1)$$

where $\Delta_r H_T^0$ and $\Delta_r S_T^0$ are, respectively, the enthalpy and entropy for the decomposition reaction and K_P is the equilibrium constant. In case of a reactant R decomposed (in accord with the dissociative evaporation mechanism [11]) into gaseous products A and B with successive condensation of low-volatility species A, that is

$$\mathrm{R}(s/l) \rightarrow a\mathrm{A}(g)\downarrow + b\mathrm{B}(g) \qquad (2)$$

the equilibrium constant is equal to

$$K_P = P_A^a P_B^b \qquad (3)$$

The so-called equivalent partial pressure P_{eq} (in bar) of product A can be calculated by the Hertz–Langmuir equation through the maximum rate of decomposition J (in kg m^{-2} s^{-1}):

$$P_{eq} = \frac{(2\pi \overline{M} RT)^{1/2} J}{\gamma M_B} \qquad (4)$$

Here $\gamma=10^5$ Pa bar^{-1} is the conversion factor from bars to pascals and $\overline{M}$ is the geometrical mean for molar masses of primary products or

$$\overline{M} = (M_A^a M_B^b)^{1/(a+b)} = (M_A^a M_B^b)^{1/\nu} \qquad (5)$$

where $\nu=a+b$.

Under high vacuum conditions (the equimolar mode), the equilibrium constant with regard to the stoichiometric coefficients in reaction (2) is equal

$$K_P = P_A^a P_B^b = \left(\frac{b}{a}\right)^b P_{eq}^{\nu} \qquad (6)$$

In the presence of the excess of gaseous product B in the reactor (the isobaric mode),

$$K_P = P_A^a P_B^b = P_{eq}^a P_B^b \qquad (7)$$

Condition of maximum-rate or free-surface decomposition in the equimolar mode means the absence of any diffusion limitations for the escape of gaseous product(s) from the surface of decomposed sample. In case of dehydration reactions, the only stable gaseous product is water vapour. The other primary products (or product) being of low volatile species immediately condense. To eliminate diffusion limitations for a water vapour escape, it is necessary to use high vacuum in the reactor.

In the presence of excess of water vapour in the reactor (the isobaric mode), the diffusion limitations for the escape of water vapour evolved during the decomposition are practically insignificant because the external partial pressure of H_2O is significantly higher than the equivalent pressure. This feature opens a remarkable opportunity of the isobaric free-surface dehydration in the presence of any foreign gas, in particular, in the air atmosphere. Indeed, the presence of air has no additional effect on the decomposition rate because (*i*) all low-volatile primary products immediately condense and (*ii*) the diffusion limitations for the escape of water vapour evolved during the decomposition are practically insignificant. It means that in the presence of the excess of water vapour in the reactor the Hertz-Langmuir equation can be used for evaluation of the equivalent pressure of primary products of dehydration not only in vacuum or at reduced pressure but even (amazingly!) at atmospheric or higher than atmospheric pressure.

As has been shown in many previous publications (e.g. [11]), the E parameter for the Arrhenius equation should be different for the equimolar and isobaric modes of decomposition, i.e.,

$$E^e = \Delta_r H_T^0 / \nu = \Delta_r H_T^0 / (a+b) \qquad (8)$$

for the equimolar mode and

$$E^i = \Delta_r H_T^0 / (\nu - b) = \Delta_r H_T^0 / a \qquad (9)$$

for the isobaric mode. In the former case, the E parameter corresponds to the enthalpy of the decomposition reaction reduced to one mole of all primary products or to the molar enthalpy, and in the latter case, to the enthalpy of the decomposition reaction reduced to one mole of primary products without including components of that present in excess.

As it follows from the further consideration of Eqs (1)–(4), using the third-law method for determination of the reaction enthalpy assumes the availability of data necessary for calculation of the entropy of reaction, $\Delta_r S_T^0$, and measuring the absolute rate of decomposition, J, what suggests a possibility for evaluation of the efficient surface area of decomposed sample. Let us consider these topics in more detail.

