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THE SELF-HEATING EFFECT IN THE PROCESS OF $KMnO_4$ DECOMPOSITION IN VACUUM

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It has been shown that the exothermic decomposition of $KMnO_4$ in vacuum is accompanied by a significant self-heating effect. It manifests itself in the reduction of the molar enthalpy of the reaction, determined by the third-law method. In comparison with the value 138.3±0.6 kJ mol^{-1} that is valid for the decomposition of $KMnO_4$ under atmospheric pressure at 493–553 K, the molar enthalpy in vacuum (10^{-4}–10^{-7} bar) at 484–511 K varies in the range of 136 to 126 kJ mol^{-1}. This is related to the reduction of the thermal conductivity of residual air in the furnace and, as a result, to the self-heating of the reactant, that accelerates the exothermic reaction. A simple method of evaluation of the self-heating effect has been developed. By analogy with the known method for evaluation of the self-cooling effect, it is based on the determination of the molar enthalpy by the third-law method at two different temperatures. The increase of sample temperature above the furnace temperature T_f in the case of the exothermic decomposition of $KMnO_4$ in a high vacuum and $T_f \geq 490$ K reaches a few tens of degrees.

Keywords: *kinetics, potassium permanganate, self-heating effect, third-law method, vacuum decomposition*

Introduction

The significance of the self-heating and self-cooling effects in the solid-state decomposition reactions has been discussed in many books and reviews on thermal analysis (e.g., [1–7]). However, until recently, there were no reliable experimental methods for their measurement. A simple method for the evaluation of the self-cooling effect was proposed only in 2002 [8]. It is based on the determination of the molar enthalpy of the reaction by the third-law method at two different temperatures.

If the only cause for the overestimation of the apparent values E_{app}, determined by the third-law method, is the self-cooling effect, then its magnitude can be easily determined. Assuming that the value of E at the lower temperature is free of this effect (i.e., that the sample temperature, T_s, is equal to the furnace temperature, T_f) and corresponds to the true value of the E parameter, E_{true}, then it becomes possible to determine the actual value of the sample temperature for any higher decomposition temperature. This temperature is equal to:

$$T_s = T_f E_{true}/E_{app} \quad (1)$$

if a small systematic decrease of both thermodynamic parameters (the entropy, $\Delta_r S_T^o$, and the enthalpy, $\Delta_r H_T^o$) with a temperature rise is neglected. Therefore, the difference, $\Delta T = T_s - T_f$, actually corresponds to the self-cooling of the sample at the higher temperature of the experiment, assuming $\Delta T=0$ at its lower temperature. This method was successfully used for the evaluation of the self-cooling effect in the process of vacuum decomposition of some hydrates [9] and carbonates [10].

The purpose of the present work was to apply this method to the evaluation of the self-heating effect in the case of the exothermic decomposition of potassium permanganate. This reactant has been recently proposed as a kinetics standard in thermal analysis [10–12].

The thermal decomposition of potassium permanganate has been the subject of a large number of studies. During the 190 years following the appearance of the first publication by Chevillot and Edwards [13, 14], the mechanism and kinetics of its decomposition have been investigated by virtually all authoritative laboratories in the world [12]. Starting at [13, 14], the resultant reaction has been represented either by the scheme:

$$10KMnO_4(s) = 5K_2MnO_4(s) + 5MnO_2(s) + 5O_2 \quad (2)$$

or by the scheme:

$$10KMnO_4(s) = 3K_2MnO_4(s) + 7MnO_2(s) + \\ + 2K_2O(s) + 6O_2 \quad (3)$$

suggested by Rüdorf more than 100 years ago [15]. The difference between these two schemes is in the

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relative amounts of solid products and free oxygen, the latter varying in the range 10–12 mass%.

However, in accordance with the mechanism of congruent dissociative vaporization and the crystal structure of $KMnO_4$ identical to that of barite $BaSO_4$, which decomposes with the evolution of free atoms of oxygen [10], the first stage of reactions (2) and (3) should be presented as follows:

$$10KMnO_4(s) \leftrightarrow 5K_2O(g) + 10MnO(g) + 25O \quad (4)$$

where K_2O and MnO are gaseous products that condense at the instant of decomposition with the formation of $K_2O(s)$, $MnO_2(s)$ and $K_2MnO_4(s)$, and O is a gaseous product, which undergoes association at the instant of decomposition to give equilibrium molecules O_2. Under these conditions, the partial pressures of the primary products and, consequently, the decomposition rate of $KMnO_4$, depend only on the stoichiometry and the thermochemical characteristics of reaction (4) and should be independent of the composition of the gas in the furnace.

