

DEHYDRATION OF SOLIDS IN DIFFERENT MODES AS A PROOF OF THEIR PRIMARY CONGRUENT DISSOCIATIVE VAPORIZATION

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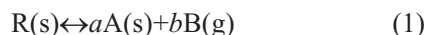
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The main purpose of this paper is to prove the applicability of the mechanism of congruent dissociative vaporization (CDV) to the solid-state decomposition kinetics through the comparison of the fundamental theoretical relationship $E_i/E_c=(a+b)/a$ resulted from this mechanism with experiment. It has been shown that the ratios of E_i and E_c parameters of the Arrhenius equation measured in the isobaric and equimolar modes (in the presence and absence of H_2O vapour) for 22 reactants with the general formula $aSalt \cdot bH_2O$ or $aOxide \cdot bH_2O$ are in agreement with the values of $(a+b)/a$. The relative standard deviation is only 17% and the correlation coefficient is close to 0.99. A probability of accidental correlation for all set of the E parameters taken from the literature is lower than $4 \cdot 10^{-16}$. This strongly supports the validity of the CDV mechanism. The problem of stability of polyatomic molecules of inorganic salts in the gaseous state, which are the primary decomposition products of crystalline hydrates, was also discussed on the basis of recent mass spectroscopy studies. It was concluded that any doubts in the applicability of the CDV mechanism as a general mechanism of solid-state decomposition reactions are unsound.

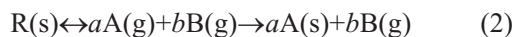
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Introduction

There are two fundamentally different approaches to interpretation of the kinetics of thermal decomposition of solids up to the solid and gaseous products and, in particular, of the dehydration of solids. The first of them (e.g. [1, 2]) is based on the traditional mechanism of incongruent dissociative vaporization of reactant



The second approach, which was proposed in 1990 [3, 4] and developed over the last decade in a number of works (e.g. [5–8]), is based on the mechanism of congruent dissociative vaporization (CDV) of reactant with the subsequent re-condensation of low-volatile product



The basic assumptions underlying this mechanism in its most recent presentation [8] may be formulated as follows.

- The primary step of thermal decomposition consists in the congruent dissociative vaporization of reactant.
- Primary decomposition products may differ of those at equilibrium.
- Part of the energy evolved in the process of condensation of low-volatile product in the reaction interface is consumed by the reactant as a fraction of the enthalpy change.

Use of the CDV mechanism allowed resolving some of the problems accumulated in this field over the last century. These include the mechanism of nucleation and the source of energy supporting the autocatalytic development of reactions, the retardation of decomposition in the presence of gaseous products, the low evaporation coefficients α_v for many substances, the effect of self-cooling on the measurement of kinetic parameters, the Topley–Smith effect and the compensation effect [5–8]. However, despite these achievements, other workers have ignored the CDV mechanism in studies of the decomposition kinetics. The most important objection against this mechanism is related to the primary stage of decomposition based on the assumption of congruent vaporization of all parts of reactant including the low-volatile species (e.g. [9]). The following question is usually raised: what sense for a low-volatility product to vaporize if in accord with its thermochemical features it should reside in the solid-state at decomposition temperature? In asking so, one leaves behind that the case in point is actually the dissociative vaporization of reactant but not the vaporization of low-volatility product. Besides, in doing so it is tacitly anticipated that the reactant is informed about thermochemical features of different reactions and capable to choose the optimal way of decomposition. As a result, the atoms of silver in the process of thermal decomposition of Ag_2O remain in their original positions in the

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solid-state but the atoms of Zn and Cd in case of ZnO and CdO decomposition transfer to the gas phase. It is difficult to agree with this anthropomorphic view. In our opinion, more logically to propose that solid products of decomposition are formed as a result of collisions and condensation of low-volatile species (atoms and molecules), which occur in free state in the gaseous phase owing to decomposition through the general (for all reactants) CDV mechanism.