For crystals or pressed pellets with a low porosity, the effective surface area of decomposition can be easily evaluated from the known geometry of samples. For powder samples, the calculation procedure consists in reduction of the decomposition rate ($\Delta m/\Delta t$) to the unit of the outer surface area (S_m) of a pellet formed by the powder sample in a cylindrical crucible. The value received is lowered additionally by the empirical factor (2.8±0.4), which takes into account a higher than S_m efficient surface area of powder sample responsible for decomposition. The magnitude of this factor, as shown in [13], does not depend on the temperature, residual pressure of air in the reactor (at $P_{H_2O} < 10^{-4}$ bar), grain size and mass of a powder sample. Therefore, the final equation for calculation of absolute rate of powder decomposition is as follows:

$$J = (\Delta m / \Delta t) / (2.8\ S_m) \qquad (10)$$

The availability of data necessary for calculation of the entropy of reaction, $\Delta_r S_T^0$, is at first glance a serious limitation for application of the third-law method. Fortunately, the situation in this field is significantly improved over the last 40 years and for majority of substances the values of entropies in standard conditions (S_{298}^0) and corresponding temperature increments ($S_T^0 - S_{298}^0$) were calculated and published in tabulated form in many handbooks. Nevertheless, for some species, for example, for low-volatility molecules in the gaseous state (e.g., metal salts), these data are absent. In some cases, it is possible to estimate the entropy value from a comparison with the known entropies of similar molecules for other metals. This approach was used, for example, for gaseous molecules of Li_2SO_4, $CaSO_4$ and $CuSO_4$ [14].

More general approach for estimation of entropy, $\Delta_r S_T^0$, for decomposition reactions was proposed in [15]. This approach is based on a very close similarity of values of molar entropy, $\Delta_r S_T^0/\nu$, for different decomposition reactions. Their average magnitude (under conditions when $P_{eq} \cong 10^{-8}$–10^{-7} bar) is 148±17 J mol^{-1} K^{-1} [15]. Moreover, the recent analysis [11] has revealed significant differences in $\Delta_r S_T^0/\nu$ between the reactants decomposed with formation of free metal atoms and reactants decomposed up to metal products in the form of free molecules. The average value of $\Delta_r S_T^0/\nu$ is equal to 136±9 J mol^{-1} K^{-1} in the first case and to 160±9 J mol^{-1} K^{-1}, in the second. The uncertainty in values of $\Delta_r S_T^0/\nu$ (± 9 J mol^{-1} K^{-1}) produces the error in determination of the E parameter to about 3%. Therefore, the impact of this factor on a background of the overall, random and systematic, error is insignificant [12].

Experimental

The experiments were carried out with Netzsch STA 429 and STA 449 instruments on the TG and TG+DSC measuring heads, respectively. The actual measured quantities were the mass change of the sample per time unit, $\Delta m/\Delta t$, and the absolute crucible temperature. The open alumina crucibles 5.7 mm inner diameter and 4.0 mm high (without lids) were used as sample containers.

The reacting materials were the analytical grade kaolinite powder and mica pieces of muscovite and talc. All materials were checked via a mass loss during dynamic firing. A powder sample (ca. 20 mg), which 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. In cases of muscovite and talc, small rectangular pieces of mica were cut (about 3–4 mm in sides and 0.2–0.5 mm in thickness). Their surface areas were estimated with the help of an MPB-2 optical (×24) microscope.

In experiments under reduced pressure performed with a STA 429 instrument, the sample chamber was evacuated to a residual pressure in the range of $n \cdot 10^{-5}$ bar with the use of rotation pump or in the range $n \cdot 10^{-8}$ bar with the use of rotation and oil-diffusion pumps. The measurements have been conducted at continuous pumping under isothermal conditions. Experiments in the presence of the excess of H_2O in the reactor (both STA 429 and STA 449 instruments were used) have been performed at atmospheric pressure in the furnace under conditions of isobaric and, at the same time (as discussed above), free-surface evaporation. The partial pressure of water vapour was evaluated from humidity percentage in the laboratory (from hygrometer readings) and the saturated pressure of H_2O at known air temperature in the room.

