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Kinetics and mechanism of free-surface decomposition of solid and melted $AgNO_3$ and $Cd(NO_3)_2$ analyzed thermogravimetrically by the third-law method

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Abstract

The third-law method and the retardation effect of the excess of gaseous product in the reactor were used for thermogravometric (TG) investigation of kinetics and mechanisms of thermal decomposition of $AgNO_3$ and $Cd(NO_3)_2$. The most important results of this study are formulated as follows. (i) In contrast to $AgNO_3$, the evolution of oxygen in the process of decomposition of $Cd(NO_3)_2$ proceeds in the form of free atoms (O). This explains, in particular, the absence of O_2 molecules in primary products of $Cd(NO_3)_2$ decomposition revealed earlier by quadrupole mass spectroscopy (QMS). (ii) The decomposition rate is reduced after reactant melting because of the absence of product/reactant interface and associated transfer of condensation energy to the reactant. This conclusion is supported by a rise of the E parameter of the Arrhenius equation by about $20\,kJ\,mol^{-1}$ after melting of $AgNO_3$ and $Cd(NO_3)_2$. (iii) The absence of layer of solid product in case of decomposition of melt provides conditions for a free evaporation in vacuum of all primary products including the low-volatility species. This phenomenon was observed in experiments on decomposition of $AgNO_3$ melt in vacuum.

Keywords: Evidence of $AgNO_3$ dissociative evaporation; Increase of E parameter after melting; Kinetics studies by third-law method; Mechanisms of nitrate decomposition

1. Introduction

The mechanism of thermal decomposition of metal nitrates has been a subject of a large number of studies, covered partially in several review papers and books [1–3]. Anhydrous nitrates of most metals decompose below 900 K. Therefore, as a rule, the reaction leaves the metal oxide, which is the main product of decomposition, in condensed state, the other products evolving in the form of gaseous molecules NO_2, NO and O_2. Accordingly, the decomposition reaction for nitrates of divalent metals is usually written as [2,3]:

$$M(NO_3)_2\,(s) \rightarrow MO\,(s) + 2NO_2 + 0.5O_2 \quad (1)$$

This traditional approach to choosing the pathway of decomposition of solids has recently been challenged dramatically [4–12]. Direct observation of the primary products evolved in decomposition of the nitrates of some metals in vacuum by quadrupole mass spectrometry (QMS) has shown that thermal decomposition of solid and melted metal nitrates involves congruent gasification (or, in other words, dissociative evaporation) of all reaction products, irrespective of their saturated vapor pressure, with subsequent condensation of the molecules of the non-volatile components as they collide with one another or with any other surface. This phenomenon was observed for anhydrous nitrates of Ag [12], Cu [8], Mg, Ca, Sr and Ba [10], Cd [9,12], Co [7], Ni [6], Cr [11] and Pb [4,5,12]. Though all known QMS investigations were performed only with metal nitrates (for the interpretation of mechanisms of analyte atomization in electrothermal atomic absorption spectrometry, where

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these compounds are of primary interest), it may be concluded that the congruent evaporation of reactant is a primary stage of decomposition of all solid and melted substances. Basing on the well-known theory of evaporation of metals proposed by Hertz and Langmuir and above conclusion, L'vov [13–17] has developed a general physical approach to the interpretation of thermal decomposition of solids and melts.

The decomposition of $AgNO_3$ and $Cd(NO_3)_2$, which are chosen for thermogravimetric investigation in the present work, was interpreted earlier [12] in accord with the dissociative evaporation mechanism as follows:

$$AgNO_3\,(l) \rightarrow Ag\,(g) + NO_2 + 0.5O_2 \qquad (2)$$

$$Cd(NO_3)_2\,(s) \rightarrow CdO\,(g) + 2NO_2 + 0.5O_2 \qquad (3)$$

These pathways were supported with a good correlation between the E parameters of the Arrhenius equation measured by QMS and the molar enthalpies for corresponding reactions [12]. However, some results of the studies reported in [12] were unexplained or explained not very clearly.

(i) In contrast to the congruent evolution of O_2 molecules in case of $AgNO_3$ decomposition, no O_2 molecules were observed in case of $Cd(NO_3)_2$ decomposition.

(ii) The drop of decomposition rate in the moment of $Cd(NO_3)_2$ melting (633 K) was explained as a result of reduction of the surface area of the sample. However, this explanation contradicts the well-known property of melts to spread over the surface of graphite (used as a support [12]) due to the wetting effect.

