

Decomposition of KMnO_4 in different gases as a potential kinetics standard in thermal analysis

Boris V. L'vov · Valery L. Ugolkov

Received: 21 May 2009 / Accepted: 26 May 2009 / Published online: 10 July 2009
© Akadémiai Kiadó, Budapest, Hungary 2009

Abstract The assumption that potassium permanganate may serve as a kinetics standard in solid decomposition kinetics made a priori on the basis of the mechanism of the congruent dissociative vaporization of KMnO_4 and its crystal structure was successfully supported experimentally. As expected, the decomposition rate of KMnO_4 does not depend on the kind of foreign gas (He, air, CO_2 and Ar) and on the measurement technique (isothermal or dynamic). Other requirements for KMnO_4 as an ideal kinetics standard are satisfied as well. The use of the third-law method for determining the molar enthalpy of a reaction ($\Delta_r H_T^0/\nu$) provides an excellent reproducibility of results. The mean value of $\Delta_r H_T^0/\nu$ from 12 experiments in different gases is $138.3 \pm 0.6 \text{ kJ mol}^{-1}$, which coincides with the value of $138.1 \text{ kJ mol}^{-1}$ calculated from the isothermal measurements in different gases by the second-law method. As predicted by theory, the random errors of the second-law and Arrhenius plot methods are 10–20 times greater. In addition, the use of these methods in the case of dynamic measurements is related to large systematic errors caused by an inaccurate selection of the geometrical (contraction) model. The third-law method is practically free of these errors.

Keywords Arrhenius plot method · Congruent vaporization · Kinetics standard ·

Potassium permanganate · Second-law method · Third-law method

Introduction

The search for an appropriate kinetics standard for studies in the thermal decomposition of solids is one of interlaboratory scientific projects initiated about 15 years ago by the Kinetics Committee at the International Confederation for the Thermal Analysis and Calorimetry (ICTAC). In the view of experts [1], the main requirements for an ideal kinetics standard are the following:

- the decomposition reaction should be irreversible;
- the absolute value of the reaction enthalpy should be low in order to restrict the effects of self-cooling or self-heating;
- the decomposition temperature should not be too low to avoid large errors in temperature calibration;
- the reactant and solid product should not react with the ambient atmosphere;
- the reaction rate should be independent of the sample preparation technique and of particle size;
- the changes to be measured to follow the course of reaction, e.g., the mass or amounts of evolved gases should be large enough to allow the use of small samples.

As demonstrated by the interlaboratory tests, summarized by the Kinetics Committee in 1994 [1], the reaction of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dehydration, chosen (rather arbitrary) as a possible kinetics standard, proved to be absolutely unsuitable for this purpose. This primarily refers to the fulfillment of requirements (1) and (3)–(5). Depending on the conditions of decomposition (in particular, the presence of H_2O vapour) and the calculation methods, the parameter E of the Arrhenius equation, measured in the most authoritative

B. V. L'vov (✉)
Department of Analytical Chemistry, St. Petersburg State
Polytechnic University, St. Petersburg 195251, Russia
e-mail: borisl'vov@rambler.ru

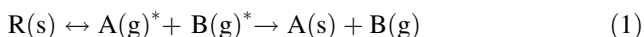
V. L. Ugolkov
Laboratory of Physics and Chemistry of Nanosized Systems,
Institute of Silicate Chemistry, St. Petersburg 199155, Russia

laboratories of the world, varied within the range 54–272 kJ mol⁻¹ [1]. The negative outcome of these tests strongly diminished the interest in this problem.

In contrast to the employed purely empirical search for a kinetics standard, the novel thermochemical approach to the mechanism and kinetics of thermal decomposition, developed by L'vov and his colleagues and summarized in the monograph [2], creates the possibility of an intelligent choice based on a preliminary theoretical analysis. The primary results of such studies have already been reported by L'vov and Ugolkov [3, 4]. The present paper describes the results of our further studies concerning this problem. In contrast to previous paper [4], devoted to the decomposition of KMnO₄ in vacuum, this work describes the peculiarities of its decomposition in different gases under atmospheric pressure.

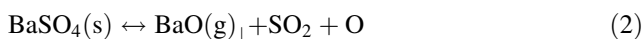
Theoretical analysis

The most important of the above requirements for an ideal kinetics standard are conditions (1) and (4), the irreversibility of the reaction and the independence of the decomposition rate from the composition of the gaseous medium. These requirements can be satisfied in the cases where all the primary products are in states that differ from their equilibrium states. To these belong, in particular, reactions of the general form:



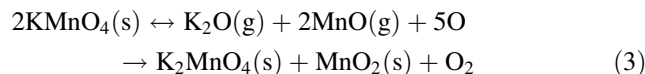
where A(g)* is a low volatile product condensed at the instant of decomposition, and B(g)* is a gaseous product that is in a non-equilibrium state at the decomposition temperature, e.g., in the form of free O or N atoms, which undergo association at the instant of decomposition to give equilibrium molecules O₂ and N₂.

