

HOW TO IMPROVE EFFICIENCY OF THERMAL ANALYSIS IN DECOMPOSITION KINETICS

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The prerequisites to use of the third-law method in decomposition kinetics and great advantages of this method compared to the routine Arrhenius-plots and second-law methods in precision, accuracy and productivity of TA measurements are discussed. Some important achievements obtained with the use of this methodology over the last two years that support potentialities of this approach are briefly reviewed.

Keywords: accuracy, Arrhenius-plots method, decomposition reactions, E parameter, kinetics, precision, productivity, third-law method

Introduction

Over a century after appearance of the first paper on thermal decomposition of silver oxide by Lewis [1] and about 80 years after publication by Bružs [2] of a paper on carbonate decomposition, where the author for the first time in heterogeneous kinetics used the Arrhenius equation for evaluation of the E parameter, this approach became the main method of thermal analysis (TA) for investigation of mechanisms of these reactions. However, despite the long story of these studies, the achievements in obtaining of reliable quantitative results are rather modest or, to be true, disappointing. As example, the situation with determination and interpretation of the E parameter for calcite can be mentioned. This problem discussed 30 years ago by Zsakó and Arz [3] and about 15 years ago by Maciejewski and Reller [4]. The reported apparent magnitudes of the Arrhenius parameters range from 110 to 1600 kJ mol⁻¹ for the E parameter and from 10² to 10⁶⁹ s⁻¹ for the A parameter [3]. (At the estimation by the authors' [4], the values of the E parameter differ even more: from 47 to 3800 kJ mol⁻¹).

The situation has not changed to the better in the recent years. In the comparative study of 'Computational aspects of kinetic analysis: The ICTAC Kinetics Project' [5, 6], all participants used the identical sets of numerical data for the decompositions of calcite in vacuum and nitrogen. In spite of this, different workers obtained from a computational procedure different kinetic parameters: from 58 to 262 kJ mol⁻¹ for the E parameter and from 3 to 36 for the ln(A/s^{-1}) parameter. This situation, which is typical not only for calcite, has led nowadays

to the appearance of some pessimistic statements on the problem of a physical meaning of kinetic parameters on the whole. Considering this problem, Maciejewski [6] claims: 'It seems to be acceptable for everybody that kinetic calculations may be the not most efficient means of determining a reaction mechanism'. This opinion is supported by Vyazovkin [7]: 'The comparison of theoretical values of the activation energy with the experimental ones may itself present a considerable challenge as the reported values tend to be widely differing'. He denies completely the concept of constant activation energy and suggests as alternative the concept of 'variable activation energy', which is an unpredictable function of temperature and/or extent of reaction [8]. It must agree with a general conclusion that 'there is evidence of stagnation in the field' [9].

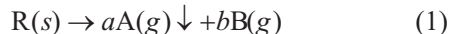
The situation began to change only recently, after application of the so-called third-law method to TA of decomposition reactions [10–21]. This method is very popular in thermochemistry of equilibrium reactions but (amazingly!) it has never been used in kinetic studies. The main purpose of the present work is to consider the advantages and limitations of this method in comparison with the traditional Arrhenius-plots and second-law methods. The basic assumptions underlying the physical approach (PA) conception and the third-law method have been discussed very recently in [21]. Therefore, a theoretical discussion below will be limited only by a short presentation of the equations necessary for further consideration. In the end of this paper, we will give a brief review of the main results obtained with this methodology in decomposition kinetics over the last two years.