It was shown [12] that, indeed, the decomposition rate of $KMnO_4$ under atmospheric pressure does not depend on the foreign gas (He, air, CO_2 and Ar), and the measurement technique (isothermal or dynamic). The use of the third-law method for the determination of the molar enthalpy of the reaction ($\Delta_r H_T^o/v$) provides an excellent reproducibility of results. The mean value of $\Delta_r H_T^o/v$ from 12 experiments in different gases and at different temperatures (493–553 K) is 138.3 ± 0.6 kJ mol^{-1}, which coincides with the value of 138.1 kJ mol^{-1} calculated from isothermal measurements in different gases by the second-law method.

However, the constancy of the molar enthalpy of the $KMnO_4$ decomposition reaction in the presence of different gases under atmospheric pressure, measured by the third-law method, does not exclude a small (by a few percent) reduction of $\Delta_r H_T^o/v$ in a vacuum. This is related to the reduction of the thermal conductivity of the gas and, as a result, to the self-heating of the reactant that accelerates the exothermic reaction. The authors observed this effect [11] even under low vacuum ($4\cdot10^{-4}$ bar). In a high vacuum ($\approx10^{-7}$ bar), it might increase.

Experimental

Measurement conditions

The main goal of the experiments was to measure the absolute decomposition rates of $KMnO_4$ under different vacuum pressures and at different temperatures by isothermal TG. This data was used to calculate the molar enthalpies of reaction (4) taking into account the partial transfer to the reactant of energy evolved in the process of transformation of the primary products of decomposition into the equilibrium products.

The change in the mass of sample per unit time and the temperature were measured using Netzsch Models STA 429 C and STA 429 CD thermal analyzers. A fine crystalline potassium permanganate (of analytically pure grade) was ground in an agate mortar and about 20 mg of powder pressed manually (at about 1 kg mm^{-2}) into a flat pellet 5.0 mm in diameter and about 0.5 mm thick. The pellet was placed in a corundum crucible with an inner diameter of 5.7 mm and a height of 3.5 mm and the crucible was closed with a small plug of glass wool (≈10 mg) to prevent the ejection of sample particles upon heating. The heating rate of the sample from the ambient to the decomposition temperature was 10 K min^{-1}. The isothermal measurements were made in a low and high vacuum: $(2–4)\cdot10^{-4}$ and $(1–2)\cdot10^{-7}$ bar, respectively. Depending on the temperature and vacuum pressure, the time of complete decomposition (disregarding the preliminary heating stage) was from 4.5 to 150 min.

The calculation scheme

The main stages of the calculation scheme were described in detail in [12]. The input parameter automatically recorded by the thermal analyzer is the relative mass loss, $\Delta m/m_0$, in a chosen time interval Δt between signal measurements. Using evident relationships, the quantities $\Delta m/\Delta t$ and $\Delta\alpha = (\Delta m/m_0)/\Sigma(\Delta m/m_0)$ are calculated. Here m_0 is the initial sample mass and $\Sigma(\Delta m/m_0)$ is the fraction of the gaseous product (O_2) with respect to the mass of the reactant. The decomposition degree at the moment of measurement, α_m, is calculated by summing the values of $\Delta\alpha$ during the period of time preceding the measurement, taking into account the loss during the time elapsed between heating the furnace and the beginning of measurements. The absolute decomposition rate of the powdered samples is calculated by the equation [10, 12]:

$$J = \frac{\Delta m/\Delta t}{2.8 s_m} \quad (5)$$

where 2.8 is the semi-empirical correction factor that accounts for the difference in the decomposition rates of powder and of a single crystal, and s_m is the surface area of the sample at the moment of measurement.

The ratio s_m/s_0 (where s_0 is the initial outer surface area of pellet) was evaluated as a function of the decomposition degree for pellets of the actual diameter-to-height ratio (d/h=10). The results of numerically modeling the s_m/s_0 variation with α_m in the process of homogeneous pellet decomposition across the entire surface for $d/h=10$ are best approximated by the function [12]:

$$s_m/s_0 = (1-\alpha_m)^{0.18} \tag{6}$$

The molar enthalpy of the decomposition reaction was calculated by the third-law method. The equilibrium pressure of atomic oxygen was found using the Hertz–Langmuir equation:

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

where M is the molar mass of oxygen; R, the gas constant, and γ, the conversion factor for recalculating the pressure from pascals to bars (10^5 Pa bar^{-1}), in which units thermodynamic calculations are carried out.