Under these conditions, the partial pressures of the primary products A(g)* and B(g)* and, consequently, the decomposition rate of the reactant R(s) depend only on the stoichiometry and the thermochemical characteristics of the reaction and should be independent of the composition and pressure of the gas in the furnace. Of particular interest among those classes of substances that have been studied so far and decompose to give oxygen or nitrogen in the atomic form [2] are potassium, rubidium and cesium permanganates. These permanganates have the crystal structure of barite BaSO₄, which decomposes according to the scheme [5, 6]:

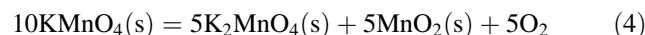


Taking into account that BaSO₄ and the permanganates mentioned above have the same crystal structure (the

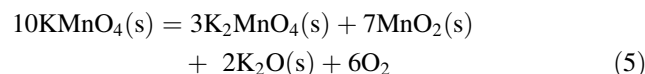
rhombic system IV), it could be expected, as first noted in monograph [2], that the primary stage of their decomposition also occurs with the evolution of atomic oxygen:



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 [7], the mechanism and kinetics of its decomposition have been investigated by virtually all authoritative laboratories in the world and, in particular, by the authors of [8–17]. Starting at [7], the resultant reaction has been represented either by the scheme:



which is equivalent to the scheme of reaction (3), or by the scheme:



suggested by Rudolf more than 100 years ago [8]. The difference between these two schemes is in the relative amounts of solid products and free oxygen, the latter varying in the range 10–12 wt%.

Experimental

Measurement conditions

The main goal of the experiments was to verify the expected independence of the decomposition rate of KMnO₄ from the composition of the gas in the furnace and the measurement technique (isothermal or dynamic). For this purpose, the absolute decomposition rate of KMnO₄ was measured in different medium by isothermal and dynamic TG. These data were used to calculate the molar enthalpy of the reaction.

The change in the mass of sample per unit time and its temperature were measured using Netzsch Models STA 429 C, STA 429 CD and STA 449 C 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 heating rate in

dynamic experiments was 3 and 10 K min^{-1} . The isothermal measurements were made in the presence of air, Ar, He and CO_2 . The dynamic measurements were made in the presence of air only.

The calculation scheme

The main stages of the calculation scheme were described briefly in [4, 18]. The input parameter automatically recorded by the thermal analyzer is the relative loss of mass, $\Delta m/m_0$, 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. (In our experiments, in accord with the reactions (4) and (5), the $\Sigma(\Delta m/m_0)$ value varied in the range from 0.10 to 0.12.) 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 since heating the furnace to the beginning of measurements. The absolute decomposition rate of powdered samples is calculated by the equation [2, 18]:

$$J = \frac{\Delta m/\Delta t}{2.8s_m} \quad (6)$$

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 different diameter-to-height ratios (d/h). The results of numerically modeling the s_m/s_0 variation with α in the process of homogeneous pellet decomposition across the entire surface for d/h ratios of 1, 3, 5, 10 and 20 were compared with the curve shapes of the function $(1 - \alpha)^n = f(\alpha)$ (7)

The best approximation of the numerical curves for the above d/h ratios is obtained for the following magnitudes of the exponent n in Eq. (7): 0.67, 0.50, 0.33, 0.18 and 0.10 (Fig. 1). The dependence of n from the d/h ratio can be analytically described by the linear ($1 \leq d/h \leq 5$) and power ($5 \leq d/h \leq 20$) relationships (Fig. 2). These relationships can be used for the interpolation of the magnitude of the exponent for any d/h value ranging from 1 to 20. In our experiments, $d/h = 10$ and therefore $n = 0.18$.

The molar enthalpy of the decomposition reaction was calculated by the third-law method. It was expected that, as in all other cases [19, 20], the application of the third-law method to these measurements will significantly increase

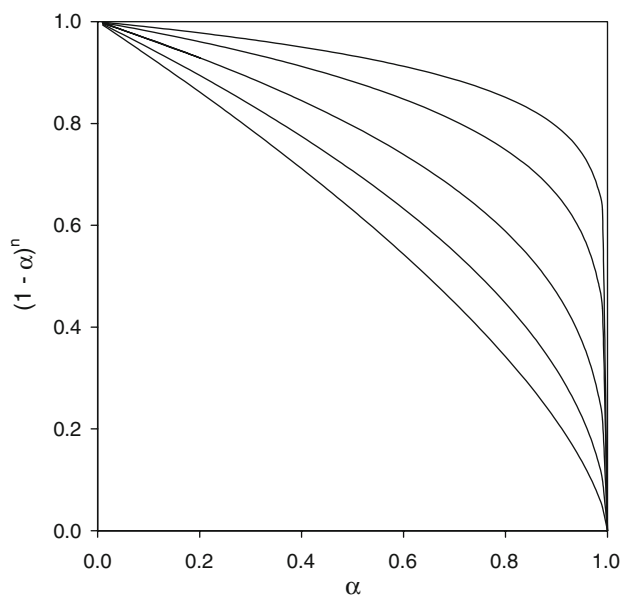


Fig. 1 The curve shapes of the function $(1 - \alpha)^n = f(\alpha)$ for different n parameters: 0.10; 0.18; 0.33; 0.50 and 0.67 (from top to bottom)