(iii) The transfer of condensation energy to the reactant, which is one of the key points of the physical approach in its up-to-date presentation [16,17], was not taken into account in calculation of the reaction enthalpies. However, as mentioned above, a good correlation between the E parameters and the molar enthalpies was observed.

This work will be devoted to investigation of these contradictions. The third-law method will be used for the determination of E parameters, and the effect of O_2 excess in the reactor on the decomposition rate will be used for the determination of chemical form of evolved oxygen (O or O_2). Both these methods were thoroughly described and applied to decomposition studies of different reactants earlier [18–20]. Therefore, our theoretical discussion below will be limited only by a short presentation of the equations necessary for further calculations.

2. Theoretical

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, that is

$$S\,(s/l) \rightarrow aA\,(g)_{\downarrow} + bB\,(g) + cC\,(g) \qquad (4)$$

the flux of each product, which ultimately determines the rate of decomposition, can be expressed through the so-called equivalent partial pressure P_{eq} (in bar) of this product corresponding to the hypothetical equilibrium of reaction (4) in a general form

$$J = \frac{\gamma M P_{eq}}{(2\pi MRT)^{1/2}} \qquad (5)$$

where M is the molar mass of product. Here $\gamma = 10^5$ Pa bar^{-1} is the conversion factor from bars to pascals. This relationship is usually called the Hertz–Langmuir equation.

2.2. Calculation of the entropy and enthalpy of decomposition reaction

The entropy change of decomposition reaction (4) was calculated from obvious equation

$$\Delta_r S_T^\circ = aS_T^\circ(A) + bS_T^\circ(B) + cS_T^\circ(C) - S_T^\circ(S) \qquad (6)$$

Calculation of the enthalpy change is more complicated. 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 introduced into calculations of the enthalpy of decomposition reaction (4), an additional term $\tau\, a\, \Delta_c H_T^\circ$ (A) where the coefficient τ corresponds to the fraction of the condensation energy consumed by the reactant. Thus, we can write

$$\Delta_r H_T^\circ = a\,\Delta_f\, H_T^\circ(A) + b\,\Delta_f\, H_T^\circ(B) + c\,\Delta_f\, H_T^\circ(C) - \Delta_f\, H_T^\circ(S) + \tau a\,\Delta_f\, H_T^\circ(A) \qquad (7)$$

The magnitudes of thermodynamic functions (the entropy and enthalpy) for the components of decomposition reactions at different temperatures are listed in Table 1 [2,21–24].

Under high-vacuum conditions (the equimolar mode of vaporization), the enthalpy of reaction (4) is related to the value of the E parameter by the obvious relationship [13–17]

$$\Delta_r H_T^\circ = \nu E \qquad (8)$$

where

$$\nu = a + b + c \qquad (9)$$

Taking into account Eqs. (7) and (8), we obtain for nitrates under investigation ($a = 1$):

$$\tau = \frac{\nu E - \Delta_f H_T^\circ(A) - b\,\Delta_f H_T^\circ(B) - c\,\Delta_f H_T^\circ(C) + \Delta_f H_T^\circ(S)}{\Delta_c H_T^\circ(A)} \qquad (10)$$

As was revealed recently [19,25], the τ parameter varies for different reactants and is in correlation with the reduced value of condensation energy, $\Delta_c H_T^\circ/RT$, at decomposition temperature.

Table 1
Thermodynamic functions for the components of decomposition reactions [2,21–24]

Function[a]	Species	State of aggregation	T (K)			
			400	500	600	700
S°_{T}	$AgNO_3$	s/l	171.1	227.1	250.5	
	Ag	s	50.2	55.9	60.9	
	Ag	g	179.0	183.4	187.4	
	$Cd(NO_3)_2$	s/l		287.1[b]	323.9[b]	386.4[b]
	CdO	s		79.7	90.0	98.3
	CdO	g		250.8[b]	257.3[b]	262.8[b]
	NO_2	g	251.5	260.8	269.0	276.4
	O_2	g	213.8	220.6	226.3	231.4
	O	g		172.1	176.0	179.2
$\Delta_f H^{\circ}_{T}$	$AgNO_3$	s/l	−114.1	−88.2	−75.4	
	Ag	s	2.6	5.2	7.9	
	Ag	g	287.0	289.1	291.2	
	$Cd(NO_3)_2$	s/l		−421.1[b]	−400.9[b]	−360.9[b]
	CdO	s		−248.0	−242.9	−237.5
	CdO	g		88.0[b]	91.6[b]	95.2[b]
	NO_2	g	38.1	42.4	46.9	51.6
	O_2	g	3.0	6.1	9.2	12.5
	O	g		253.5	255.6	257.7

[a] All S°_{T} values are in $\mathrm{J\,mol^{-1}\,K^{-1}}$ and all $\Delta_f H^{\circ}_{T}$ values are in $\mathrm{kJ\,mol^{-1}}$.
[b] High-temperature increments for the corresponding Ba compounds [21,24] were used.