Further, the equilibrium constant of reaction (4) was found:

$$K_P = (P_{eqp})^{\nu}/\delta \tag{8}$$

Where ν is the number of moles of the reaction products and δ the factor that accounts for the congruent nature of the decomposition. This factor is determined using the molar masses and the stoichiometric coefficients of the decomposition products. For reaction (4), this factor is equal to $\delta=2.907$ [12].

The enthalpy of the reaction was calculated by the equation:

$$\Delta_r H_T^o = T(\Delta_r S_T^o - R\ln K_P) \tag{9}$$

where $\Delta_r S_T^o$ is the entropy change of the decomposition reaction. Its value at 500 K, which was accepted on the base of thermodynamic consideration [12], is equal to $\Delta_r S_T^o/\nu \approx 141$ J mol^{-1} K^{-1}. This value is used in our calculations.

It should be noted that the difference in the mean values of $\Delta_r H_T^o/\nu$ measured under atmospheric pressure in our previous papers (145.7 kJ mol^{-1} [11] and 138.3 kJ mol^{-1} [12]) is related to the inaccurate value of the molar entropy (160 J mol^{-1} K^{-1}) that was used in the third-law calculations in [11] and an incorrect value of the exponent in Eq. (6): 0.5 [11] instead of 0.18 in [12].

Results and discussion

The conditions and final results of the isothermal determination of the molar enthalpies of the $KMnO_4$ decomposition under different vacuum pressures and at different temperatures are presented in Table 1 in order of decreasing vacuum pressure, and in order of increasing temperature for each pressure value. Table 2 contains an example of calculations of the molar enthalpies for the $KMnO_4$ decomposition in vacuum ($2\cdot10^{-4}$ bar) at 502.6 K (run 6).

It is necessary to comment some of the quantities in Table 1.

Twofold differences in pressure for a low and high vacuum are related to some instrumental features of the thermal analyzers used in the experiments (STA 429 C and STA 429 CD models manufactured in 1988 and 2007, respectively).

The values for the thermal conductivity, λ_{500}, of residual gas in the furnace were evaluated on the base of the known value of λ_{500} for air at 500 K and 1 bar (40 mW m^{-1} K^{-1} [16]) and the 'critical distance', d_c, which defines the decrease of λ_{500} with vacuum pressure. This distance depends on the size of sample micro particles inside the tablet and the average distance between the tablet and the crucible wall and can be estimated as $d_c \approx 10^{-4}$ m. The 'critical pressure' that corresponds to the equality of the free-paths of air molecules to this distance was calculated by the equation [7, p. 103]: $P_c=2.5\cdot10^{-10}\ T/d_c$. The corresponding critical pressure at 500 K is equal to $P_c=1.25\cdot10^{-3}$ bar. The decrease of thermal conductivity in vacuum is proportional to the ratio of the actual pressure P_a to the P_c value. For example, for the actual vacuum pressure $P_c=2\cdot10^{-4}$ bar, $\lambda_{500}=40\cdot2\cdot10^{-4}/1.25\cdot10^{-3}=6.4$ mW m^{-1} K^{-1}. (Because of the uncertainty in the d_c value, these estimations are naturally approximate).

To prove that the decrease of molar enthalpy is related to the self-heating effect, the quantity 'decomposition rate' was used. Its value is equal to $\Delta\alpha_m/(\Delta tn)$ where $\Delta\alpha_m$ is the interval of measurement in values of α_m and Δt is the registration time for each of the n measurement points in this interval. The value of $\Delta\alpha_m/(\Delta tn)=0.1$ min^{-1}, for example, signifies that one-tenth of the sample decomposes in 1 min. As would be expected, this value, $\Delta\alpha_m/(\Delta tn)$, is proportional to P_{eqp} (Fig. 1).

The last column in Table 1 contains the ΔT values calculated by Eq. (1), by taking into account that $\Delta T=T_s-T_f$ and $E_{true}=138.3$ kJ mol^{-1}. The effect of the decomposition rate on the molar enthalpy and on the temperature increase of the decomposing samples, ΔT, is illustrated in Figs 2 and 3, respectively.

The analysis of the data presented in Table 1 and Figs 2 and 3 yields the following statements.