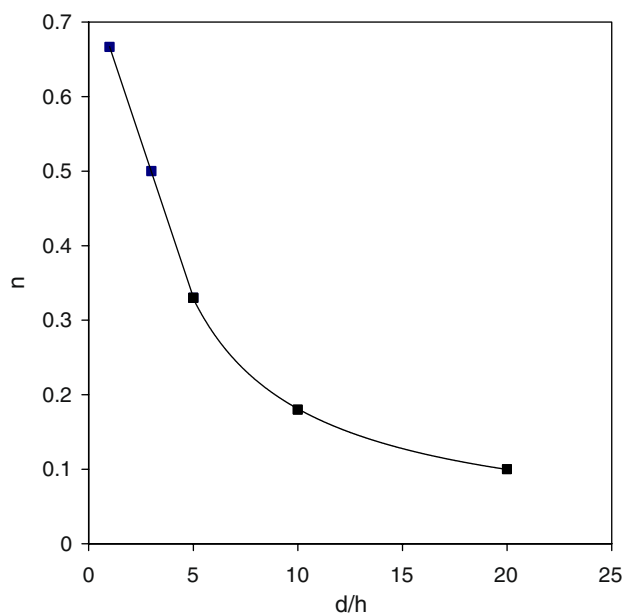


Fig. 2 The dependence of n parameter from d/h ratio described by the linear and power equations: $n = 0.7514 - 0.0842d/h$ ($1 \leq d/h \leq 5$) and $n = 1.3157(d/h)^{-0.8612}$ ($5 \leq d/h \leq 20$)

the precision and accuracy of experimental results. The equilibrium pressure of atomic oxygen (the primary product of reaction (3)) was found using the Hertz–Langmuir equation:

$$P_{\text{eqp}} = \frac{(2\pi MRT)^{1/2} J}{\gamma M} \quad (8)$$

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 (3) was found:

$$K_p = (P_{\text{eqp}})^{\nu} / \delta \quad (9)$$

Here 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 stoichiometric coefficients of the decomposition products [2]. For reaction (3), which involves three products, $\delta = 2.907$.

The enthalpy of the reaction was calculated by the equation:

$$\Delta_r H_T^{\circ} = T(\Delta_r S_T^{\circ} - R \ln K_p) \quad (10)$$

where $\Delta_r S_T^{\circ}$ is the entropy of the reaction. Thermodynamic functions for potassium permanganate and its decomposition products at 298 K are given in Table 1 [21–23]. It is easy to calculate that $\Delta_r S_{298}^{\circ} / \nu = 150.0 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$ (assuming that the deviations in the values of the S_{298}° function from their true values for gaseous MnO and K_2O species are the same in sign). The difference between the entropy change for the reaction (3) at 298 K and at 500 K can be estimated using the BaSO_4 decomposition reaction (2) for comparison. (The values of thermal increments in the entropy of KMnO_4 are unknown.) In the case of BaSO_4 , this difference ($\Delta_r S_{298}^{\circ} / \nu - \Delta_r S_{500}^{\circ} / \nu$) is about $9 \text{ J mol}^{-1} \text{ K}^{-1}$ [22]. Therefore, it should be expected that for KMnO_4 , $\Delta_r S_{500}^{\circ} / \nu \approx 141 \text{ J mol}^{-1} \text{ K}^{-1}$. This value was used in our further calculations. When reliable data for the entropy of KMnO_4 at 500 K becomes known, the final values of molar enthalpy for reaction (3) should be recalculated.

Table 1 Values of thermodynamic functions for KMnO_4 and the products of its decomposition at 298 K [21–23]

Species	$\Delta_f H_{298}^{\circ} (\text{kJ mol}^{-1})$	$S_{298} (\text{J mol}^{-1} \text{ K}^{-1})$
$\text{KMnO}_4(\text{s})$	−829.5	171.7 ± 0.4
$\text{K}_2\text{MnO}_4(\text{s})$	−1179.9	175.6 ± 0.4^a
$\text{MnO}_2(\text{s})$	−521.8	53.2 ± 0.4
$\text{MnO}(\text{g})$	123.8	226.4 ± 6.3
$\text{K}_2\text{O}(\text{s})$	−361.7	96.0 ± 4
$\text{K}_2\text{O}(\text{g})$	−74.1	286.4 ± 6
O_2	0	205.0 ± 0.1
O	249.2	160.9 ± 0.1

^a For K_2SO_4

Results and discussion

Basic result

The conditions and final results of the isothermal and dynamic determination of the molar enthalpies of the KMnO_4 decomposition in different media are presented in Table 2 in order of decreasing thermal conductivity (λ) of the gases: helium, air, CO_2 and argon, and in order of increasing temperature among each of the gases. Tables 3 and 4 contain as examples the results of calculations of the molar enthalpies in the isothermal and non-isothermal decomposition of KMnO_4 in air.