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

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

$$\Delta_r H^{\circ}_{T} = T(\Delta_r S^{\circ}_{T} - R \ln K_P) \qquad (11)$$

where K_P is the equilibrium constant for the reaction (4)

$$K_P = P_A^a \times P_B^b \times P_C^c \qquad (12)$$

Taking into account Eqs. (8), (9) and (12), Eq. (11) in the case of decomposition of nitrates in vacuum can be reduced to the equation

$$E = T\left(\frac{\Delta_r S^{\circ}_{T}}{\nu} - R \ln P_{eq}\right) \qquad (13)$$

The equivalent pressure of the gaseous product (B or C) is related to the total absolute rate of decomposition, J (in $\mathrm{kg\,m^{-2}\,s^{-1}}$), by the Hertz–Langmuir equation (Eq. (5)) which is rewritten as

$$P_{eq} = \frac{(2\pi \overline{M} RT)^{1/2} J}{\gamma M} \qquad (14)$$

Here $\overline{M}$ is the geometrical mean for molar masses of products or $\overline{M} = (M_A^a \times M_B^b \times M_C^c)^{1/(a+b+c)}$ and M is the sum of the molar masses of gaseous species, i.e. $M = bM_B + cM_C$.

2.4. The retardation effect of excess of gaseous product on the decomposition

In case of dissociative evaporation of metal nitrate at two different external partial pressures of oxygen, i.e. $P_1(O_2)$ and $P_2(O_2)$, the evaporation rates should be related [15,16] as

$$\frac{J_1}{J_2} = \left(\frac{P_2(O_2)}{P_1(O_2)}\right)^{c/(a+b)} \qquad (15)$$

if evolution of oxygen proceeds in the form of molecules. In case of evolution of oxygen in the form of atoms, the difference in the partial pressures of O_2 at temperatures lower than 1500 K (when the dissociation degree of O_2 into atomic oxygen is negligible) should have no effect on the evaporation rate, i.e.

$$\frac{J_1}{J_2} = 1 \qquad (16)$$

Therefore, a comparison of the decomposition rates of nitrates at two different external partial pressures of O_2 can be used as a criterion for choosing the true mechanism of dissociative evaporation.

3. Experimental

The experiments were carried out with a Netzsch STA 429 instrument on the TG and DSC measuring head. The actual measured quantities were the mass change of the sample per time unit, $\Delta m/\Delta t$, and the absolute crucible temperature. An open alumina crucible, 5.7 mm inner diameter and 4.0 mm high was used as a sample container. The reacting materials were high-purity $AgNO_3$ and $Cd(NO_3)_2$ (melting points are 483 and 633 K). Anhydrous $Cd(NO_3)_2$ was obtained after preliminary dehydration of commercial $Cd(NO_3)_2{\cdot}4H_2O$ in air at 200 °C and its thorough grinding.

A powder sample (20 mg in all cases), 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. To eliminate spreading of $AgNO_3$ melt out of crucible in the process of heating, the experiments with melted $AgNO_3$ were performed with a mixture of $AgNO_3$ and Al_2O_3 powders taken in the ratio of 1:1 and 1:5. The same technique (with a mixture of 1:1) was used for $Cd(NO_3)_2$ melt.