- In all cases of the vacuum decomposition of $KMnO_4$, the molar enthalpy of the reaction is appreciably lower (126.3–136.4 kJ mol^{-1}) than that under atmospheric pressure (138.3±0.6 kJ mol^{-1}). The only exception is the experiment at 489.9 K and a vacuum pressure of $4\cdot10^{-4}$ bar (run 4), for

Table 1 The conditions and results of isothermal determination of the molar enthalpies of $KMnO_4$ decomposition in vacuum by the third-law method

Run	Instrument	Vacuum/ bar	T/ K	m_0/ mg	λ_{500}/ mW m^{-1} K^{-1}	$\Sigma(\Delta m/m_0)$/ %	$\Delta\alpha_m$	n	Δt/ s	P_{eqp}/ bar	$[\Delta\alpha_m/(\Delta tn)]$/ min^{-1}	$(\Delta_r H^\circ_T/\nu)$/ kJ mol^{-1}	ΔT/ K
1	STA 429 C	$4\cdot10^{-4}$	495.5	20.4	12.8	10.1	0.33–0.83	5	300	$1.1\cdot10^{-7}$	0.020	136.4±0.4	7
2	STA 429 C	$4\cdot10^{-4}$	500.3	20.1	12.8	10.7	0.36–0.90	4	300	$1.7\cdot10^{-7}$	0.027	136.1±0.8	8
3	STA 429 C	$4\cdot10^{-4}$	500.5	20.5	12.8	10.9	0.39–0.93	4	300	$1.7\cdot10^{-7}$	0.027	136.0±1.1	9
4	STA 429 CD	$2\cdot10^{-4}$	489.9	20.3	6.4	6.9	0.44–0.90	10	180	$4.8\cdot10^{-8}$	0.015	138.3±0.4	0
5	STA 429 CD	$2\cdot10^{-4}$	499.6	20.5	6.4	15.0	0.29–0.82	10	120	$1.7\cdot10^{-7}$	0.027	135.9±0.6	9
6	STA 429 CD	$2\cdot10^{-4}$	502.6	20.6	6.4	12.8	0.16–0.76	11	60	$2.9\cdot10^{-7}$	0.055	134.5±1.0	14
7	STA 429 CD	$2\cdot10^{-4}$	510.3	20.7	6.4	13.0	0.23–0.86	8	60	$4.7\cdot10^{-7}$	0.079	134.5±1.0	14
8	STA 429 CD	$2\cdot10^{-7}$	484.6	20.8	0.0064	12.4	0.25–0.87	11	300	$6.1\cdot10^{-8}$	0.011	135.9±0.6	9
9	STA 429 CD	$2\cdot10^{-7}$	489.5	20.7	0.0064	14.8	0.22–0.86	18	120	$8.5\cdot10^{-8}$	0.018	135.9±0.8	9
10	STA 429 CD	$2\cdot10^{-7}$	499.5	20.8	0.0064	16.2	0.28–0.82	8	120	$2.5\cdot10^{-7}$	0.034	134.3±1.0	15
11	STA 429 CD	$2\cdot10^{-7}$	503.7	20.7	0.0064	11.4	0.17–0.79	11	60	$2.7\cdot10^{-7}$	0.056	134.9±0.2	13
12	STA 429 CD	$2\cdot10^{-7}$	511.2	20.9	0.0064	12.6	0.30–0.72	7	30	$7.0\cdot10^{-7}$	0.120	132.9±0.5	21
13	STA 429 C	$1\cdot10^{-7}$	484.0	21.0	0.0032	6.5	0.07–0.50	12	120	$7.6\cdot10^{-8}$	0.018	134.8±0.4	13
14	STA 429 C	$1\cdot10^{-7}$	494.0	21.0	0.0032	9.5	0.13–0.75	9	60	$3.2\cdot10^{-7}$	0.069	131.7±0.8	25
15	STA 429 C	$1\cdot10^{-7}$	502.0	21.2	0.0032	11.2	0.29–0.87	8	30	$7.5\cdot10^{-7}$	0.145	130.2±0.7	30
16	STA 429 C	$1\cdot10^{-7}$	504.0	20.4	0.0032	17.1	0.16–0.76	8	15	$2.2\cdot10^{-6}$	0.300	126.3±0.8	46