The heating rate of the sample from the room temperature to intermediate one (5 K lower than the desired temperature) was 30 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 5–10 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, 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. All primary signals ($\Delta m/\Delta t$) were corrected also for the blank signal measured independently with an empty crucible. Its value varied in the range of 0.02–0.07 μg s^{-1} depending on the gas pressure and temperature of the furnace.

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 15–30 min) did not exceed ±0.2 K.

Results and discussion

This work

There are two problems in determination of the decomposition rates and calculation of the enthalpies for these reactants. Firstly, all three materials have a very low emittance factor and their heating by radiation is low. Therefore, to reduce the self-cooling effect, it is preferable to work at a residual air pressure higher than ca. 10^{-4} bar or, what is still better, at atmospheric pressure when the heat transfer by the gas molecules (for powder samples) reaches its maximum. Secondly, any literature data on the temperature increments of entropy ($S_T^0 - S_{298}^0$) for kaolinite, muscovite and talc are absent. Therefore, the only way to evaluate the entropy change for dehydration reactions is to use the approximate value of molar entropy $\Delta_r S_T^0/\nu=160\pm9$ J mol^{-1} K^{-1}, which is valid for reactants decomposed up to metal products in the form of free molecules. The number of moles of primary decomposition products, ν, is related to the stoichiometry of these compounds and in cases of kaolinite, muscovite and talc is as follows: 5, 12 and 8. Therefore, the entropy change $\Delta_r S_T^0$ should be equal, respectively, to 800, 1920 and 1280 J mol^{-1} K^{-1}.

Experimental conditions and results of calculations of the enthalpy values for a dehydration of kaolinite, muscovite and talc are presented in Tables 1–4. From the analysis of these data, the following conclusions might be deduced.

- As can be seen from Tables 1 and 2, under high-vacuum conditions ($n \cdot 10^{-8}$ bar), the enthalpy values are about 9% higher than those at atmospheric pressure. This is the result of self-cooling effect, which manifests in an increase of values calculated by the third-law method [13, 14]. For talc (Table 3), this difference is lower (4%), probably, due to the higher decomposition temperature. As expected, under low-vacuum conditions ($8 \cdot 10^{-5}$ bar) for the kaolinite decomposition (Table 1) the enthalpy values are only 3% higher than those at atmospheric pressure. All results measured in vacuum were omitted in calculations of the mean values listed in Table 4.
- The relative standard deviation from the mean in all cases is smaller than 2 percent (Table 4). This supports a high precision (reproducibility) of the third-law method that was theoretically substantiated in [11, 12] and demonstrated in many our previous publications [13–15].
- The similarity of the results obtained under very different conditions of decomposition (in vacuum at low values of P_{H_2O} and in atmosphere of air at high values of P_{H_2O}) means that the dissociative evaporation mechanism of dehydration of these reactants, as described by reactions in Table 4, is valid.
- The values of the E parameter for the equimolar and isobaric modes of decomposition listed in the two last columns of Table 4 are calculated by Eqs (8) and (9). It is remarkable that of the different parameters obtained by this approach ($\Delta_r H_T^0$, E^e and E^i), the molar enthalpy ($\Delta_r H_T^0/\nu=E^e$) is the only parameter directly related to the decomposition temperature in the equimolar mode. Indeed, in all cases, in accord with the theory [15], the ratio $T/E^e \cong 3.5\pm0.1$ K kJ^{-1} mol. To relate the $\Delta_r H_T^0$ or E^i parameter to decomposition temperature, the stoichiometry coefficients (a, b and ν) should be additionally taken into account.