In experiments on determination of the E parameter, the sample chamber was evacuated to a residual pressure in the range of $n \times 10^{-8}$ to $n \times 10^{-7}$ bar with the use of rotation and oil-diffusion pumps. All measurements have been conducted at continuous pumping under isothermal conditions. The heating rate of the sample from the room temperature to intermediate one (10 K lower than the desired temperature) was 10 K min^{-1} and from intermediate to the desired temperature was 1 K min^{-1}. In case of decomposition of melted $Cd(NO_3)_2$, 50 K min^{-1} heating rate was used in the first stage to reduce the decomposition loss of sample before its melting. At the beginning of each measuring cycle the system was heated at the temperature chosen, usually for 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 checked experimentally, was found to be proportional to $(1 - \alpha)^{2/3}$ where α is the decomposition degree. This dependence can be interpreted as a combined result of the reduction of number and size of particles in the process of decomposition. Temperature was measured with Pt–Pt10%Rh thermocouple placed with its junction immediately below the crucible. Temperature variations in the process of mass-change measurements (usually, during 30–40 min) did not exceed ±0.2 K.

The absolute value of the decomposition rate for powder samples was estimated using the method proposed in our previous work [26]. It consists of 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 calculation of the E parameter by the third-law method. The value of this geometrical factor (2.8 ± 0.4), as was shown in [19,20,25,26], does not depend on the temperature, residual pressure of gas in the reactor, grain size and mass of a powder sample. After melting of nitrates in cases of their mixture with Al_2O_3, such mixtures retain the powder structure of Al_2O_3 so that evaluation of the absolute decomposition rate remains the same as described above for solid reactants. To check this assumption, experiments with melted $AgNO_3$ were performed with mixtures of $AgNO_3$ with Al_2O_3 taken in different ratios (1:1 and 1:5).

The experiments on the retardation effect of oxygen on the decomposition of $Cd(NO_3)_2$ were carried out in two different gases: nitrogen and air at atmospheric pressure (under constant volume conditions). In this case, only relative losses of mass were measured under isothermal conditions.

4. Results and discussion

Comparative results on decomposition rate of $Cd(NO_3)_2$ in the atmosphere of air and nitrogen are presented in Table 2. Table 3 contains the experimental conditions and results of determination of the E parameter for decomposition of $AgNO_3$ and $Cd(NO_3)_2$ in vacuum. The following conclusions can be deduced from the analysis of these data.

1. As it follows from Eq. (15), in cases of evolution of oxygen in accord with reaction (3), the ratio of decomposition rates for $Cd(NO_3)_2$ in nitrogen and air should be equal to $2100^{1/6} \cong 3.6$. Here 2100 is the ratio of partial pressures of oxygen in air (0.21 bar) and pure nitrogen after preliminary evacuation of the furnace up to 5×10^{-4} bar (or the residual partial pressure of O_2 about 1×10^{-4} bar). In case of evolution of oxygen in the form of atoms, the difference in the partial pressures of O_2 should have no effect on the evaporation rate, i.e. $J(N_2)/J(\text{Air}) = 1$. The experimental data for $Cd(NO_3)_2$ are close to the last value (Table 2). It means that evolution of oxygen occurs in the form of atoms and the corresponding decomposition reaction, unlike Eq. (3), should be written as follows:

$$Cd(NO_3)_2\,(s) \rightarrow CdO\,(g)_{\downarrow} + 2NO_2 + O \tag{17}$$

   This conclusion is in agreement with direct QMS measurements [12], which, as noted above could not reveal any O_2 molecules in primary products of $Cd(NO_3)_2$ decomposition. The assumption expressed by L'vov and Novichikhin [12] in relation to this fact ("We find it difficult to propose a reasonable explanation for the absence of the $O_2{}^+$ signal except to assume that the oxygen is released in another species whose signal was not measured in this work") was absolutely correct (the O^+ signal was not measured in [12]).
2. The absolute rates of decomposition of melted $AgNO_3$ diluted with Al_2O_3 in the ratio of 1:1 and 1:5 are practically identical (Table 3). Three-fold difference in concentration

Table 2
Kinetics of isothermal decomposition of melted $Cd(NO_3)_2$ in atmosphere of nitrogen[a] and air

T (K)	J^b (μg s^{-1})		$J(N_2)/J(\text{Air})$		
	N_2	Air	Experiment	Theory: Eq. (3)	Theory: Eq. (17)
680 ± 1	1.67	1.68	1.0	3.6	1.0
679 ± 1	1.35	1.51	0.9	3.6	1.0
679 ± 1	1.50	2.13	0.7	3.6	1.0

[a] Pure nitrogen was introduced after evacuation of the furnace chamber up to $P_{air} = 5 \times 10^{-4}$ bar or $P_{O_2} = 1 \times 10^{-4}$ bar.

[b] Averaged value for 30 min.