Table 2 The results of isothermal determination of the molar enthalpy for $KMnO_4$ decomposition in vacuum ($2\cdot10^{-4}$ bar) at 502.6 K (run 6)[a]

t/ min	$\Delta m/m_0$	$(\Delta m/\Delta t)$/ μg s^{-1}	$\Delta\alpha$	α_m	s_m/s_0	J/ kg m^{-2} s^{-1}	P_{eqp}/ bar	$-\ln K_P$	$(\Delta_r H^o_T/\nu)$/ kJ mol^{-1}
1	0.0007	0.24	0.005	0.005	0.999	$1.82\cdot10^{-6}$	$2.34\cdot10^{-8}$	141.6	144.9
2	0.0005	0.17	0.004	0.009	0.998	$1.30\cdot10^{-6}$	$1.67\cdot10^{-8}$	144.3	146.3
3	0.0005	0.17	0.004	0.013	0.998	$1.30\cdot10^{-6}$	$1.67\cdot10^{-8}$	144.3	146.3
4	0.0007	0.24	0.005	0.019	0.997	$1.83\cdot10^{-6}$	$2.34\cdot10^{-8}$	141.6	144.8
5	0.0012	0.41	0.009	0.028	0.995	$3.14\cdot10^{-6}$	$4.02\cdot10^{-8}$	137.3	142.6
6	0.0015	0.52	0.012	0.040	0.993	$3.93\cdot10^{-6}$	$5.04\cdot10^{-8}$	135.5	141.6
7	0.0029	1.00	0.022	0.062	0.989	$7.64\cdot10^{-6}$	$9.78\cdot10^{-8}$	130.2	138.9
8	0.0022	0.76	0.017	0.079	0.985	$5.81\cdot10^{-6}$	$7.45\cdot10^{-8}$	132.4	140.0
9	0.0044	1.51	0.034	0.113	0.979	$1.17\cdot10^{-5}$	$1.50\cdot10^{-7}$	126.8	137.1
10	**0.0058**	**1.99**	**0.045**	**0.158**	**0.969**	$\mathbf{1.56\cdot10^{-5}}$	$\mathbf{2.00\cdot10^{-7}}$	**124.5**	**135.9**
11	**0.0078**	**2.68**	**0.060**	**0.219**	**0.957**	$\mathbf{2.12\cdot10^{-5}}$	$\mathbf{2.72\cdot10^{-7}}$	**122.0**	**134.6**
12	**0.0095**	**3.26**	**0.074**	**0.292**	**0.940**	$\mathbf{2.63\cdot10^{-5}}$	$\mathbf{3.37\cdot10^{-7}}$	**120.3**	**133.7**
13	**0.0102**	**3.50**	**0.079**	**0.371**	**0.920**	$\mathbf{2.89\cdot10^{-5}}$	$\mathbf{3.70\cdot10^{-7}}$	**119.5**	**133.3**
14	**0.0100**	**3.43**	**0.078**	**0.449**	**0.898**	$\mathbf{2.90\cdot10^{-5}}$	$\mathbf{3.71\cdot10^{-7}}$	**119.5**	**133.3**
15	**0.0097**	**3.33**	**0.075**	**0.524**	**0.875**	$\mathbf{2.89\cdot10^{-5}}$	$\mathbf{3.70\cdot10^{-7}}$	**119.6**	**133.3**
16	**0.0080**	**2.75**	**0.062**	**0.586**	**0.853**	$\mathbf{2.44\cdot10^{-5}}$	$\mathbf{3.13\cdot10^{-7}}$	**120.9**	**134.0**
17	**0.0061**	**2.09**	**0.047**	**0.633**	**0.835**	$\mathbf{1.90\cdot10^{-5}}$	$\mathbf{2.44\cdot10^{-7}}$	**122.9**	**135.1**
18	**0.0066**	**2.27**	**0.051**	**0.684**	**0.812**	$\mathbf{2.11\cdot10^{-5}}$	$\mathbf{2.71\cdot10^{-7}}$	**122.0**	**134.6**
19	**0.0053**	**1.82**	**0.041**	**0.726**	**0.792**	$\mathbf{1.74\cdot10^{-5}}$	$\mathbf{2.23\cdot10^{-7}}$	**123.6**	**135.4**
20	**0.0044**	**1.51**	**0.034**	**0.760**	**0.774**	$\mathbf{1.48\cdot10^{-5}}$	$\mathbf{1.90\cdot10^{-7}}$	**124.9**	**136.1**
21	0.0036	1.24	0.028	0.788	0.757	$1.24\cdot10^{-5}$	$1.59\cdot10^{-7}$	126.3	136.9
22	0.0041	1.41	0.032	0.819	0.735	$1.45\cdot10^{-5}$	$1.86\cdot10^{-7}$	125.0	136.2
23	0.0032	1.10	0.025	0.844	0.716	$1.16\cdot10^{-5}$	$1.49\cdot10^{-7}$	126.8	137.1
24	0.0032	1.10	0.025	0.869	0.694	$1.20\cdot10^{-5}$	$1.54\cdot10^{-7}$	126.6	137.0
25	0.0024	0.82	0.019	0.888	0.675	$9.26\cdot10^{-6}$	$1.19\cdot10^{-7}$	128.6	138.1
26	0.0024	0.82	0.019	0.906	0.653	$9.57\cdot10^{-6}$	$1.23\cdot10^{-7}$	128.4	137.9
27	0.0019	0.65	0.015	0.921	0.633	$7.81\cdot10^{-6}$	$1.00\cdot10^{-7}$	130.0	138.8
28	0.0019	0.65	0.015	0.936	0.610	$8.11\cdot10^{-6}$	$1.04\cdot10^{-7}$	129.7	138.6
29	0.0022	0.76	0.017	0.953	0.577	$9.92\cdot10^{-6}$	$1.27\cdot10^{-7}$	128.1	137.8
30	0.0015	0.52	0.012	0.964	0.549	$7.12\cdot10^{-6}$	$9.12\cdot10^{-8}$	130.8	139.2
31	0.0010	0.34	0.008	0.972	0.525	$4.96\cdot10^{-6}$	$6.35\cdot10^{-8}$	133.6	140.7
32	0.0015	0.52	0.012	0.984	0.477	$8.19\cdot10^{-6}$	$1.05\cdot10^{-7}$	129.6	138.6
33	0.0007	0.24	0.005	0.989	0.443	$4.11\cdot10^{-6}$	$5.27\cdot10^{-8}$	135.1	141.5
34	0.0005	0.17	0.004	0.993	0.409	$3.18\cdot10^{-6}$	$4.08\cdot10^{-8}$	137.2	142.5
35	0.0002	0.07	0.002	0.995	0.391	$1.33\cdot10^{-6}$	$1.71\cdot10^{-8}$	144.2	146.2