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Theoretical

Equivalent partial pressure

In case of a reactant R decomposed in vacuum into gaseous products A and B with simultaneous condensation of low-volatility species A , that is



the flux of each product, which ultimately determines the maximum rate of decomposition, can be expressed through the so-called equivalent partial pressure P_{eq} (in bar) of the gaseous product, which is related to the maximum rate of decomposition, J (in $\text{kg m}^{-2} \text{s}^{-1}$), by the Hertz–Langmuir equation rewritten as

$$P_{eq} = \frac{(2\pi\overline{MRT})^{1/2} J}{\gamma M_B} \quad (2)$$

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

$$\overline{M} = (M_A^a \cdot M_B^b)^{1/(a+b)} \quad (3)$$

Entropy and enthalpy of decomposition reaction

The entropy change for decomposition reaction (1) is calculated from the obvious equation

$$\Delta_r S_T^0 = aS_T^0(A) + bS_T^0(B) - S_T^0(R) \quad (4)$$

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 introduce into calculations of the enthalpy of decomposition reaction (1) an additional term $\tau a \Delta_c H_T^0(A)$, where the parameter τ corresponds to the fraction of the condensation energy consumed by the reactant. Thus, we can write

$$\begin{aligned} \Delta_r H_T^0 = & a\Delta_f H_T^0(A) + b\Delta_f H_T^0(B) - \\ & -\Delta_f H_T^0(R) + \tau a \Delta_c H_T^0(A) \end{aligned} \quad (5)$$

As was revealed recently [18, 21], the τ parameter varies for different reactants and is in correlation with the reduced value of condensation energy, $\Delta_c H_T^0/RT$, at decomposition temperature. This correlation can be approximated as follows:

$$\tau = -0.1312x^2 + 1.5762x - 3.9757 \quad (6)$$

where $x = \ln(-\Delta_c H_T^0/RT)$.

In accord with the PA conception [21], the E parameter for the equimolar mode of decomposition (in vacuum) is equal to the molar enthalpy of reaction:

$$E = \Delta_r H_T^0 / \nu = \Delta_r H_T^0 / (a + b) \quad (7)$$

The third-law method

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

$$\Delta_r H_T^0 = T(\Delta_r S_T^0 - R \ln K_p) \quad (8)$$

Here K_p is the equilibrium constant for the reaction (1):

$$K_p = P_A^a \cdot P_B^b \quad (9)$$

and $a+b=\nu$. Taking into account Eqs (7) and (9), Eq. (8) in case of decomposition of reactant in vacuum can be reduced to the final equation used in calculation of the E parameter

$$E = T(\Delta_r S_T^0 / \nu - R \ln P_{eq}) \quad (10)$$

Prerequisites to use of the third-law method

As it follows from consideration of Eq. (10), using the third-law method for determination of the E parameter assumes a possibility of evaluation of the equivalent pressure, P_{eq} , in conditions of free-surface decomposition of reactant and the availability of data necessary for calculation of the molar entropy of reaction, $\Delta_r S_T^0 / \nu$. In its turn, calculation of P_{eq} value from the Hertz–Langmuir equation assumes a possibility of measuring the absolute rate of decomposition, J (in $\text{kg m}^{-2} \text{s}^{-1}$), what suggests a possibility for evaluation of the efficient surface area of decomposed sample. Let us consider these topics in more detail.

Free-surface decomposition

Condition of free-surface decomposition means the absence of any diffusion limitations for the escape of gaseous product from the surface of decomposed sample. This condition is usually referred to high vacuum in the reactor ($<10^{-8}$ bar). However, in many cases, this prerequisite is too high. It is easy to estimate an allowable level for the presence of foreign (inert) gas in the reactor if to compare the decomposition rate in high vacuum described by Eq. (2) with the decomposition rate in the presence of inert gas described by one-dimensional diffusion equation. As shown in [21], the allowable pressure, P , of inert gas in the reactor can be evaluated from the relationship:

$$P \leq 4 \cdot 10^{-8} T^{1/3} \quad (11)$$

It can be seen from Eq. (11) that $P \cong 3 \cdot 10^{-4}$ bar at 1000 K and $2 \cdot 10^{-4}$ bar at 700 K. This means that in

many cases the condition of free-surface decomposition can be achieved at evacuation of reactor with only a rotation pump (if only the primary products of reaction do not include O_2 and/or N_2). For illustration, the rate of decomposition of dolomite at 800 K is practically identical ($2.3 \cdot 10^{-5}$ and $1.8 \cdot 10^{-5}$ $kg\ m^{-2}\ s^{-1}$) at residual pressure of air, respectively, $2 \cdot 10^{-4}$ and $8 \cdot 10^{-8}$ bar [13]. (A small increase of the rate in low vacuum is related to reduction of the self-cooling effect).