The literature data

- The average value of the E parameter measured for kaolinite in the absence of water vapor in the reactor (the equimolar mode) in different works (159 [3], 172 [8], 182 [4], 213 [7] and 233 kJ mol^{-1} [10]) is equal to 192±30 kJ mol^{-1}. This value is in excellent agreement with E^e=196±3 kJ mol^{-1} obtained in the present work. However, the standard deviation differs dramatically.
- Of the E parameters for kaolinite measured in the presence of water vapor in the reactor (the isobaric mode), the values that are similar to our result (327±5 kJ mol^{-1}) were obtained by Brindley *et al.* [7]. At 6 and 18 mbar of water vapour pressure, the E^i parameter was 351.5 and 376.6 kJ mol^{-1} (average: 364±18 kJ mol^{-1}). It should be noted that in the absence of water vapor, Brindley *et al.* [7] obtained 213 kJ mol^{-1}, which is also close to our result (196±3 kJ mol^{-1}).
- A very unusual result for kaolinite dehydration in the presence of water vapour has been obtained recently by Nahdi *et al.* [10]. With the help of the rate-jump method at three-fold different rates (0.14 and 0.42 mg h^{-1}) and a total time of decomposition of about 140 h for 200 mg powder sample, they found E=188±10 kJ mol^{-1} at P_{H_2O}=5 mbar, which is in strong contradiction with the previously published data [7] (see above). However, from the analysis of data reported in [10] it follows that the total water loss corresponding to Fig. 2 [10] is erroneous. It turned out much higher (0.14 mg h$^{-1}\cdot$70 h+ +0.42 mg h$^{-1}\cdot$70 h=39.2 mg) than that expected from the reactant stoichiometry (200 mg·0.1395= 27.9 mg). It means that the actual decomposition rate at higher temperatures should be lower than 0.42 mg h^{-1}, i.e. (27.9 mg–0.14 mg h$^{-1}\cdot$70 h)/70 h= 0.26 mg h^{-1}. As a result, the E parameter, instead of 188 kJ mol^{-1} [10], should be equal to (188ln3)/ln(0.26/0.14)=334 kJ mol^{-1}. This value coincides with our result: 327 kJ mol^{-1}.

To support this conclusion, we calculated the enthalpy of dehydration reaction at two different P_{H_2O} values ($1\cdot10^{-6}$ bar and 5 mbar) by the third-law method. The results of these calculations are listed in Table 5. The primary data (T, $\Delta m/\Delta t$ and P_{H_2O}) that are re-

Table 1 Experimental conditions and results of calculation of the enthalpy for a dehydration reaction of $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ (kaolinite) by the third-law method

Sample	STA	P_{air}/bar	P_{H_2O}/bar	T/K	S_0/mm^2	$^a\alpha_m$	^bS_m/mm^2	$(\Delta m/\Delta t)$/μg s^{-1}	^cJ/kg m^{-2} s^{-1}	$^dP_{eq}$/bar	K_P/bar^5	$\Delta_rH^0_T$/kJ mol^{-1}
Powder	429	$6{\cdot}10^{-8}$	$6{\cdot}10^{-10}$	661.9	61.8	0.14	55.9	0.063	$4.03{\cdot}10^{-7}$	$4.06{\cdot}10^{-9}$	$1.10{\cdot}10^{-42}$	1061
Powder	429	$6{\cdot}10^{-8}$	$6{\cdot}10^{-10}$	672.6	61.8	0.16	55.0	0.083	$5.39{\cdot}10^{-7}$	$5.47{\cdot}10^{-9}$	$4.90{\cdot}10^{-42}$	1070
Powder	429	$8{\cdot}10^{-5}$	$1.2{\cdot}10^{-6}$	673.2	61.8	0.08	58.4	0.147	$8.99{\cdot}10^{-7}$	$9.13{\cdot}10^{-9}$	$1.10{\cdot}10^{-36}$	1002
Powder	429	$8{\cdot}10^{-5}$	$1.2{\cdot}10^{-6}$	673.8	61.8	0.08	58.4	0.111	$5.32{\cdot}10^{-7}$	$5.40{\cdot}10^{-9}$	$2.27{\cdot}10^{-37}$	1012
Powder	429	$8{\cdot}10^{-5}$	$1.2{\cdot}10^{-6}$	674.6	61.8	0.13	56.2	0.108	$6.86{\cdot}10^{-7}$	$6.97{\cdot}10^{-9}$	$4.88{\cdot}10^{-37}$	1009
Powder	429	1	$1.4{\cdot}10^{-2}$	715.0	61.8	0.15	55.5	0.062	$3.99{\cdot}10^{-7}$	$4.17{\cdot}10^{-9}$	$1.42{\cdot}10^{-29}$	967
Powder	429	1	$1.4{\cdot}10^{-2}$	728.8	61.8	0.22	52.4	0.137	$9.34{\cdot}10^{-7}$	$9.87{\cdot}10^{-9}$	$1.88{\cdot}10^{-28}$	970
Powder	449	1	$7.9{\cdot}10^{-3}$	750.0	58.7	0.25	48.0	0.422	$3.14{\cdot}10^{-6}$	$3.36{\cdot}10^{-8}$	$2.37{\cdot}10^{-27}$	982
Powder	449	1	$7.7{\cdot}10^{-3}$	770.0	58.2	0.46	38.6	0.568	$5.26{\cdot}10^{-6}$	$5.71{\cdot}10^{-8}$	$1.10{\cdot}10^{-26}$	999