Nevertheless, the above logical consideration of the problem is, probably, not enough to convince that the CDV mechanism actually prevails in solid-state decomposition reactions. Some other (direct and indirect) proofs are necessary. The present work is dedicated to this goal. It will be shown below that the decomposition kinetics of reactants in the equimolar and isobaric modes (in the absence of gaseous product in the reactor and in its presence) is obedient to the simple law resulted from the CDV mechanism. Recently, for the same goal, this method has been successfully applied to decomposition of CaCO_3 , SrCO_3 and BaCO_3 in CO_2 [7, 8]. Now we will use it for analysis of a rather large group of dehydration reactions with water vapour as a gaseous product.

One more argument against the CDV mechanism is related to the supposedly low stability of polyatomic molecules of inorganic salts, which are the decomposition products of crystalline hydrates, in the gaseous-state. This topic will be shortly discussed on the basis of recent literature data in the end of paper.

Theoretical

The common Arrhenius approach that based on the empirical equation

$$k = A \exp(-E/RT) \quad (3)$$

does not allow to explain the difference in the kinetics (in values of the E and A parameters) of solid decomposition in different (equimolar and isobaric) modes. As alternative to the Arrhenius approach, the Hertz–Langmuir approach to the solid-state kinetics can be used. It is based on the well-known equation that resulted from statistical mechanics (molecule physics)

$$J = \frac{P}{(2\pi MRT)^{1/2}} \quad (4)$$

where J means the maximum vapour flow (in moles) from the reactant surface in the absence of any diffusion limitations and P is the equilibrium vapour pressure of this substance at temperature T . The change of sample mass related to escape of the gas-

eous product B in case of solid decomposition in accord with reactions (1) and (2) is determined, respectively, by the equation

$$J_B [\text{kg m}^{-2} \text{s}^{-1}] = \frac{\gamma M_B}{(2\pi M_B RT)^{1/2}} P_B [\text{bar}] \quad (5)$$

where $\gamma=10^5 \text{ Pa bar}^{-1}$ is the conversion factor from bars (usually used in thermodynamic calculations of P_B) to pascals.

The equilibrium value of P_B is determined by the third law of thermodynamics

$$\Delta_r H_T^0 = T(\Delta_r S_T^0 - R \ln K_p) \quad (6)$$

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. For a primary stage of reaction (2) that defines its kinetics on the whole,

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

The congruency condition for this reaction can be written as

$$\frac{P_A}{a(2\pi M_A RT)^{1/2}} = \frac{P_B}{b(2\pi M_B RT)^{1/2}} \quad (8)$$

From this, it follows

$$\frac{P_B}{P_A} = \frac{b}{a} \left(\frac{M_B}{M_A} \right)^{1/2} \equiv \beta \quad (9)$$

Taking into account Eqs (6)–(9), we receive for the equimolar mode:

$$P_B^e = (\beta^a K_p)^{1/\nu} = \beta^{a/\nu} \exp \frac{\Delta_r S_T^0}{\nu R} \exp \left(-\frac{\Delta_r H_T^0}{\nu RT} \right) \quad (10)$$

and for the isobaric mode

$$P_B^i = \beta P_A^i = \beta \frac{K_p^{1/a}}{(P_B^{\text{ext}})^{b/a}} = \frac{\beta}{(P_B^{\text{ext}})^{b/a}} \exp \frac{\Delta_r S_T^0}{aR} \exp \left(-\frac{\Delta_r H_T^0}{aRT} \right) \quad (11)$$

where P_B^{ext} is the external pressure of gaseous product B in the reactor and

$$\nu = a + b \quad (12)$$

Equations (10) and (11) are, undoubtedly, the key item of this derivation. They determine the effect of the external pressure of gaseous product on the equilibrium pressure of this product and its dependence on temperature and stoichiometry of reaction. If we now install the values of P_B^e and P_B^i into Eq. (5), we will eventually receive:

$$\begin{aligned}
 J_B^c &= \frac{\gamma M_B}{(2\pi M_B RT)^{1/2}} \beta^{a/v} \exp \frac{\Delta_r S_T^0}{vR} \exp \left(-\frac{\Delta_r H_T^0}{vRT} \right) = \\
 &= A_B^c \exp \left(-\frac{\Delta_r H_T^0}{vRT} \right) \quad (13)
 \end{aligned}$$