Table 3
Experimental conditions and results of calculation of the E parameter for $AgNO_3$ and $Cd(NO_3)_2$ decomposition by the third-law method

Nitrate	Aggregate state	Vacuum (bar)	T (K)	S_0 (mm^2)	α_m [a]	S_m [b] (mm^2)	$\Delta m/\Delta t$ ($\mu g\,s^{-1}$)	J_{corr} [c] ($kg\,m^{-2}\,s^{-1}$)	P_{eq} (bar)	$\Delta_r S^\circ_T$ [d] ($J\,mol^{-1}\,K^{-1}$)	E ($kJ\,mol^{-1}$)
$AgNO_3$	s	9×10^{-8}	472.5	58.2	0.071	55.4	0.059	3.80×10^{-7}	2.4×10^{-9}	357.1	145.5
$AgNO_3$	s	2×10^{-7}	472.0	58.2	0.017	57.5	0.047	2.92×10^{-7}	1.8×10^{-9}	357.1	146.4
$AgNO_3$	s	8×10^{-8}	471.8	58.2	0.016	57.6	0.050	3.10×10^{-7}	1.9×10^{-9}	357.1	146.2
$AgNO_3$	l[e]	8×10^{-8}	573.5	61.8	0.185	53.9	0.130	8.61×10^{-7}	5.9×10^{-9}	321.3	164.1
$AgNO_3$	l[e]	7×10^{-8}	574.5	61.8	0.187	53.8	0.100	6.64×10^{-7}	4.6×10^{-9}	321.3	165.5
$AgNO_3$	l[e]	7×10^{-8}	574.2	61.8	0.180	54.1	0.124	8.19×10^{-7}	5.6×10^{-9}	321.3	164.5
$AgNO_3$	l[f]	1×10^{-7}	572.4	61.8	0.121	56.8	0.128	8.05×10^{-7}	5.4×10^{-9}	321.4	164.2
$AgNO_3$	l[f]	5×10^{-7}	571.6	61.8	0.165	54.8	0.123	8.02×10^{-7}	5.4×10^{-9}	321.4	164.0
$Cd(NO_3)_2$	s	5×10^{-8}	573.7	58.2	0.371	42.7	1.10	9.20×10^{-6}	3.2×10^{-8}	649.9	175.5
$Cd(NO_3)_2$	s	7×10^{-8}	553.5	58.2	0.377	42.5	0.48	4.03×10^{-6}	1.4×10^{-8}	651.9	173.4
$Cd(NO_3)_2$	l[e]	1×10^{-7}	658.6	62.7	0.50	39.5	1.43	1.29×10^{-5}	4.7×10^{-8}	612.6	193.3
$Cd(NO_3)_2$	l[e]	1×10^{-7}	660.7	62.7	0.49	40.0	1.21	1.08×10^{-5}	4.0×10^{-8}	612.4	194.7
$Cd(NO_3)_2$	l[e]	1×10^{-7}	651.4	62.7	0.49	40.0	0.76	6.79×10^{-6}	2.5×10^{-8}	613.4	194.7

[a] The decomposition degree by the time of measurement.
[b] The surface area by the time of measurement.
[c] $J_{cor} = (\Delta m/\Delta t)/(2.8\ S_m)$ in all cases.
[d] Interpolated for temperatures used taking into account the values listed in Table 1.
[e] Mixture of $AgNO_3$ or $Cd(NO_3)_2$ with Al_2O_3 (1:1).
[f] Mixture of $AgNO_3$ with Al_2O_3 (1:5).

of $AgNO_3$ in Al_2O_3 samples has no effect on the rate of decomposition. It means that the initial distribution of melted reactant over the tablet at any concentration of melt reproduces the morphology of solid sample (structure of Al_2O_3 powder). Therefore, the geometrical factor (2.8) deduced for powdered tablets should be equally valid for melted reactant distributed in these tablets. However, further investigation of this statement would be desirable.

3. Tremendous importance is a comparison of the decomposition rates for solid and melted reactants in vacuum (Table 3). As can be seen, in spite of about 100 K difference in temperature, the decomposition rates for $AgNO_3$ in $Cd(NO_3)_2$ in both cases are rather similar. (Difference of the two–three orders of magnitude is expected based on the values of the E parameter). It means that, on some reasons, the decomposition of solid reactants slows down after their melting. This conclusion is in contradiction to the widespread opinion: "Melting is an important feature in theoretical considerations of crystal reactivity because chemical changes often proceed more rapidly in a melt than in the solid state" [27]. This opinion is based on the following reasonable though, at best, only a priori assumptions. "Reasons why reactions of solids may proceed more rapidly in a molten zone than within a crystalline reactant, include: (i) relaxation of the regular stabilising intercrystalline forces; (ii) establishment of a favorable configuration for chemical change may be possible due to mobility in a liquid but inhibited within a rigid crystal structure, and (iii) the influences of intermediates and impurities may be greater (or different) in a molten phase" [3].