Molar enthalpy

The availability of data necessary for calculation of the molar entropy of reaction, $\Delta_r S_T^0 / \nu$, is at first glance a serious limitation for application of the third-law method. Fortunately, the situation in this field is significantly improved over the last 40 years and for majority of substances the values of entropies in standard conditions (S_{298}^0) and corresponding temperature increments ($S_T^0 - S_{298}^0$) were calculated and published in tabulated form in many handbooks (e.g. in [23]). Nevertheless, for some species, for example, for low-volatility molecules in the gaseous state (e.g., metal salts), these data are absent. In some cases, it is possible to estimate the entropy value from a comparison with the known entropies of similar molecules for other metals. This approach was used, for example, for gaseous molecules of Li_2SO_4 , $CaSO_4$ and $CuSO_4$ [13].

More general approach for estimation of molar entropy was demonstrated in [10]. Instead of true values of $\Delta_r S_T^0 / \nu$ for 20 different reactants, their average magnitude (148 ± 17 $J\ mol^{-1}\ K^{-1}$) was used for all these reactants. The correlation between the E parameters and the molar enthalpies for corresponding decomposition reactions was a bit worse for the approximate version: the mean value of R.S.D. was 5% compared with 3% for the precise version.

Our recent analysis of $\Delta_r S_T^0 / \nu$ values for 50 different reactants has revealed significant differences in $\Delta_r S_T^0 / \nu$ between the reactants decomposed with formation of free metal atoms and reactants decomposed up to metal products in the form of free molecules [21]. The average value of $\Delta_r S_T^0 / \nu$ is equal to 136 ± 9 $J\ mol^{-1}\ K^{-1}$ in the first case and to 160 ± 9 $J\ mol^{-1}\ K^{-1}$, in the second. In both cases, R.S.D. values are only one-half its value for all 50 reactants. Under these circumstances, the approximate and precise versions of calculation of the E parameter are not distinguished in precision [21].

Absolute rate of decomposition

For application of the third-law method to the determination of the E parameter, it is necessary to

know the absolute rate of sample decomposition J (in $kg\ m^{-2}\ s^{-1}$). For crystals or pressed pellets with a low porosity, the effective surface area of decomposition could be evaluated from the known geometry of samples. The evaluation of the efficient surface area of powders with the undefined grain size and number of particles presents a serious problem. In principle, the application of the B.E.T. technique permits to determine this value. However, the decomposition of powders is not spatially homogeneous. Because of the self-cooling effect, the temperature of inner parts of the powder is lower than that of the surface. This fact was noted in many works though no one tried to investigate this problem quantitatively.

L'vov *et al.* [22] proposed a fairly simple theoretical model and developed a program to compute the temperature of individual crystals and the layer-by-layer temperature distribution in powder samples during the course of their decomposition in vacuum and in the presence of foreign gases. L'vov and Ugolkov [12] performed such calculations for the decomposition of dolomite (crystals and powders) in high and low vacuum as a function of a total number of powder layers and different values of the emittance parameter.

The theoretical conclusions deduced from these calculations were verified experimentally on different samples of dolomite taken in the form of natural crystals and powders [12]. The absolute rate of decomposition for powders (J_p) in all cases was higher than that for the crystals (J_c) and, as was shown, the difference in the decomposition rates for powders and crystals is rather constant and does not depend on the temperature, residual pressure of air in the reactor, the mass of powder samples and the size of grains. The mean value of the ratio J_p/J_c at different temperatures was equal to 2.8 ± 0.4 .