for the equimolar mode and

$$\begin{aligned}
 J_B^i &= \frac{\gamma M_B}{(2\pi M_B RT)^{1/2}} \frac{\beta}{(P_B^{\text{ext}})^{b/a}} \exp \frac{\Delta_r S_T^0}{aR} \exp \left(-\frac{\Delta_r H_T^0}{aRT} \right) = \\
 &= A_B^i \exp \left(-\frac{\Delta_r H_T^0}{aRT} \right) \quad (14)
 \end{aligned}$$

for the isobaric mode. Here

$$A_B^c = \frac{\gamma M_B}{(2\pi M_B RT)^{1/2}} \beta^{a/v} \exp \frac{\Delta_r S_T^0}{vR} \quad (15)$$

and

$$A_B^i = \frac{\gamma M_B}{(2\pi M_B RT)^{1/2}} \frac{\beta}{(P_B^{\text{ext}})^{b/a}} \exp \frac{\Delta_r S_T^0}{aR} \quad (16)$$

As can be seen from a comparison of Eq. (3) with Eqs (13) and (14), the E parameter for reaction (2) should be different for the equimolar and isobaric modes of decomposition, i.e.,

$$E_c = \Delta_r H_T^0 / v \quad (17)$$

for the equimolar mode and

$$E_i = \Delta_r H_T^0 / a \quad (18)$$

for the isobaric mode. In both cases, the E parameter corresponds to the molar enthalpy, i.e., the enthalpy of the decomposition reaction reduced to one mole of primary products without including components of that present in excess. Therefore, the ratio of the E parameters for the isobaric and equimolar modes is equal to

$$\frac{E_i}{E_c} = \frac{v}{a} = \frac{a+b}{a} = 1 + \frac{b}{a} \quad (19)$$

Equations (15) and (16) have been used for the quantitative evaluation of the A parameters and, in particular, explanation of the compensation effect [5]. However, for brevity sake, we omit here this topic. It is remarkable that for the first time all these theoretical conclusions were described and proved experimentally more than 20 years ago [10]. Nevertheless, no worker except of this author tried to use them in the kinetics of solid-state reactions, probably, because of a priori unbelief in applicability of the CDV mechanism to these (especially, dehydration) reactions.

Results and discussion

Correlation between the experimental ratios of E_i/E_c and theoretical ratios of v/a

In selection of the primary data on the E parameters from the available literature, we have used (with rare exceptions) the following criteria.

- Values of the E parameter for the equivalent and isobaric modes were determined and described by the same group of authors, in most cases, in one work.
- Isothermal TG measurements were used.
- All E_c values were measured in high vacuum (at continuous pumping).
- The same kinetic model was used for calculation of the decomposition rates in the different modes.
- The Arrhenius-plots method was used for evaluation of the E parameter.
- In case of determination of the E_i parameter at different $P_{\text{H}_2\text{O}}$, the result for highest $P_{\text{H}_2\text{O}}$ was chosen (outside the range of $P_{\text{H}_2\text{O}}$ typical for the Topley–Smith effect).

As a result of thorough analysis of available literature (monographs, collections of papers, proceedings and periodicals) published over the last 45 years, we could select 22 different reactions (Table 1) that were kinetically investigated in two different decomposition modes under above-mentioned conditions. The list of corresponding reactants includes 3 layer silicates (clays), 3 metal hydroxides, 15 hydrates of metal salts and 1 anhydrous carbonate (which was included to demonstrate that the presence of H_2O vapour has no effect on the decomposition kinetics of anhydrous reactants). They are arranged in order of increasing of v/a ratio. As can be seen from the reference list, 13 from 22 reactants were investigated in the laboratory of the Institute of General and Inorganic Chemistry in Minsk (Byelorussia) in 1970–1985 under the leadership of Pavlyuchenko and Prodan (the authors of many books and papers on the solid-state kinetics). It is remarkable that these 13 reactants cover all range of v/a ratios (from 1 to 13). What's more, we could not find any data on the E parameters from other laboratories for v/a ratios higher than three.