   Meanwhile, the retardation effect of melting can easily be explained and quantitatively evaluated in the framework of the physical approach to decomposition kinetics. As stated in [16], the formation of product/reactant interface in the process of solid decomposition with a partial transfer of condensation energy to the reactant ($\tau\ a\ \Delta_c H^\circ_T$) reduces the enthalpy of reaction and increases the decomposition rate. In the absence of such interface for a liquid reactant, the enthalpy of reaction corresponds to the condition $\tau = 0$. Therefore, the difference in the E parameter for a liquid and solid reactant should be equal to $\tau\ a\ \Delta_c H^\circ_T/\nu$. Indeed, the experimental values of the E parameter for liquid and solid $AgNO_3$ (Table 3) differ by the value of $\tau\ a\ \Delta_c H^\circ_T/\nu \cong 165-146\,kJ\,mol^{-1} = 19\,kJ\,mol^{-1}$. The corresponding difference in case of $Cd(NO_3)_2$ decomposition is equal to $194-174\,kJ\,mol^{-1} = 20\,kJ\,mol^{-1}$. Now it is easy to understand the actual reason of the drop of decomposition rate in the moment of $Cd(NO_3)_2$ melting observed by QMS in [12]. On the whole, the peculiarities of decomposition of solid and melted nitrates that were discussed above strongly support the basic principles of physical approach theory. It needs to be ascertained if these findings are common to decomposition of other reactants, in particular, of some low-melting hydrates.

4. If we calculate further the enthalpy and the E parameter of decomposition reaction (3) without taking into account the energy transfer (i.e., at $\tau = 0$), we receive $E = 169\,kJ\,mol^{-1}$, which is only $5\,kJ\,mol^{-1}$ lower than the E parameter measured for true reaction (17). The error in the chemical form of evolved oxygen (O_2 instead of O) made in [12] was practically compensated by the error associated with neglecting the condensation energy transfer. This brought to apparent agreement between theory and experiment in [12].

Table 4
The final kinetic parameters for nitrate decomposition

Nitrate	T (K)	Primary products[a]	E (kJ mol^{-1})	T/E (K kJ^{-1} mol)	$\Delta_r H_T^\circ/\nu$ (kJ mol^{-1})	$\Delta_c H_T^\circ$ (kJ mol^{-1})	τ	
							Eq. (10)	Eq. (18)
$AgNO_3$ (s)	472	$Ag(g)_{\downarrow} + NO_2 + 1/2O_2$	146.0 ± 0.5	3.2		−284.2	0.21	0.33
$AgNO_3$ (l)	573	$Ag(g) + NO_2 + 1/2O_2$	164.5 ± 0.6	3.5	167.7 ± 1.0		0	0
$Cd(NO_3)_2$ (s)	563	$CdO(g)_{\downarrow} + 2NO_2 + O$	174.5 ± 1.5	3.2		−335.4	0.43	0.33
$Cd(NO_3)_2$ (l)	660	$CdO(g) + 2NO_2 + O$	194.2 ± 0.8	3.4	204.3 ± 1.0		0	0

[a] An arrow (↓) implies taking into account part τ of condensation energy consumed by the reactant.

5. The final values of kinetic parameters for decomposition of nitrates are presented in Table 4. As can be seen, the T/E ratios in all cases are equal to 3.3 ± 0.1 K kJ^{-1} mol what is in agreement with the theoretically predicted value for $P_{eq} = 1 \times 10^{-8}$ bar [18]. This is an additional proof of validity of the data received. The values of τ parameter determined from Eq. (10) are in satisfactory agreement with their values calculated from approximate Eq. (18)

$$\tau = 0.423 \ln\left(\frac{-\Delta_c H_T^\circ}{RT}\right) - 1.48 \quad (18)$$