Based on above results, a simple procedure was proposed for determination of the E parameter by the third-law method from the data obtained for powder samples [3]. It consists in 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 empirical factor and then used for the calculation of the E parameter by the third-law method. The magnitude of this factor (2.8 ± 0.4), as noted above, does not depend on the temperature, residual pressure of air in the reactor, grain size and mass of a powder sample. This procedure permitted to greatly expand the application of the third-law method to the determination of decomposition kinetics for many solids available only in the powder form [10–21].

The similar technique can be applied to investigation of melts. To eliminate spreading of melt over the surface of crucible in the process of heating, a mixture of reactant with some chemically neutral and thermostable powder (e.g., Al_2O_3) taken in the ratio of 1 to 1 is used. After melting of reactant, such mixture retains the powder structure of Al_2O_3 so that evaluation of the absolute decomposition rate remains identical to that described above. The technique was applied to melted Ag and Cd nitrates [19]. Therefore, the absolute rate of decomposition can be measured for any materials available in form of crystals, powders or melts.

Efficiency

Precision (reproducibility)

As can be seen from the analysis of results reported in [23] for several hundreds of substances (mainly related to their enthalpies of formation or sublimation), the data calculated by the third-law method are in general the order of magnitude more precise than those calculated by the second-law method and Arrhenius-plots methods. This is connected with the different impact of systematic and random errors in the determination of the true temperature of reactant and J , P or k variables on ΔH_T^0 or E values. It is clear if we compare Eq. (10) with Eq. (12) valid in cases of the Arrhenius-plots and second-law methods:

$$E = \frac{1}{T_{\min}^{-1} - T_{\max}^{-1}} R \ln \frac{P_{\max}}{P_{\min}} = \frac{T_{\max} T_{\min}}{T_{\max} - T_{\min}} R \ln \frac{k_{\max}}{k_{\min}} \quad (12)$$

where k_{\max} and k_{\min} are the rate constants at the maximum (T_{\max}) and minimum (T_{\min}) temperatures of the experiment (in case of the second-law method, the partial pressures, P , or absolute rates, J , are usually used in place of k values). As can be seen from comparison of Eq. (10) with Eq. (12), the main difference between these formulas consists in the presence of additional factor in Eq. (12), namely, $T_{\max}/(T_{\max}-T_{\min})$ or $T_{\max}/\Delta T$. The other (minor) difference is in using of the ratio of two variables, k_{\max}/k_{\min} , in Eq. (12) instead of single variable, P_{eq} , in Eq. (10).

Under rather typical measurement conditions, e.g., at $T_{\min}=900$ K and $T_{\max}=1000$ K, a twofold difference in the absolute rate of decomposition can introduce 5.2 kJ mol^{-1} error in the determination of the E parameter at 900 K by the third-law method. In case of the Arrhenius-plots method (Eq. (12)), a twofold difference in the ratio k_{\max}/k_{\min} should introduce 52 kJ mol^{-1} error in the determination of the E parameter. Therefore, precision of the third-law method is, on the average, the order of magnitude

higher than that of the second-law and Arrhenius-plots methods. Use of the ratio of two variables, k_{\max}/k_{\min} , in Eq. (12) instead of single variable, P_{eq} , in Eq. (10) should obviously increase the overall error still more. The effect reverses if the number of points used for plotting is higher than 4. However, on the whole, the impact of this factor on precision is relatively small.

It is of interest to consider the real distribution of $T_{\max}/\Delta T$ values throughout different publications on determination of the E parameter by the Arrhenius-plots method. For this purpose, we handled the corresponding data reported in a recent book by Galwey and Brown [24]. The frequency of occurrence of $T_{\max}/\Delta T$ -values in steps of equal increment (0.3) throughout 220 items is presented in Fig. 1. A maximum point of this distribution corresponds to $T_{\max}/\Delta T=10$ and the average value of $T_{\max}/\Delta T$ for all 220 items is equal to 16. As can be seen, there are some cases when this ratio and therefore a loss of precision (in comparison with the third-law method) reach the values of 30–50.