[a] The magnitudes of parameters in the interval of steady-state decomposition (used in data averaging) are marked with bold

which $\Delta_r H^o_T/\nu$=138.3±0.4 kJ mol^{-1}. The reason for that is unknown. (The data of this experiment are excluded of all further calculations and diagrams).

- In contrast to the invariability of the molar enthalpy with the change of decomposition rate in atmospheric experiments, the rise of the decomposition rate in vacuum experiments monotonously reduces the molar enthalpy (Fig. 2). The molar enthalpy in the latter case is related to the decomposition rate (and therefore to the heat generation rate) by the linear equation:

$$\Delta_r H^o_T/\nu \approx 136.4 - 34.7\Delta\alpha_m/(\Delta t n) \qquad (10)$$

- This proves unambiguously that the origin of the molar enthalpy reduction in vacuum is self-heating.

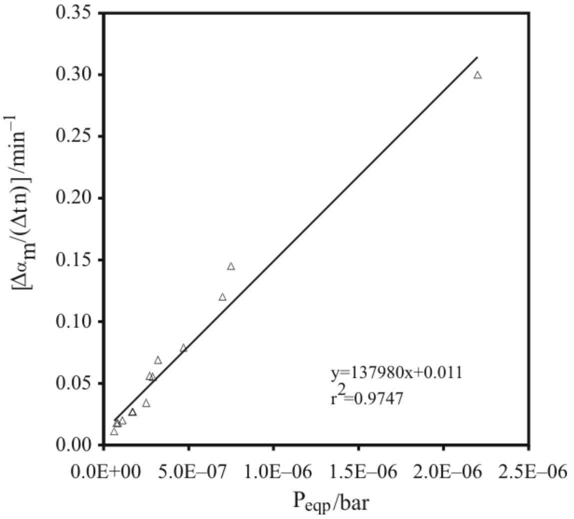

Fig. 1 The correlation between the rate of $KMnO_4$ decomposition $[\Delta\alpha_m/(\Delta tn)]$ and the equivalent pressure of primary products P_{eqp}