Special note should be made of some cases when the above-mentioned criteria were not fulfilled. The E_i and E_c values for talc, muscovite and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ have been obtained by different workers. For some reactants ($\text{Zn}(\text{OH})_2$, $\text{LiCl} \cdot \text{H}_2\text{O}$, $\text{Er}(\text{HCOO})_3 \cdot 2\text{H}_2\text{O}$, $\text{NiNa}_3\text{P}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$ and $\text{ZnNa}_3\text{P}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$), the E_i and E_c parameters were calculated or re-calculated by the author on the base of primary data reported in corresponding publications. It was related to the absence of appropriate calculations in original publications [27, 35] or to

Table 1 Kinetic parameters of dehydration reactions in different modes

Reactant	$\Delta T/K$	a	b/a	v/a	$E/kJ\ mol^{-1}$		E_i/E_c	$\Delta\%$	P_{H_2O} in isobaric mode/mbar	Reference	
					isobaric	equimolar				isobaric	equimolar
$Na_2CO_3 \cdot 3NaHCO_3$	351–403	4	0	1	105	102	1.03	3.0	20	[11]	[11]
$3MgO \cdot 4SiO_2 \cdot H_2O$	1220–1295	7	0.143	1.143	423	366	1.15	0.6	zero-grade Ar	[12]	[13]
$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	1051–1101	10	0.2	1.2	377	341	1.11	-7.5	air static	[14]	[13]
$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	663–748	3	0.667	1.667	351	213	1.65	-1.0	6	[15]	[15]
$Mg(OH)_2$	543–643	1	1	2	238	121	1.97	-1.5	5	[16]	[16]
$Cd(OH)_2$	343–393	1	1	2	272	116	2.34	17.0	7	[17]	[18]
$Zn(OH)_2$	348–394	1	1	2	209 ^a	95	2.20	10.0	18	[19]	[19]
$CaC_2O_4 \cdot H_2O$	382–465	1	1	2	281	147	1.91	-4.5	air dynamic	[20]	[20]
$LiCl \cdot H_2O$	353–373	1	1	2	177 ^b	98 ^b	1.81	-9.5	20	[21]	[21]
$Li_2SO_4 \cdot H_2O$	300–382	1	1	2	160	86	1.86	-7.0	air static	[22]	[23, 24]
$BaCl_2 \cdot H_2O$	318–333	1	1	2	151	80	1.89	-5.5	20	[25]	[25]
$Ca(H_2PO_4)_2 \cdot H_2O$	313–373	1	1	2	159	67	2.37	18.5	10	[26]	[26]
$Er(HCOO)_3 \cdot 2H_2O$	377–417	1	2	3	187 ^c	87 ^c	2.15	-28.3	11	[27]	[27]
$Y(HCOO)_3 \cdot 2H_2O$	387–407	1	2	3	200	82	2.44	-18.7	7	[28]	[28]
$(NH_4)_5P_3O_{10} \cdot 2H_2O$	262–333	1	2	3	100	46	2.17	-27.7	1	[29]	[29]
$MnHPO_4 \cdot 3H_2O$	303–375	1	3	4	250	57	4.39	9.8	24	[30]	[30]
$Y_2(CO_3)_3 \cdot 4H_2O$	298–453	1	4	5	154	35	4.40	-12.0	12	[31]	[31]
$Na_3P_3O_{10} \cdot 6H_2O$	303–370	1	6	7	236	59	4.00	-42.9	6	[32]	[32]
$Na_3P_3O_9 \cdot 6H_2O$	260–308	1	6	7	264	41	6.44	-8.0	12	[33]	[33]
$La_2(CO_3)_3 \cdot 8H_2O$	270–430	1	8	9	515	65	7.92	-12.0	13	[34]	[34]
$NiNa_3P_3O_{10} \cdot 12H_2O$	283–333	1	12	13	431 ^d	40	10.78	-17.1	18	[35]	[35]
$ZnNa_3P_3O_{10} \cdot 12H_2O$	273–328	1	12	13	461 ^e	48 ^e	9.60	-26.1	20	[36]	[36]