[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]$J=(\Delta m/\Delta t)/(2.8S_m)$;
[d]At $\overline{M}=0.039$ kg mol^{-1} and $M_B=0.036$ kg mol^{-1}.

Table 2 Experimental conditions and results of calculation of the enthalpy for a dehydration reaction of $K_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2H_2O$ (muscovite) by the third-law method

Sample	STA	P_{air}/bar	P_{H_2O}/bar	T/K	m/mg	S_0/mm^2	$^a\alpha_m$	^bS_m /mm^2	$(\Delta m/\Delta t)$/μg s^{-1}	^bJ/kg m^{-2} s^{-1}	$^bP_{eq}$/bar	K_P/bar^{12}	$\Delta_rH^0_T$/kJ mol^{-1}
Crystal	429	$8{\cdot}10^{-8}$	$8{\cdot}10^{-10}$	1070	10.6	99.3	0.75	39.4	0.023	$5.84{\cdot}10^{-7}$	$9.12{\cdot}10^{-9}$	$3.31{\cdot}10^{-97}$	4031
Crystal	429	$4{\cdot}10^{-8}$	$4{\cdot}10^{-10}$	1084	10.2	74.5	0.60	40.4	0.019	$4.70{\cdot}10^{-7}$	$7.40{\cdot}10^{-9}$	$2.68{\cdot}10^{-98}$	4106
Crystal	429	1	$9.8{\cdot}10^{-3}$	1051	16.5	93.6	0.17	82.7	0.100	$1.21{\cdot}10^{-6}$	$1.87{\cdot}10^{-8}$	$5.02{\cdot}10^{-82}$	3654
Crystal	429	1	$7.5{\cdot}10^{-3}$	1051	13.1	110	0.48	71.1	0.054	$7.56{\cdot}10^{-7}$	$1.17{\cdot}10^{-8}$	$2.70{\cdot}10^{-84}$	3699
Crystal	449	1	$7.6{\cdot}10^{-3}$	1070	9.30	64.7	0.40	46.0	0.090	$1.95{\cdot}10^{-6}$	$3.05{\cdot}10^{-8}$	$4.02{\cdot}10^{-80}$	3681
Crystal	429	1	$5.2{\cdot}10^{-3}$	1081	13.7	103	0.40	73.3	0.113	$1.55{\cdot}10^{-6}$	$2.43{\cdot}10^{-8}$	$1.94{\cdot}10^{-81}$	3746
Crystal	449	1	$9.0{\cdot}10^{-3}$	1101	9.21	65.3	0.23	54.9	0.212	$3.86{\cdot}10^{-6}$	$6.13{\cdot}10^{-8}$	$6.07{\cdot}10^{-77}$	3720
Crystal	429	1	$8.4{\cdot}10^{-3}$	1101	18.1	97.3	0.50	61.3	0.162	$2.64{\cdot}10^{-6}$	$4.19{\cdot}10^{-8}$	$1.18{\cdot}10^{-78}$	3757