   This equation was proposed in our previous work [25] for a priori estimation of τ parameter, as a function of the reduced value of condensation energy, and probably, it needs a further improvement.
6. The E parameter for decomposition of liquid $AgNO_3$ (164.5 ± 0.6 kJ mol^{-1}) measured in this work is in excellent agreement with its theoretical value (167.7 ± 1 kJ mol^{-1}) calculated from the enthalpy of reaction (2) at 570 K and with the literature data: 167 ± 3 kJ mol^{-1} measured by QMS [12] and 174 ± 1 kJ mol^{-1} determined by non-isothermal TG [28]. The E parameter for decomposition of solid $Cd(NO_3)_2$ (175 ± 2 kJ mol^{-1}) is in agreement with the only literature data (177 ± 3 kJ mol^{-1}) determined by QMS [12]. The E parameter for decomposition of liquid $Cd(NO_3)_2$ (194 ± 1.0 kJ mol^{-1}) is in satisfactory agreement with its theoretical value (204 ± 1 kJ mol^{-1}) calculated from the enthalpy of reaction (17) at 660 K and with the literature data: 186 ± 11 kJ mol^{-1} [29]. The departure of the E parameter (194 kJ mol^{-1}) from a theoretical value is probably due to additional (unaccounted) heat generated in the process of recombination of oxygen atoms. In contrast to the present work, the Arrhenius plots method was used in [12,28,29] for determination of the E parameters.
7. The last but not least conclusion that was deduced from this study is a possibility of direct observation of evaporation of low-volatility products in the process of decomposition of melted nitrates. This conclusion follows as a logical consequence of the previous deduction (item 3) about the absence of product/reactant interface in case of decomposition of melts. The surface of melted reactant is free from the layer of solid product, which usually prevents escape of low-volatility species from the reaction interface (even through a porous layer), and this provides conditions for the congruent evaporation of all primary products. The validity of this conclusion is supported with our experiments with melted $AgNO_3$. As noted above, this melt is very active to spread over the alumina surface, and in case of mass of sample higher than 1 mg escapes from the crucible and covers its entire inner and outer surfaces. In the process of decomposition of $AgNO_3$ in vacuum, atoms of Ag that congruently evaporate from the outer surface of the crucible should condense on the surface of nearby objects. Indeed, after heating (10 K min^{-1}) 20 mg of $AgNO_3$ in vacuum, from the room temperature to up to 600 K, the surface of the neighboring reference crucible opposite to the sample crucible was found to be covered by a brown layer of silver oxide. (Brown color is related to oxidation of Ag up to Ag_2O after cooling of crucible in the air atmosphere). It should be noted that at 600 K the saturation vapor pressure of metallic Ag is only 8.8×10^{-19} bar. This is about 10 orders of magnitude lower than the partial pressure necessary for a noticeable evaporation of metal. (For comparison, $P_{eq} = 1.3 \times 10^{-8}$ bar for decomposition of $AgNO_3$ at 600 K). Therefore, a typical objection against the dissociative vaporization mechanism that evaporation is improbable if the saturation vapor pressure of solid product is very low (see e.g. [30]) is not true.

5. Conclusions

The third-law method and the retardation effect of the excess of gaseous product in the reactor were used for TG investigation of kinetics and mechanisms of thermal decomposition of $AgNO_3$ and $Cd(NO_3)_2$. The most important results of this study can be formulated as follows:

(i) In contrast to $AgNO_3$, the evolution of oxygen in the process of decomposition of $Cd(NO_3)_2$ (and probably, of some other metal nitrates) proceeds in the form of free atoms (O). This explains, in particular, the absence of O_2 molecules in primary products of $Cd(NO_3)_2$ and $Pb(NO_3)_2$ decomposition observed by QMS in [12].

(ii) The absence of product/reactant interface and transfer of condensation energy to the reactant after its melting increases by about 20 kJ mol^{-1} the value of the E

parameter and reduces the decomposition rate of melt. This conclusion is in contradiction with the widespread opinion that "chemical changes often proceed more rapidly in a melt than in the solid state" [27]. Further studies are desirable to clarify the validity and generality of each of these alternatives.

(iii) The absence of layer of solid product in case of decomposition of melt, which usually prevents escape of low-volatility species from the reaction interface (even through a porous layer), provides conditions for a free evaporation in vacuum of all primary products including the low-volatility species. This phenomenon was observed in our experiments on decomposition of $AgNO_3$ melt. Complete agreement of this observation with earlier studies of metal nitrate decomposition by QMS [4–12] is obvious.

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