^aCalculated from the data in Fig. 22 [19] at 90, 95 and 100°C; ^bcalculated from the data in Table 1 [21] at 80 and 85°C for the isobaric mode and at 95 and 100°C for the equimolar mode;^ccalculated from the data in Fig. 3 [27] at 114, 124, 134 and 144°C for the isobaric mode and from Table 2 at 104, 114, 124 and 144°C for the equimolar mode; ^dcalculated from the data in Fig. 3 [35] at 60, 62 and 65°C; ^ecalculated from the data in Fig. 2 [36] at 0 and 15°C for the equimolar mode and at 47 and 50°C for the isobaric mode

some obvious disagreements between the primary experimental data and the reported results of calculations [19, 21, 36]. Reliability of E_i/E_c ratios for this group of reactants is, probably, lower than that in other cases though hardly they differ from the true values more than 10–20%.

From consideration of the data presented in Table 1, the following conclusions can be deduced.

- First of all, attention should be drawn to a good correlation between experimental values of E_i/E_c and theoretical values of v/a . The mean value of the relative standard deviation, s_r , for all 22 reactants is only 17% though for two of them it reaches 28% and for one, 43%.
- As can be seen from the same data (with the exception of the latter, most deviated result for $\text{Na}_5\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$) presented in Fig. 1, the correlation coefficient r is close to 0.99. However, the slope of the correlation line is only 0.78. Partly this can be explained by underestimated experimental results for the reactants with $v/a=13$. If we omit additionally these points (Fig. 2), the slope is increased up to 0.87. Nevertheless, the systematic underestimation of experimental results on the whole is obvious. In 16 instances, the results are lower than expected and only in 4 instances, essentially higher. One of the reasons could be the difference in compositions of solid product in different modes. It is known that in the presence of H_2O vapour the dehydration of some reactants proceeds up to formation mono- or dihydrates but in vacuum, up to anhydrous salts. In particular, it has been proved for $\text{ZnNa}_3\text{P}_3\text{O}_{10}$

$\cdot 12\text{H}_2\text{O}$ [36] and $\text{NiNa}_3\text{P}_3\text{O}_{10}\cdot 12\text{H}_2\text{O}$ [35]. This should reduce the enthalpy of dehydration reaction compared to the value expected for the dehydration up to anhydrous product.

- Our potential opponents may argue that the above correlation is accidental. To estimate the probability of this event, it is necessary to calculate the number of statistically independent sections in 13-fold interval of v/a variation with the relative width $v/a \pm 2s$ for each section and $s=0.17v/a$. (Criterion $2s$ for a definition of section independence corresponds to the 95% significance level). If to take into account that the relative width increase for adjacent sections is 1.68, then their number should be equal to 5 ($1 \cdot 1.68^5 \cong 13$). In this case, the probability of accidental correlation between E_i/E_c and v/a is 0.2 for a single reactant and only $0.2^{22} \cong 4 \cdot 10^{-16}$ for 22 reactants. Therefore, on the whole, this correlation is in no way random in nature.
- The mean magnitude of E_c parameter at low dehydration temperatures (≤ 300 K), typical for the last 8 reactants, is equal to 49 ± 10 kJ mol $^{-1}$. As expected this value is higher than the enthalpy of vaporization of free water at 298 K ($=44.0$ kJ mol $^{-1}$). However, in three cases the E parameter is lower than 44 kJ mol $^{-1}$. This is a direct evidence of errors in measurements related apparently to the self-cooling effect. Hopefully, this systematic error is equally valid in determination of both E_c and E_i parameters so that their ratio is close to the true value.
- It is generally agreed [2] that the mechanism of dehydration of layer silicates differs from that for crys-