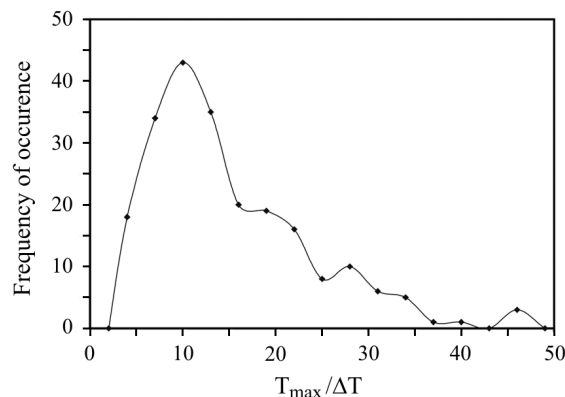


Fig. 1 The distribution of publications on determination of the E parameter by the Arrhenius-plots method as a function $T_{\max}/\Delta T$ ratio, in steps of equal increment (0.3). A total of 220 items are included

The analysis of the data reported in [10–21] shows that in all cases of determination of the E parameter by the third-law method the R.S.D. is lower than 2% (this value corresponds to reproducibility in measurements of rates of decomposition, J , within of factor two [21]). In many cases (more than one-half), the R.S.D. is lower than 1%. Therefore, the difference in precision of the methods evaluated by $T_{\max}/\Delta T$ -factor agrees with actual R.S.D. values typical for these methods.

Accuracy

Besides the random variations of measured values, some systematic variations might occur. The most

typical one is related to overestimation of decomposition temperatures because of the self-cooling effect. The impact of this factor is obviously more important for higher temperatures used in Arrhenius-plots and second-law experiments. Under measurement conditions noted above, e.g., at $T_{\min}=900$ K and $T_{\max}=1000$ K, an error of 10 K because of the self-cooling effect (i.e., at $T_{\max}=990$ K instead of 1000 K) results in the error in E calculation about 9% instead of only 1% in case of the third-law method applied at T_{\max} . We can see that at the same error in temperature, the final error of E determination by the third-law method is the order of magnitude lower. In real conditions, when the third-law method is applied at T_{\min} , the final error is reduced still more.

These theoretical estimations have been supported by the experimental results on decomposition in high vacuum of carbonates [10–12,14], hydrates [13], sulfates [16] and hydroxides [18] (see also [21]). In full accord with the theoretical (model) evaluations, the temperature difference between the temperature controlled heater (e.g., a crucible) and the sample in high vacuum constitutes several ten degrees and can reach (in extreme cases) about 10% of the heater temperature [21]. This systematic error manifests in 15–30% underestimation of the E parameters in many cases of application of the second-law and Arrhenius-plots methods.

The other typical systematic error in determination of the E parameter by the Arrhenius-plots method is connected with a rather arbitrary choice of the kinetic model for estimation of k values from the primary TA data. This is illustrated by the results reported in numerous publications, e.g., in [5, 6]. In case of the third-law method, the equivalent pressure, P_{eq} , used in calculation is unambiguously related to the absolute rate of decomposition, J , measured under steady-state conditions and, therefore, this type of systematic error is completely excluded.

The error related to uncertainty in the value of molar entropy calculated from the available thermochemistry data (<1 J mol⁻¹ K⁻¹) is not higher than 0.3% and can be obviously neglected. However, if (in the absence of true values) the average magnitudes of $\Delta_r S_T^0 / \nu$ are used, the uncertainty in their values (± 9 J mol⁻¹ K⁻¹) becomes perceptible: the error in determination of the E parameter amounts to about 3%. Nevertheless, even so, the impact of this factor on a background of the overall, random and systematic, error is insignificant [21].