As can be seen from the results in Table 2, the values of the molar enthalpy, regardless of gas features, in particular, of the eightfold difference in thermal conductivity, measurement technique (isothermal and dynamic), of the decomposition temperature (493–553 K) and the type of thermal analyzer used, vary in a very narrow interval (137.3 – $139.2 \text{ kJ mol}^{-1}$), such that the average value of $\Delta_r H_T^{\circ} / \nu$ is equal to 138.3 ± 0.6 (SD). This value is in reasonable agreement with the results obtained in other studies by the Arrhenius plot method: 141 kJ mol^{-1} for single crystals [11], and 162 [11], 130 ± 5 [13], 165 ± 10 [16] and 143 kJ mol^{-1} [17] for powders. All these results have been obtained in a vacuum. The average value of the E parameter reported in these works is $148 \pm 15 \text{ kJ mol}^{-1}$. (The E parameter is equivalent to the molar enthalpy in the thermochemical approach.) The most important difference of our result from the literature data is about a 20-fold reduction of random errors. As expected, this is due to using the third-law method instead of the Arrhenius plot method for determining the E parameter. This conclusion is additionally supported by the results described below.

Precision and accuracy of the second-law and third-law methods

The results of our dynamic measurements, in addition to the third-law method, were used for determining the molar enthalpy by the second-law method (Fig. 3). Furthermore, the second-law method was applied to the data obtained by the isothermal measurements (Fig. 4). As can be seen from these diagrams, the points are rather scattered (e.g., for run 8 in Fig. 3). The average value of $\Delta_r H_T^{\circ} / \nu$ from all four results (138, 146, 152 and 161 kJ mol^{-1}) is equal to $149 \pm 10 \text{ kJ mol}^{-1}$. This practically coincides with the mean value from the literature data ($148 \pm 15 \text{ kJ mol}^{-1}$), but is about 10 kJ mol^{-1} higher than the molar enthalpy obtained by the third-law method ($138.3 \pm 0.6 \text{ kJ mol}^{-1}$). Again, the random error is an order of magnitude higher than that for the third-law method.

Table 2 The conditions and final results of isothermal and dynamic determination of the molar enthalpies for KMnO_4 decomposition in different medium by the third-law method

Run	Medium	Instrument	Technique	T (K)	m_0 (mg)	λ at 500 K [24] ($\text{mW m}^{-1} \text{K}^{-1}$)	Measurement range (α_m)	Point number	Integration time (s)	P_{exp} (bar)	$\Delta_r H_T^0/v$ (kJ mol^{-1})
1	He	STA 429 CD	Isothermal	493.6	20.0	214	0.29–0.90	11	300	5.4×10^{-8}	138.8 ± 0.4
2	Air	STA 429 C	Isothermal	494.3	20.5	40	0.23–0.87	7	300	8.2×10^{-8}	137.3 ± 0.3
3	Air	STA 429 C	Isothermal	499.0	20.3	40	0.30–0.75	5	300	9.8×10^{-8}	137.9 ± 0.5
4	Air	STA 429 C	Isothermal	504.0	19.8	40	0.38–0.83	4	300	1.3×10^{-7}	138.0 ± 0.3
5	Air	STA 429 C	Isothermal	506.8	20.5	40	0.13–0.89	22	60	1.5×10^{-7}	138.3 ± 0.5
6	Air	STA 429 C	Isothermal	520.0	20.6	40	0.44–0.90	14	30	3.5×10^{-7}	138.2 ± 0.4
7	Air	STA 429 CD	Dynamic: 3 K min^{-1}	510–531	21.2	40	0.14–0.67	8	60	1.4×10^{-7}	139.1 ± 0.4
8	Air	STA 429 C	Dynamic: 10 K min^{-1}	525–545	20.1	40	0.11–0.59	11	12	3.1×10^{-7}	139.2 ± 0.7
9	Air	STA 429 C	Dynamic: 10 K min^{-1}	523–553	20.6	40	0.11–0.95	7	30	3.7×10^{-7}	138.1 ± 0.3
10	CO_2	STA 449 C	Isothermal	493.7	21.1	33	0.29–0.83	8	300	2.5×10^{-6}	138.9 ± 0.6
11	Ar	STA 429 C	Isothermal	493.2	20.1	26	0.29–0.81	9	300	6.2×10^{-8}	138.2 ± 0.3
12	Ar	STA 429 C	Isothermal	493.6	20.9	26	0.21–0.77	8	300	6.9×10^{-8}	137.8 ± 0.2

The application of the second-law method to the data obtained by isothermal measurements (Fig. 4) is much more reliable than for dynamic measurements. This becomes apparent in comparing the integration time spent on the registration of each point in the plots for these two cases. In isothermal measurements, this time is in the range 8–60 min, while in dynamic measurements, it is only 12–60 s. Therefore, the proximity of the $\Delta_r H_T^0/v$ value ($138.1 \text{ kJ mol}^{-1}$) obtained by the second-law method (Fig. 4) and the mean $\Delta_r H_T^0/v$ value ($138.3 \pm 0.6 \text{ kJ mol}^{-1}$) obtained by the third-law method cannot be accidental. One of the reasons for the systematic deviation of results from the true value in the case of the second-law method applied to dynamic measurements is related to an inaccurate choice of the contraction model. As illustration, Table 5 presents the results of calculations of the molar enthalpies for one of our dynamic experiments (run 7) by all three methods (including the Arrhenius plot method) for the different contraction models. The relative differences in $\Delta_r H_T^0/v$ values for the contraction models with $n = 0.10$ and 0.67 are only 1% for the third-law method and 40% for the two other methods. Two other reasons are related to reactant self-cooling or self-heating (for the endothermic and exothermic reactions in a high vacuum) and the condensation effect [25–27].