[a]The decomposition degree by the time of measurement; [b]$J=(\Delta m/\Delta t)/S_m$, where $S_m=S_0(1-\alpha_m)^{2/3}$; [c]At $\overline{M}=0.0582$ kg mol^{-1} and $M_B=0.036$ kg mol^{-1}

Table 3 Experimental conditions and results of calculation of the enthalpy for a dehydration reaction of $3MgO\cdot 4SiO_2\cdot H_2O$ (talc) by the third-law method

Sample	STA	P_{air} /bar	P_{H_2O} /bar	T/K	m_0 /mg	S_0/mm^2	$^a\alpha_m$	^bS_m /mm^2	$(\Delta m/\Delta t)$/μg s^{-1}	^bJ/kg m^{-2} s^{-1}	$^cP_{eq}$/bar	K_P/bar^8	$\Delta_r H_T^0$/kJ mol^{-1}
Crystal	429	$8\cdot 10^{-8}$	$8\cdot 10^{-10}$	1248.2	16.60	58.0	0.52	35.6	0.182	$5.11\cdot 10^{-6}$	$1.51\cdot 10^{-7}$	$2.75\cdot 10^{-55}$	2902
Crystal	429	$8\cdot 10^{-8}$	$8\cdot 10^{-10}$	1258.8	15.00	55.3	0.55	32.5	0.184	$5.66\cdot 10^{-6}$	$1.68\cdot 10^{-7}$	$6.22\cdot 10^{-55}$	2918
Crystal	449	1	$1.4\cdot 10^{-2}$	1220.7	6.01	37.2	0.35	27.9	0.053	$1.90\cdot 10^{-6}$	$5.55\cdot 10^{-8}$	$2.27\cdot 10^{-53}$	2793
Crystal	449	1	$1.2\cdot 10^{-2}$	1220.7	8.03	47.1	0.33	36.1	0.070	$1.94\cdot 10^{-6}$	$5.66\cdot 10^{-8}$	$2.24\cdot 10^{-53}$	2793
Crystal	429	1	$9.9\cdot 10^{-3}$	1250.5	13.30	49.3	0.41	34.7	0.099	$2.85\cdot 10^{-6}$	$8.44\cdot 10^{-8}$	$3.03\cdot 10^{-52}$	2834
Crystal	449	1	$1.3\cdot 10^{-2}$	1250.7	5.88	34.6	0.46	22.9	0.063	$2.75\cdot 10^{-6}$	$8.14\cdot 10^{-8}$	$3.08\cdot 10^{-52}$	2834
Crystal	449	1	$1.1\cdot 10^{-2}$	1250.7	6.66	42.2	0.53	25.5	0.076	$2.98\cdot 10^{-6}$	$8.82\cdot 10^{-8}$	$4.57\cdot 10^{-52}$	2830
Crystal	429	1	$9.9\cdot 10^{-3}$	1275.0	10.80	35.8	0.37	26.3	0.462	$1.76\cdot 10^{-5}$	$5.23\cdot 10^{-7}$	$1.07\cdot 10^{-46}$	2754
Crystal	449	1	$1.1\cdot 10^{-2}$	1275.0	12.90	39.2	0.34	29.7	0.584	$1.97\cdot 10^{-5}$	$5.86\cdot 10^{-7}$	$2.61\cdot 10^{-46}$	2745
Crystal	449	1	$8.9\cdot 10^{-3}$	1294.8	15.20	69.8	0.16	62.2	1.630	$2.62\cdot 10^{-5}$	$7.89\cdot 10^{-7}$	$1.69\cdot 10^{-45}$	2767
Crystal	449	1	$8.4\cdot 10^{-3}$	1294.8	13.80	73.7	0.30	58.1	1.230	$2.12\cdot 10^{-5}$	$6.37\cdot 10^{-7}$	$3.57\cdot 10^{-46}$	2784

[a] The decomposition degree by the time of measurement, [b] $J=(\Delta m/\Delta t)/S_m$., [c] At $\overline{M}=0.0445$ kg mol^{-1} and $M_B=0.018$ kg mol^{-1}.