Productivity

The application of the third-law method at only one temperature greatly reduces (by a factor of ten or

more) the total time spent for the experiment in comparison with that for the second-law and Arrhenius-plots methods. This is easy to understand by considering the total number of points usually used for plotting. Most of the workers who applied the second-law and Arrhenius-plots methods under isothermal measurement conditions used, by our estimation [10], from 10 to 60 points. Even in the non-isothermal experiments, at least three heating rates are recommended in order to correctly describe the course of reaction. In case of the third-law method, a single measurement of the decomposition rate takes entirely not more than 2–3 h. Therefore, productivity of this method is much higher in comparison with the second-law and Arrhenius-plots methods under isothermal measurement conditions and comparable to that for the non-isothermal techniques.

What has been achieved

Some important results obtained over the last two years with the use of the third-law method are summarized below:

- For the first time over the century elapsed after a pioneer work by Lewis [1], kinetics and decomposition mechanisms of a large group of reactants from different classes of compounds (non-metals, oxides, peroxides, hydroxides, sulfides, selenides, nitrides, azides, carbonates, nitrates, sulfates and hydrates) are identified on a single PA basis [10–21].
- The validity of fundamental theoretical relationship between the initial temperature of decomposition, T_i , in vacuum and the E parameter ($T_i[\text{K}] \cong 3.5 E [\text{kJ mol}^{-1}]$) was supported by experimental results reported in the literature for 100 different reactants [10].
- The results of TG experiments on the decompositions of CaCO₃, SrCO₃ and BaCO₃ in the presence of CO₂ and some data reported in the literature were used for the determination of the E parameter by the third-law method [15]. The values obtained (495, 569 and 605 kJ mol⁻¹) are twice as much compared with the values of the E parameter obtained for these carbonates in the absence of CO₂. This fact together with the invariance of the E parameter with partial pressure of CO₂ (P_{CO_2}) and a hyperbolic dependence of the rate of decomposition on P_{CO_2} are in excellent agreement with the theoretical predictions deduced from the mechanism of decomposition that includes the primary stage of dissociative evaporation of reactant [15].
- The third-law method was used for TG investigation of kinetics and mechanisms of

thermal decomposition of AgNO_3 and $\text{Cd}(\text{NO}_3)_2$ [19]. The decomposition rate is reduced after reactant melting because of the absence (disappearance) of product/reactant interface and associated transfer of condensation energy to the reactant. This conclusion is supported by a rise of the E parameter by about 20 kJ mol^{-1} after melting of these nitrates.

- On the basis of critical comparison of experimental and theoretical values of the E parameter and investigation of the retardation effect of oxygen on the evaporation rate of ZnO , CdO and HgO , it was concluded that the dissociative evaporation of ZnO and HgO proceeds with releasing of atomic oxygen (O) as a primary product of decomposition [17]. By contrast, the mechanism of dissociative evaporation of CdO corresponds to the equilibrium reaction with releasing of molecular oxygen (O_2). As was shown, this difference in mechanisms is not related with interatomic O–O distances in these oxides. From the analysis of crystal structure for 12 different oxides, which evaporate with releasing of molecular oxygen, and for 13 compounds, which evaporate with releasing of atomic oxygen, it was revealed that the first mechanism is observed for all oxides with the cubic crystal structure [17]. It was proposed that a decisive role in this difference belongs to a local symmetry in the position of O atoms. The similar features were revealed for decomposition of Group IIA, IIIA and IVA nitrides [20].

Conclusions

Using the third-law method in TA might be decisive in transformation of decomposition kinetics from one of the stagnant fields of physical chemistry, as it is [25], into a region of rigorous fundamental science based on the new PA conception and efficient methodology of investigation. However, the final result mainly depends on attention of thermoanalytical community to this prospect, in particular, of young generation of workers, who are not related to obsolete conceptions through their past activity in this field and feel interest in new ideas.

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