The requirements for an ideal kinetics standard and their fulfillment

It would be useful to consider the obtained results in a framework of the main requirements for an ideal kinetics standard formulated above. (The first sentence in each item repeats the corresponding requirement.)

The decomposition reaction should be irreversible. The choice of KMnO_4 as a candidate for a kinetics standard was based on this very requirement (in contrast to the use of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ in previous investigations [1]).

The absolute value of the reaction enthalpy should be low in order to reduce the effects of self-cooling or self-heating. The enthalpy values for reactions (4) and (5) calculated with the data in Table 1 are as follows: $\Delta_r H_{298}^0 = -21.4 \text{ kJ mol}^{-1}$ in the first case and $\Delta_r H_{298}^0 = 95.5 \text{ kJ mol}^{-1}$ in the second. The calculated value ($-21.4 \text{ kJ mol}^{-1}$) is about twice the value measured by DSC ($-10.4 \pm 1.5 \text{ kJ mol}^{-1}$ [15]). The self-heating effect at such a value of the reaction enthalpy and under atmospheric pressure should not be too high.

The decomposition temperature should not be too low in order to avoid large errors in temperature calibration. In the case of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, the decomposition temperature is below 300 K. TG instruments are difficult to calibrate accurately in this range [1]. The decomposition temperature in the case of KMnO_4 is in a range optimal for calibration: 480–520 K.

Table 3 The results of isothermal determination of the molar enthalpy for KMnO_4 decomposition in air at 520 K (run 6)^a

t (min)	$\Delta m/m_0$	$(\Delta m/\Delta t)$ ($\mu\text{g s}^{-1}$)	$\Delta\alpha$	α_m	s_m/s_0	J ($\text{kg m}^{-2} \text{s}^{-1}$)	P_{eqp} (bar)	$-\ln K_P$	$\Delta_r H_T^0/v$ (kJ mol^{-1})
0.5	0.0027	1.85	0.023	0.311	0.935	1.50×10^{-5}	1.96×10^{-7}	124.6	140.7
1.0	0.0035	2.40	0.030	0.341	0.928	1.96×10^{-5}	2.56×10^{-7}	122.5	139.5
1.5	0.0035	2.40	0.030	0.371	0.920	1.98×10^{-5}	2.58×10^{-7}	122.4	139.5
2.0	0.0037	2.54	0.032	0.403	0.911	2.11×10^{-5}	2.75×10^{-7}	121.9	139.2
2.5	0.0039	2.68	0.034	0.437	0.902	2.25×10^{-5}	2.93×10^{-7}	121.4	138.9
3.0	0.0040	2.75	0.034	0.471	0.892	2.34×10^{-5}	3.04×10^{-7}	121.1	138.8
3.5	0.0043	2.95	0.037	0.508	0.880	2.54×10^{-5}	3.31×10^{-7}	120.4	138.4
4.0	0.0045	3.09	0.039	0.547	0.867	2.70×10^{-5}	3.52×10^{-7}	119.9	138.1
4.5	0.0045	3.09	0.039	0.586	0.853	2.75×10^{-5}	3.58×10^{-7}	119.8	138.1
5.0	0.0045	3.09	0.039	0.625	0.838	2.80×10^{-5}	3.64×10^{-7}	119.7	138.0
5.5	0.0044	3.02	0.038	0.663	0.822	2.79×10^{-5}	3.63×10^{-7}	119.7	138.0
6.0	0.0043	2.95	0.037	0.700	0.805	2.78×10^{-5}	3.62×10^{-7}	119.7	138.0
6.5	0.0040	2.75	0.034	0.734	0.788	2.64×10^{-5}	3.44×10^{-7}	120.1	138.2
7.0	0.0042	2.88	0.036	0.770	0.767	2.85×10^{-5}	3.71×10^{-7}	119.5	137.9
7.5	0.0042	2.88	0.036	0.807	0.744	2.94×10^{-5}	3.83×10^{-7}	119.3	137.8
8.0	0.0041	2.82	0.035	0.842	0.717	2.98×10^{-5}	3.88×10^{-7}	119.2	137.7
8.5	0.0038	2.61	0.033	0.875	0.688	2.88×10^{-5}	3.75×10^{-7}	119.4	137.9
9.0	0.0033	2.27	0.028	0.903	0.657	2.62×10^{-5}	3.41×10^{-7}	120.2	138.3
9.5	0.0025	1.72	0.022	0.925	0.628	2.07×10^{-5}	2.70×10^{-7}	122.1	139.3
10.0	0.0019	1.30	0.016	0.941	0.601	1.65×10^{-5}	2.15×10^{-7}	123.9	140.3
10.5	0.0014	0.96	0.012	0.953	0.576	1.26×10^{-5}	1.65×10^{-7}	126.0	141.4
11.0	0.0009	0.62	0.008	0.961	0.558	8.40×10^{-6}	1.09×10^{-7}	129.3	143.2