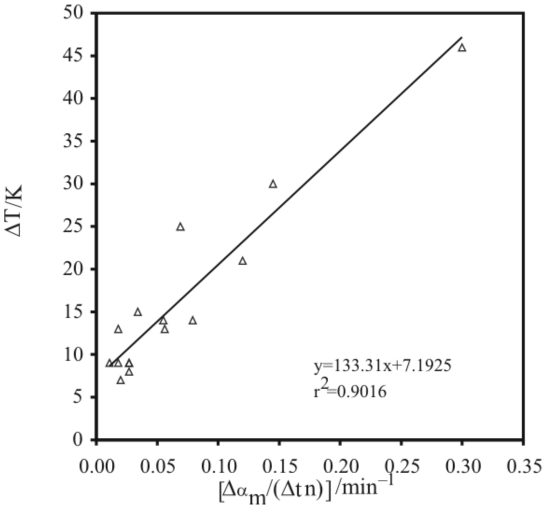

Fig. 3 The dependence of the temperature increase ΔT of the decomposing sample on the rate of $KMnO_4$ decomposition $[\Delta\alpha_m/(\Delta tn)]$

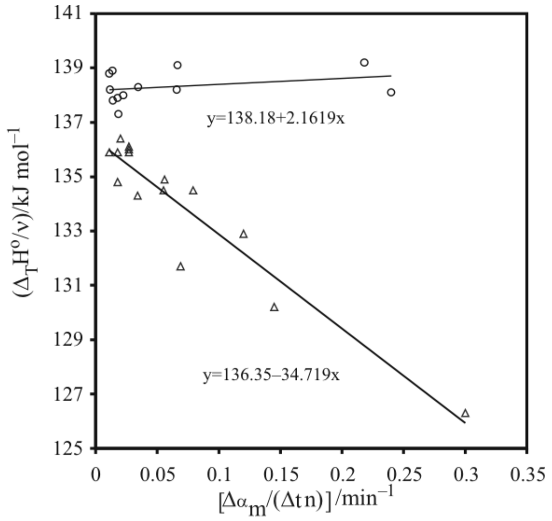

Fig. 2 The dependence of the molar enthalpy $(\Delta_r H^o_T/\nu)$ on the rate of $KMnO_4$ decomposition $[\Delta\alpha_m/(\Delta tn)]$; ○ – under atmospheric pressure and △– in a vacuum

- As should be expected from the above, the temperature increase, ΔT, of the decomposing sample as a function of the decomposition rate (Fig. 3), is also described by the linear equation:

$$\Delta T \approx 7.2 + 133\Delta\alpha_m/(\Delta tn) \qquad (11)$$

- The maximum magnitude of ΔT for $\Delta\alpha_m/(\Delta tn)$= 0.3 min^{-1} is 46 K (run 16). This value corresponds to about 10% of the furnace temperature. The self-heating effect appears to be very high considering that the absolute value of the reaction enthalpy of exothermic reaction (2) measured by the DSC technique is only 10.4±1.5 kJ mol^{-1} [17]. This contradicts the wide-spread opinion that the self-heating effect is insignificant if the reaction enthalpy is small.
- The difference between the values of $\Delta_r H^o_T/\nu$ measured by DSC [17] and by TG techniques (–10 and +138 kJ mol^{-1}) is rather obvious. The first value was measured for a closed system (pan+sample+lid) as a whole, the second, for the reactant only, when a part of the condensation energy is transferred to the solid product(s). Such a difference is typical for all solid-state decomposition reactions. In this particular case, the difference is especially high because the primary gaseous product, the free atoms of oxygen, recombines with the evolution of heat outside the reaction interface: $2O \rightarrow O_2$+500 kJ mol^{-1}. This difference is erroneously identified in the literature as the difference between two quantities: the 'molar enthalpy' (in the case of DSC) and the so-called 'activation energy' (in the case of TG). The latter actually has no physical meaning in solid-state kinetics [18].
- Of interest is the deviation of the oxygen yield, $\Sigma(\Delta m/m_0)$, in some of the vacuum experiments from the expected value of 10–12% (Table 1). In two cases (runs 4 and 13), the $\Sigma(\Delta m/m_0)$ value is 6.9 and 6.5%, and in three cases (runs 5, 10 and 16), it is 15.0, 16.2 and 17.1%, respectively. We can propose that in these cases the reaction develops in accordance with the schemes:

$$3KMnO_4 = K_3(MnO_4)_2 + MnO_2 + O_2 \qquad (12)$$

and

$$10KMnO_4(s) = 5K_2MnO_4(s) + 5MnO(s) + 7.5O_2 \qquad (13)$$

- The yield of oxygen for reaction (12) is 6.7%, and for reaction (13), it is 15%. Reaction (12) has been observed by Boldyrev *et al.* [19] and later by Herbstein *et al.* [20] in a high vacuum at temperatures near 488 K. (In our experiments, the temperature was 489.9 and 484.0 K). The development of the decomposition according to reaction (13) can be explained by the inadequate stability of MnO_2 at high temperatures. Taking into consideration the addition of the ΔT value, the actual temperature of the sample in runs 5, 10 and 16 amounts to 509, 515 and 550 K. However, the high yield can be related to the partial ejection of sample particles upon heating at $T\geq500$ K. This problem deserves further investigation.