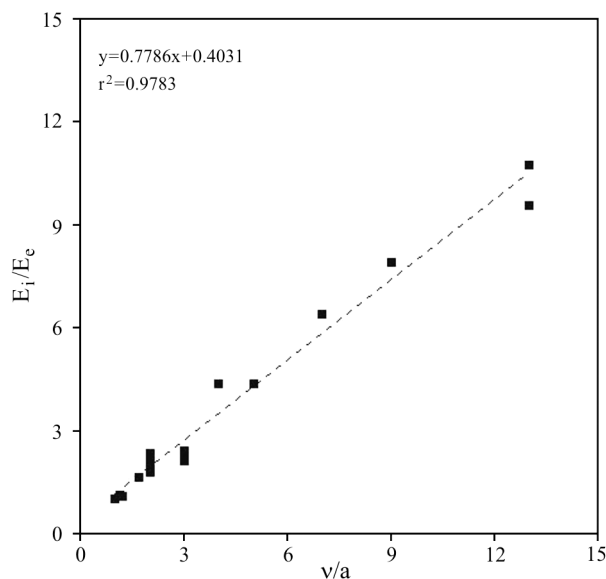


Fig. 1 Correlation between the experimental ratios of the Arrhenius parameters E_i/E_c and theoretical ratios of stoichiometric coefficients v/a for all reactants (Table 1) except of $\text{Na}_5\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$

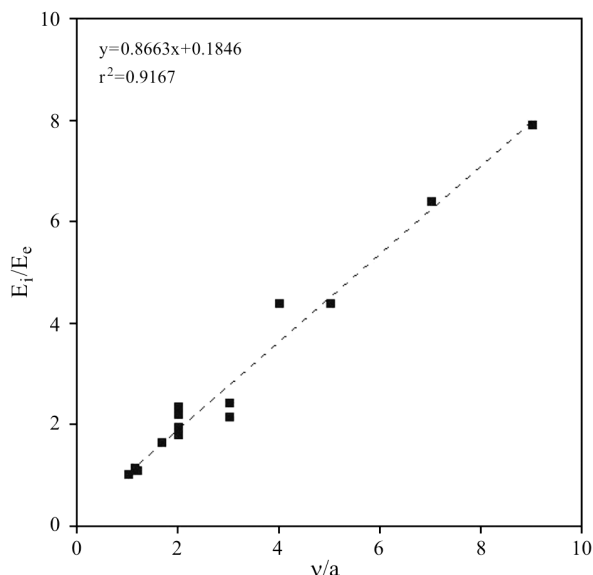


Fig. 2 Correlation between the experimental ratios of the Arrhenius parameters E_i/E_c and theoretical ratios of stoichiometric coefficients v/a for all reactants (Table 1) except of $\text{Na}_5\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$ and two reactants with $v/a=13$

talline hydrates and this explains the differences in the E_c parameters (in vacuum) and decomposition temperatures. This view is reflected, in particular, in the fact that the term 'dehydroxylation' usually applied in the literature to clay dehydration. However, this is not the case. As can be seen from Table 1, increase of temperature and the molar enthalpy (the E_c parameter) for clay dehydration is accompanied by a sharp increase of a coefficient. It means that in case of talc, for example, for removing of one mole of water it is necessary, in agreement with the CDV mechanism, to vaporize additionally (as a ballast) 7 moles of other low-volatility components (3MgO and 4SiO_2). As a result, the temperature and molar enthalpy of talc dehydration increase significantly (by a factor of 4–8) compared to those for the hydroxides and, especially, hydrates with $a=1$.

Gaseous molecules of inorganic salts

Our discussion would be incomplete if we do not consider another argument against the CDV mechanism that related to the supposedly low stability of polyatomic molecules of inorganic salts in the gaseous state. It is generally agreed that the stability of these compounds is low and their existence in the gaseous phase is improbable. This opinion has been demolished in the last few years by the results of mass spectroscopy (MS) studies. In a recently published monograph 'Vaporization Thermodynamics of Double Oxides' by Kazenas [37], the author collected, systematized and generalized a huge material on the vapour pressure and composition under metal borates, aluminates, carbonates, silicates, nitrates, sulfates, phosphates, chromates and other double oxides. This material is based on studies by Kazenas and his group and the results reported in the literature. In a foreword to this book, Kazenas claims: 'Observation of new types of molecules completely disproved the view on the high-temperature vapour as a media, which is poor in molecular forms. It has been established, in particular, that molecular composition of vapour phase for many chemical compounds is more complex and diverse than it was suggested earlier'. By the use of effusion MS, many molecules were revealed and thermodynamically described at about 1000–1200 K. Of among them are, for example, molecules of M_2SO_4 (Li_2SO_4 , in particular), MNO_3 , MPO_3 , $\text{M}(\text{PO}_3)_3$, M_2CO_3 , M_2CrO_4 , MMoO_4 and MWO_4 . It should be noted that effusion MS does not allow to study the vapour composition at low temperatures typical for the decomposition of hydrates. However, in principle, the stability of molecules at lower temperatures can only increase.