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

The reactant and solid product/products should not react with the ambient atmosphere. This is probably the most important requirement for the selected decomposition reaction. As can be seen from the results presented in Table 2, the presence of O_2 in the furnace (0.21 bar) has no effect on the decomposition rate of KMnO_4 . This is a strong indication that oxygen is released in the form of free atoms, which is in line with our prediction based on the identity of crystal structures of KMnO_4 and BaSO_4 . This conclusion is also confirmed by the exquisite experiments performed by Herbstein et al. [17]. A mixture of KMnO_4 crystals labeled with oxygen isotopes ^{16}O and ^{18}O was used in their experiments. The evolving oxygen analyzed by mass-spectrometry was composed of a 1:1:2 mixture of $^{32}\text{O}_2$, $^{36}\text{O}_2$ and $^{34}\text{O}_2$ species. The formation of $^{34}\text{O}_2$ molecules indicates unambiguously that oxygen is primarily released as free ^{16}O and ^{18}O atoms, which associate upon mutual collisions into $^{34}\text{O}_2$ molecules. The same conclusion was made on the basis of a more complicated decomposition mechanism by Herbstein et al. [17]. The decomposition

rate of KMnO_4 , in contrast to $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, is independent of the presence of H_2O vapour. This was confirmed by Brown et al. [16].

The reaction rate should be independent of the sample preparation technique and of particle size. Our own experiments concerning this were limited up to now only to pressed pellets prepared from powders crushed at different moments (with no effect of this factor). Therefore, further investigations are desirable to estimate the impact of the sample preparation techniques and of particle size on the kinetics of KMnO_4 decomposition. For comparison, the reaction rate of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ decomposition is very dependent upon particle-size and prehistory [1].

The changes to be measured should be large enough to allow the use of small samples. In this respect, both reactants have similar features. The changes in mass are about 11% for KMnO_4 and 14% for $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. This is enough for the use of samples with a mass of a few milligrams. To illustrate, Prout and Tompkins [11] used the samples of KMnO_4 up to 2 mg.

Table 4 The results of dynamic measurement (3 K/min) of the molar enthalpy for KMnO_4 decomposition (run 7)^a

t (min)	T (K)	$\Delta m/m_0$	$\Delta m/\Delta t$ ($\mu\text{g s}^{-1}$)	Δz	α_m	s_m/s_0	J ($\text{kg m}^{-2} \text{s}^{-1}$)	P_{eqp} (bar)	$-\ln K_P$	$(\Delta_r H_T^0/v$ (kJ mol^{-1}))
1	483	0.0002	0.071	0.002	0.002	1.000	5.36×10^{-7}	6.73×10^{-9}	151.6	144.2
2	486	0.0002	0.071	0.002	0.004	0.999	5.36×10^{-7}	6.75×10^{-9}	151.6	145.1
3	489	0.0050	1.767	0.043	0.046	0.991	1.35×10^{-5}	1.71×10^{-7}	125.7	132.8
4	492	0.0002	0.071	0.002	0.048	0.991	5.41×10^{-7}	6.85×10^{-9}	151.5	146.8
5	495	0.0007	0.247	0.006	0.054	0.990	1.89×10^{-6}	2.41×10^{-8}	141.4	142.5
6	498	0.0007	0.247	0.006	0.060	0.989	1.90×10^{-6}	2.42×10^{-8}	141.4	143.4
7	501	0.0009	0.318	0.008	0.068	0.987	2.44×10^{-6}	3.12×10^{-8}	139.3	143.2
8	504	0.0019	0.671	0.016	0.084	0.984	5.17×10^{-6}	6.63×10^{-8}	133.3	140.9
9	507	0.0024	0.848	0.021	0.105	0.980	6.56×10^{-6}	8.44×10^{-8}	131.4	140.7
10	510	0.0038	1.343	0.032	0.137	0.974	1.05×10^{-5}	1.35×10^{-7}	127.6	139.6
11	513	0.0052	1.837	0.044	0.181	0.965	1.44×10^{-5}	1.87×10^{-7}	125.0	139.0
12	516	0.0066	2.332	0.056	0.238	0.952	1.86×10^{-5}	2.41×10^{-7}	123.0	138.7
13	519	0.0075	2.650	0.064	0.302	0.937	2.14×10^{-5}	2.79×10^{-7}	121.8	138.9
14	522	0.0086	3.039	0.074	0.376	0.919	2.51×10^{-5}	3.27×10^{-7}	120.5	139.0
15	525	0.0101	3.569	0.086	0.462	0.894	3.03×10^{-5}	3.96×10^{-7}	119.0	139.0
16	528	0.0115	4.063	0.098	0.560	0.863	3.57×10^{-5}	4.69×10^{-7}	117.6	139.0
17	531	0.0132	4.664	0.113	0.673	0.818	4.32×10^{-5}	5.69×10^{-7}	116.1	138.9
18	534	0.0118	4.169	0.101	0.774	0.765	4.13×10^{-5}	5.45×10^{-7}	116.4	139.9
19	537	0.0101	3.569	0.086	0.860	0.702	3.86×10^{-5}	5.11×10^{-7}	117.0	141.0
20	540	0.0090	3.180	0.077	0.937	0.608	3.97×10^{-5}	5.27×10^{-7}	116.7	141.6
21	543	0.0038	1.343	0.032	0.970	0.533	1.91×10^{-5}	2.54×10^{-7}	122.6	145.7
22	546	0.0013	0.459	0.011	0.981	0.492	7.08×10^{-6}	9.46×10^{-8}	130.5	151.0
23	549	0.0008	0.283	0.007	0.987	0.455	4.71×10^{-6}	6.31×10^{-8}	133.7	153.7
24	552	0.0005	0.177	0.004	0.992	0.422	3.18×10^{-6}	4.26×10^{-8}	136.8	156.3
25	555	0.0005	0.177	0.004	0.996	0.370	3.62×10^{-6}	4.88×10^{-8}	135.8	156.6