- A monotonous decrease of the molar enthalpy with a rise in temperature leads to the large systematic overstating of the parameter *E*, calculated by the Arrhenius plot method. This statement is illustrated in Fig. 4. As an example, the primary data for the $KMnO_4$ decomposition at 484–511 K and $2\cdot10^{-7}$ bar were used. A decrease of $\Delta_r H^o_T/\nu$ in this temperature interval by 3 kJ mol^{-1} manifested itself in the *E* value (178.6 kJ mol^{-1}) that is 40 kJ mol^{-1} above the true value. This effect, theoretically predicted by L'vov [10], should be taken into account when evaluating the accuracy of the reported values of the *E* parameter in vacuum: 162 kJ mol^{-1} [21] and 165 kJ mol^{-1} [22].
- Taking into account the significant underestimation of molar enthalpy in vacuum (10^{-4}–10^{-7} bar) at 484–511 K, the possible application of potassium permanganate as a kinetics standard [11, 12] should be limited to atmospheric pressure.

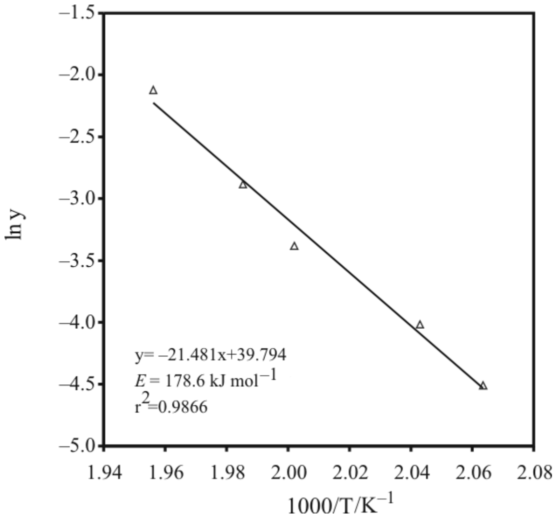

Fig. 4 The Arrhenius plot of ln*y* *vs.* 1000/*T* where $y\equiv[\Delta\alpha_m/(\Delta tn)]/min^{-1}$ for the decomposition of $KMnO_4$ under vacuum pressure of $2\cdot10^{-7}$ bar (runs 8–12)

Conclusions

It has been shown that the exothermic decomposition of $KMnO_4$ in vacuum is accompanied by a significant self-heating effect. It manifests itself in the reduction of the molar enthalpy of the reaction, determined by the third-law method. In comparison with the value 138.3±0.6 kJ mol^{-1} that is valid for the decomposition of $KMnO_4$ under atmospheric pressure at 493–553 K [12], the molar enthalpy in vacuum (10^{-4}–10^{-7} bar) at 484–511 K varies in the range of 136.4 to 126.3 kJ mol^{-1}. This is related to the reduction of the thermal conductivity of the residual air in the furnace and, as a result, to the self-heating of the reactant, that accelerates the exothermic reaction.

A simple method of quantitative evaluation of the self-heating effect has been developed. By analogy with the method for evaluation of the self-cooling effect [9], it is based on the determination of the molar enthalpy by the third-law method at two different temperatures. It has been shown that the increase of sample temperature above the furnace temperature, T_f, in the case of the exothermic decomposition of $KMnO_4$ in a high vacuum and $T_f\geq490$ K reaches a few tens of degrees.

A monotonous decrease of the molar enthalpy with a rise in temperature leads to the systematic overstating of the parameter *E*, calculated by the Arrhenius plot method. This effect should be taken into account when evaluating the accuracy of the literature data obtained in a vacuum. Taking into account the significant underestimation of molar enthalpy in vacuum (10^{-4}–10^{-7} bar), the possible application of potassium permanganate as a kinetics standard [11, 12] should be limited to atmospheric pressure.

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