Table 4 The mean values of the reaction enthalpy and the *E* parameter for the equimolar and isobaric modes of dehydration

Reactant	Dehydration reaction (primary stage)	$\Delta_r H_T^0$/kJ mol^{-1}	E/kJ mol^{-1}	
			Equimolar	Isobaric
Kaolinite	$Al_2O_3\cdot 2SiO_2\cdot 2H_2O \rightarrow Al_2O_3(g)\downarrow + 2SiO_2(g)\downarrow + 2H_2O$	980±15	196±3	327±5
Muscovite	$K_2O\cdot 3Al_2O_3\cdot 6SiO_2\cdot 2H_2O \rightarrow K_2O(g)\downarrow + 3Al_2O_3(g)\downarrow + 6SiO_2(g)\downarrow + 2H_2O$	3710±39	309±3	371±4
Talc	$3MgO\cdot 4SiO_2\cdot H_2O \rightarrow 3MgO(g)\downarrow + 4SiO_2(g)\downarrow + H_2O$	2793±34	349±4	399±5

Table 5 Values of the enthalpy for a dehydration reaction of kaolinite at different partial pressure of water vapour calculated by the third-law method from the data reported in [10]

Temperature/K	P_{H_2O}/ bar	$(\Delta m/\Delta t)$/mg h^{-1}	$^a J$/kg m^{-2} s^{-1}	$^a P_{eq}$/bar	K_P/bar^5	$\Delta_r H^0_T$/kJ mol^{-1}
643	$1\cdot10^{-6}$	0.42	$1.4\cdot10^{-7}$	$1.4\cdot10^{-9}$	$2.7\cdot10^{-39}$	989
663	$5\cdot10^{-3}$	0.26^c	$8.6\cdot10^{-8}$	$8.6\cdot10^{-10}$	$1.6\cdot10^{-32}$	934

$^a J=(\Delta m/\Delta t)/(2.8S_0)$ where $S_0 \cong 300$ mm^2 (at r=4.9 mm and h=5 mm) [10]; ^{b}Calculated by Eq. (4) at $\overline{M}$=0.039 kg mol^{-1} and M_B=0.036 kg mol^{-1}; ^{c}Recalculated from Fig. 2 [10] as explained in the text

ported in [10] were used. The outer surface area, S_0, of powder sample was estimated from the sample mass (m=200 mg) and apparent (bulk) density of kaolinite powder (530 kg m^{-3}), under assumption that the crucible radius and height of powder bed are equal (about 5 mm). As can be seen, the enthalpy values are equal to 989 and 934 kJ mol^{-1} (average: 962±40 kJ mol^{-1}). The last value agrees very well with our result: 980±15 kJ mol^{-1}.

Therefore, it can be concluded that the above-mentioned discrepancy in the E^i parameter with the reported data (in particular, in [7]) and with our value (327±5 kJ mol^{-1}) is due to shortages of the methods used in [10]. It can be assumed, in particular, that at high inlet pressure of water vapour (P_1=5 mbar), the outlet pressure (P_2) may be different for diaphragms with one and three holes and, as a result, the mass ratio for gas (H_2O) transferred through these diaphragms (and proportional to $P_1^2 - P_2^2$) is smaller than three. Be it as it may, this discrepancy (of methodological importance) deserves further study.

- The literature data for dehydration of muscovite are the values of E^e=226 kJ mol^{-1} [16] measured in vacuum and E^i=376 kJ mol^{-1} [17] measured under atmospheric pressure. For dehydration of talc, the value of E^i=423±17 kJ mol^{-1} [18] was determined in a flow of zero-grade Ar. Two last E^i values are in a good agreement with our data: 371±4 kJ mol^{-1} and 399±5 kJ mol^{-1} (Table 4). The value of E^e=226 kJ mol^{-1} measured for muscovite in high vacuum by the Arrhenius-plots method is most likely underestimated as a result of self-cooling.