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

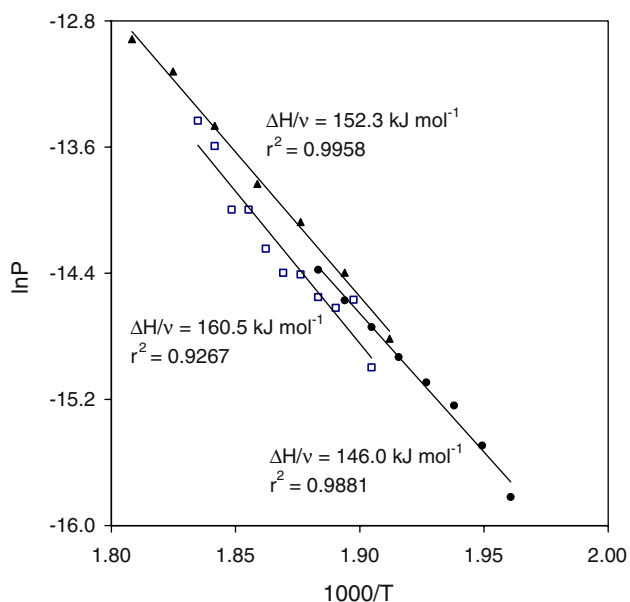


Fig. 3 Second-law plots of $\ln(P_{\text{eqp}}/\text{bar})$ versus $(1000/T)/\text{K}^{-1}$ for different runs of the dynamic measurements: filled circles Run 7; open squares Run 8 and filled triangles Run 9

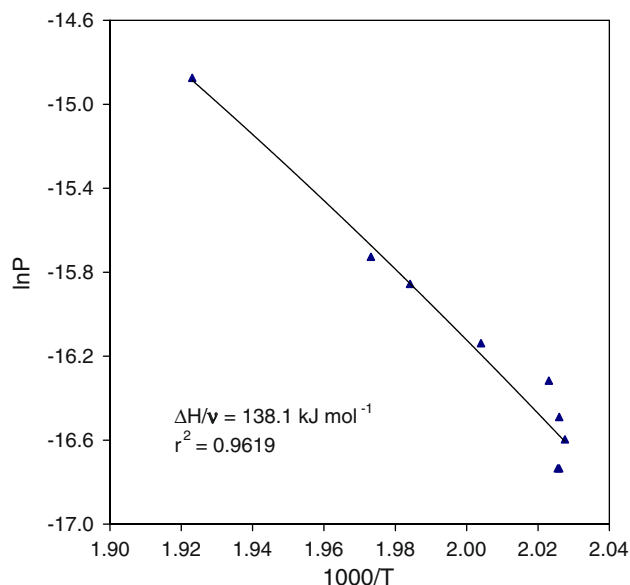


Fig. 4 Second-law plot of $\ln(P_{\text{eqp}}/\text{bar})$ versus $(1000/T)/\text{K}^{-1}$ for the isothermal measurements

Table 5 Effect of a contraction model on the results of dynamic measurement (run 7) of the molar enthalpy by different methods

Model	$\Delta_r H_T^0/v(\text{kJ mol}^{-1})$		
	Third-law	Second-law	Arrhenius plot
$n = 0.10$	139.3	138.2	136.0
$n = 0.18$	139.1	146.0	143.9
$n = 0.33$	138.7	160.8	158.6
$n = 0.50$	138.2	177.5	175.4
$n = 0.67$	137.8	194.0	191.8

Conclusions

The assumption that potassium permanganate may serve as a kinetics standard in solid decomposition kinetics made a priori [2] on the basis of the mechanism of the congruent dissociative vaporization of KMnO_4 and its crystal structure was successfully supported experimentally. As expected, the decomposition rate of KMnO_4 does not depend on the kind of foreign gas (He, air, CO_2 and Ar) and on the measurement technique (isothermal or dynamic). Other requirements for KMnO_4 as an ideal kinetics standard are satisfied as well. The use of the third-law method for determining the molar enthalpy of a reaction ($\Delta_r H_T^0/v$) provides an excellent reproducibility of results. The mean value of $\Delta_r H_T^0/v$ from 12 experiments in different gases is $138.3 \pm 1.1 \text{ kJ mol}^{-1}$, where 1.1 kJ mol^{-1} is equal, with a 95% confidence interval, to two standard deviations (2σ).

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 its reduction in a vacuum. This is related to the reduction of the thermal conductivity of the residual gas and, as a result, to the self-heating of the reactant that accelerates the exothermic reaction. The authors observed this effect [3, 4] under low ($\approx 10^{-3}$ bar) and high ($\approx 10^{-7}$ bar) vacuum. Therefore, the possible application of KMnO_4 as a kinetics standard should be limited by its decomposition in different gases at atmospheric pressure.