Quadrupole free-surface MS is a more efficient technique for the direct investigation of gaseous phase

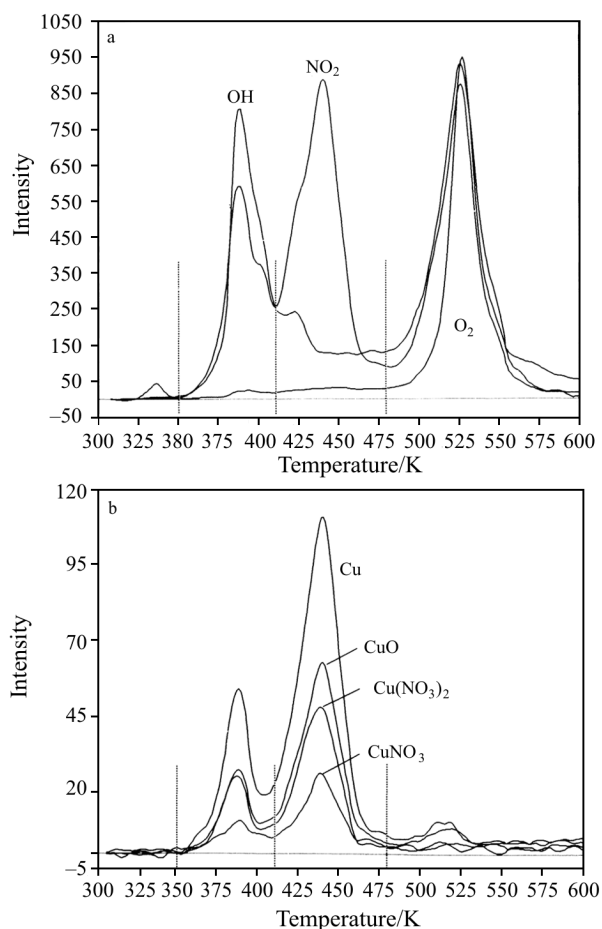


Fig. 3 Mass spectral signals for decomposition of 12 μg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ heated with a rate 1 K s^{-1} on the graphite platform: a – volatile and b – non-volatile species (reproduced from L'vov and Novichikhin [38])

under dehydrated compounds, especially for melted reactants uncovered by a solid shell of product [8]. This is illustrated in Fig. 3 by the example of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ dehydration [38]. The process of two-step decomposition of this hydrate (the melted point is 387 K), with the formation of intermediate $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{Cu}(\text{OH})_2$, is accompanied by appearance of $\text{Cu}(\text{NO}_3)_2$ molecules and also, CuNO_3 , CuO and Cu species (as daughter ions). The E_c parameter for this process is equal to 101 kJ mol^{-1} [38]. Unfortunately, quadrupole free-surface MS is used for such investigations very rarely. Some results (mainly, for metal nitrates) were summarized in [5].

Conclusions

The main purpose of this paper was to prove the applicability of the CDV mechanism as a general mechanism in solid-state decomposition kinetics. For this purpose, the fundamental theoretical relationship ($E_i/E_c = \nu/a$) that unambiguously follows from this mechanism was com-

pared with experiment. The literature values of E_i and E_e parameters of the Arrhenius equation for 22 different dehydration reactions were used. It has been shown that the relative standard deviation of E_i/E_e values from theory is equal to 17% and the correlation between E_i/E_e and v/a ratios is about 0.99 (with the exception of only one from 22 points). A probability of accidental correlation for all set of results is lower than $4 \cdot 10^{-16}$. We are conscious of necessity of further efforts for improving accuracy of such experiments and increasing the number of tests. Nevertheless, already now we can claim that any doubts in the applicability of the CDV mechanism as a general mechanism of solid-state decomposition reactions are groundless. Strange enough that in our age of general application of the chemical vapour deposition (CVD) technologies [39] it is necessary to prove the reality of its converse, the CDV mechanism.

Acknowledgements

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