Conclusions

The third-law method has been applied to determine the enthalpies, $\Delta_r H^0_T$, for dehydration reactions of kaolinite, muscovite and talc. The $\Delta_r H^0_T$ values measured in the equimolar (vacuum) and isobaric (in the presence of water vapour) modes practically coincide. It means, in accord with the results of our previous publications [19], that the effect of water vapour on the dehydration is governed by the laws of equilibrium thermodynamics applied to primary gaseous products of solid decomposition. This fact strongly supports the mechanism of dissociative evaporation of these reactants in accordance with the schemes listed in Table 4.

In connection with the controlling role of water molecules in the decomposition of all these compounds, the term ‘dehydroxylation’ applied in the literature to these reactions [5–10, 16, 18] provokes obvious objections.

The magnitudes of the E parameter deduced from values for different modes of decomposition are in agreement with quite a few early results reported in the literature in 1960s [4, 7, 8, 17, 18].

A possibility of simple, fast, precise and reliable (free from the self-cooling effect) investigation into kinetics of dehydration reactions at atmospheric pressure of air (under conditions of isobaric free-surface evaporation!), which has been realized in this work for the first time, is undoubtedly the important methodological innovation that can be applied to innumerable hydrated compounds including various crystalline hydrates. (It is a shame that we have come to this obvious idea so late! Two years ago, we used the same methodology for investigation of decomposition of $CaCO_3$, $SrCO_3$ and $BaCO_3$ in atmosphere of argon with the addition of CO_2 [19]. However, a possibility of its application to dehydration reactions has remained unnoticed. Probably, it is true ‘that «having an idea» is not necessarily the result of some great mental leap: it is often the result of merely being able, for one sublime moment, to avoid being stupid!’ [20]).

References

1 M. E. Brown, D. Dollimore and A. K. Galwey, Reaction in the Solid State, Elsevier, Amsterdam 1980.

2 A. K. Galwey and M. E. Brown, Thermal Decomposition of Ionic Solids, Elsevier, Amsterdam 1999.

3 T. Jacobs, Nature, 182 (1958) 1086.

4 J. B. Holt, I. B. Cutler and M. E. Wadsworth, J. Am. Ceram. Soc., 45 (1962) 133.

5 F. Toussaint, J. J. Fripiat and M. C. Gastuche, J. Phys. Chem., 67 (1963) 26.

6 J. N. Weber and R. Roy, Am. Mineral., 50 (1965) 1038.

7 G. W. Brindley, J. H. Sharp, J. H. Patterson and B. N. Nakahira, Am. Mineral., 52 (1967) 201.

8 H. B. Johnson and F. Kessler, J. Am. Ceram. Soc., 52 (1969) 199.

9 G. D. Anthony and P. D. Garn, J. Am. Ceram. Soc., 57 (1974) 132.
10 K. Nahdi, P. Llewellyn, F. Rouquerol, J. Rouquerol, N. K. Ariguib and M. T. Ayedi, Thermochim. Acta, 390 (2002) 123.
11 B. V. L’vov, Thermochim. Acta, 424 (2004) 183.
12 B. V. L’vov, J. Therm. Anal. Cal., 79 (2005) 151.
13 B. V. L’vov and V. L. Ugolkov, Thermochim. Acta, 401 (2003) 139.
14 B. V. L’vov and V. L. Ugolkov, J. Therm. Anal. Cal., 74 (2003) 697.
15 B. V. L’vov, Thermochim. Acta, 389 (2002) 199.
16 H. Kodama and J. E. Brydon, Trans. Faraday Soc., 64 (1968) 3112.
17 J. B. Holt, I. B. Cutler and M. E. Wadsworth, in 12th Nat. Conf. Clay and Clay Minerals, Macmillan London, (1964) p. 55.
18 J. R. Ward, Thermochim. Acta, 13 (1975) 7.
19 B. V. L’vov and V. L. Ugolkov, Thermochim. Acta, 410 (2004) 47.
20 A. Walsh, Spectrochim. Acta Part B, 35 (1980) 639.

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