We do not call to the immediate use of KMnO_4 as a kinetics standard. However, we are sure that this difficult problem can be successively resolved, at least in principle. The present paper is one of the steps in this direction. Besides, the mechanism of KMnO_4 decomposition remains one of the most intriguing puzzles in TA. The novel approach to this problem used in our paper might stimulate the other studies and/or provoke the open debates in the literature.

Acknowledgements The authors thank Nikita L'vov (Montreal, Canada) for the linguistic improvement of the manuscript.

References

1. Brown M, Flynn RM, Flynn JH. Report on the ICTAC Kinetics Committee. *Thermochim Acta*. 1995;256:477–83.
2. L'vov BV. Thermal decomposition of solids and melts. New thermochemical approach to the mechanism, kinetics and methodology. Berlin: Springer; 2007.
3. L'vov BV, Ugolkov VL. Use of potassium permanganate as a possible kinetic standard in thermal analysis. *Russ J Appl Chem*. 2007;80:1289–94.
4. L'vov BV, Ugolkov VL. The self-heating effect in the process of KMnO_4 decomposition in vacuum. *J Therm Anal Calorim*. 2008; 94:453–60.
5. L'vov BV, Novichikhin AV. Quantitative interpretation of the evaporation coefficients for the decomposition or sublimation of some substances in vacuo. *Thermochim Acta*. 1997;290: 239–51.
6. L'vov BV, Ugolkov VL. Kinetics of free-surface decomposition of magnesium and barium sulfates analyzed thermogravimetrically by the third-law method. *Thermochim Acta*. 2004;411:73–9.
7. Chevillot PF, Edwards WE. Mémoire. Sur le caméléon mineral. *Ann Chim Phys*. 1817;4:287–97.
8. Rudolf G. Über die Einwirkung der Hitze auf übermangansaures Kalium. *Z Anorg Chem*. 1901;27:58–61.
9. Hinshelwood CN, Bowen EJ. The influence of physical conditions on the velocity of decomposition of certain crystalline solids. *Proc R Soc Lond A*. 1921;99:203–12.
10. Roginsky SZ. On the role of supersaturation and on the limiting stage in topochemical reactions. *Trans Faraday Soc*. 1938;34: 959–69.
11. Prout EG, Tompkins FC. The thermal decomposition of potassium permanganate. *Trans Faraday Soc*. 1944;40:488–98.
12. Erofeev BV, Smirnova II. Kinetics of thermal decomposition of potassium permanganate. *Russ J Phys Chem*. 1952;26:1233–43 (in Russian).
13. Hill RAW, Richardson RT, Rodger BW. Kinetics of decomposition of potassium permanganate in the temperature range 110 to 230°C. *Proc R Soc Lond A*. 1966;291:208–23.
14. Boldyrev VV. Mechanism of thermal decomposition of potassium permanganate in the solid phase. *J Phys Chem Solids*. 1969;30:1215–20.
15. Brown ME, Sole KC, Beck MW. Isothermal DSC study of the thermal decomposition of potassium permanganate. *Thermochim Acta*. 1985;89:27–37.
16. Brown ME, Galwey AK, Mohamed AM, Tanaka H. A mechanism for the thermal decomposition of potassium permanganate crystals based on nucleation and growth. *Thermochim Acta*. 1994;235:255–70.
17. Herbststein FH, Kapon M, Weissman A. Old and new studies of the thermal decomposition of potassium permanganate. *J Therm Anal*. 1994;41:303–22.
18. L'vov BV, Ugolkov VL. Kinetics and mechanisms of free-surface vaporization of groups IIA, IIIA and IVA nitrides analyzed thermogravimetrically by the third-law method. *Thermochim Acta*. 2005;438:1–8.
19. L'vov BV. Application of the third-law methodology to investigation of decomposition kinetics. *Thermochim Acta*. 2004;424: 183–9.
20. L'vov BV. How to improve efficiency of thermal analysis in decomposition kinetics. *J Therm Anal Calorim*. 2005;79:151–6.

21. Glushko VP, editor. Thermodynamic constants of substances. Moscow: Akademii Nauk SSSR; 1962–1982 (in Russian).
22. Gurvich LV, Veits IV, Medvedev VA, et al. Thermodynamic properties of individual substances. Moscow: Nauka; 1978–1982 (in Russian).
23. Kireev VA. Methods of practical calculations in thermodynamics of chemical reactions. Moscow: Khimiya; 1975. (in Russian).
24. Grigor'ev IS, Melikhov EZ, editors. Physical constants. Handbook. Moscow: Energoatomizdat; 1991. (in Russian).
25. L'vov BV. Fundamental restrictions of the second-law and Arrhenius plot methods used in the determination of reaction enthalpies in decomposition kinetics. *J Therm Anal Calorim.* 2008;92:639–42.
26. L'vov BV. Role of vapour oversaturation in the thermal decomposition of solids. *J Therm Anal Calorim.* 2009;96:321–30.
27. L'vov BV. Thermochemical approach to solid-state decomposition reactions against the background of traditional theories. *J Therm Anal Calorim.* 2009;96:487–93.