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THERMOLYSIS OF POTASSIUM TETRAPEROXOCHROMATE(V). II. LINEAR HEATING

A.I. LESNIKOVICH, S.V. LEVCHIK and V.G. GUSLEV

Institute of Physico-Chemical Problems, Byelorussian State University, Minsk 220080 (U.S.S.R.)

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ABSTRACT

The method of estimating effective invariant kinetic characteristics in non-isothermal kinetics is developed, its connection with general methods for describing multiparametric dependencies and improving the unambiguity of inverse problem solution as well as with the main initial non-isothermal equation of kinetics is discussed. The method is applied to K_3CrO_8 thermolysis whose study is difficult because decomposition tends to develop into thermal explosion.

INTRODUCTION

It is shown [1] that potassium tetraperoxochromate(V) (K_3CrO_8) is a long-term test subject in topochemistry. Its thermolysis by the equation $K_3CrO_8 \rightarrow K_2CrO_4 + KO_2 + O_2$ proceeds without fusing and is characterized by a typical sigmoid kinetic curve under isothermal conditions. The high-sensitive ESR method illustrates the development of thermolysis and exposes profound changes in the paramagnetic salt component (CrO_8^{3-} ions) as early as at the induction period. The kinetics of isothermal decomposition of K_3CrO_8 is described by autocatalytic equations, the value of the effective activation energy being $E = 69 \pm 12$ kJ mol^{-1} and the pre-exponential factor being $\log(A/\mathrm{s}^{-1}) = 7 \pm 2$. Joint kinetic and instrumental tests have allowed the conclusion that thermolysis follows the nucleation mechanism with the most important contribution to defect generation being during the induction period throughout the solid. The findings of Part I of this communication [1] serve as a basis for studying K_3CrO_8 thermolysis under the conditions of a linear temperature rise. The knowledge of the main specificities of this process gives a basis for testing the validity of the conclusions obtained from non-isothermal tests whose interpretation is more difficult than in an isothermal case.

The accuracy of non-isothermal methods has been widely discussed, but this question is still open to discussion [2–4]. For several reasons [2,3],

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kinetic characteristics are ambiguously estimated from non-isothermal data, i.e., the inverse kinetic problem has multiple solutions, and this invalidates the scientific, and reduces the practical, importance of the kinetic parameters obtained and imparts to them a purely empiric character. As a whole, non-isothermal methods are not recommended for solving the inverse kinetic problem [5]. However, decomposition under non-isothermal conditions gives a better modelling of such practically important processes as solid combustion, since variations of the heating rate and transition to non-isothermal conditions may change the mechanism of the process. The application of non-isothermal methods in these cases seems to be inevitable.

Part III of this series, dealing with K_3CrO_8 thermolysis, will consider the decomposition of this substance under combustion conditions. The quantitative physical combustion model requires the knowledge of the parameters E and A and the form of the kinetic function $f(\alpha)$. The above-mentioned ambiguity of the solution, poor conditionality of the inverse kinetic problem and, hence, false compensation effect (CE), greatly hinder the choice of E, A and $f(\alpha)$. Because of the CE, extrapolation of kinetic data to combustion temperatures seems to be a dubious procedure even when the process kinetics do not change a transition from low temperatures, at which kinetic data are obtained, to combustion temperatures. Therefore, the intention is to obtain invariant, i.e., uniquely determined and independent of the experimental conditions (provided changing conditions do not change the process mechanism), effective kinetic characteristics, $\hat{E}$, $\hat{A}$, $\hat{f}(\alpha)$, of K_3CrO_8 thermolysis during linear temperature rise and to compare them with the data obtained by isothermal methods in order to elucidate the sensitivity of the kinetic characteristics of K_3CrO_8 thermolysis to changes in heating conditions.

During the heating of this substance its strongly exothermal decomposition may change into thermal explosion. This complicates the kinetic studies with linear heating and specifies stringent requirements to the investigation methods. The latter impelled the use of K_3CrO_8 for verifying the method of estimating invariant kinetic parameters. In ref. 6 it was verified in a more simple way. The method of finding $\hat{f}(\alpha)$ is still to be developed, which requires the analysis of its relationship to other most general approaches for the description of multiparametric relationships and for inverse problem solution. These are the subjects of the present communication.

DESCRIPTION, DEVELOPMENT AND ANALYSIS OF THE METHOD

The method of estimating the invariant ($\hat{}$ above) parameters $\hat{E}$ and $\hat{A}$ suggested in refs. 6 and 7 implies the following, when applied to non-isothermal conditions. Some of the approaches are used to estimate E and A with discrimination of the function $f_j(\alpha)$ through verification of linearity of an appropriate expression for all j functions. Because of the strong temperature dependence of the reaction rate, $\mathrm{d}\alpha/\mathrm{d}t$, the linearization procedure has a low sensitivity to functions of the form $\mathrm{f}_j(\alpha)$. The discrimination of these functions is, therefore, ineffective. The set of E_j and A_j values, corresponding to the above functions, is formally related by the following compensation law whose quantitative form expresses ambiguity in A and E estimation

$$\log A_j = B + lE_j \tag{1}$$

where $B = \log \hat{k}$; $l = 1/2.3\ R\hat{T}$; k is the rate constant. However, as the invariant $\hat{A}$ and $\hat{E}$ belong to locus (1), they may be found as an intersection of straight lines (1). The essence of the method is to obtain a pencil of lines (1) by varying the experimental conditions, to find the coordinates of its centre, i.e., $\hat{A}$ and $\hat{E}$, from the condition of forming the pencil with straight lines (1)

$$B = \log \hat{A} - \hat{E}l \tag{2}$$

and to use $\hat{A}$ and $\hat{E}$ for discriminating $\mathrm{f}_j(\alpha)$ models. In fact, a common prolonged ellipsoidal confidence domain rather than a straight line (1) appears in the space of $\log A_j$ and E_j factors, but this may be taken into account only at the stage of finding an error in $\hat{A}$ and $\hat{E}$.

Note that the above method of $\hat{A}$ and $\hat{E}$ estimation corresponds to the modification of the basic non-isothermal kinetic equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{1}{\beta}\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\mathrm{f}(\alpha) \tag{3}$$

whose disadvantages are exposed rather convincingly in refs. 2 and 3, to become a three-exponential equation of the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \hat{A}\exp\left(-\frac{\hat{E}}{R\hat{T}_v}\right)\exp\left(\frac{E_j}{R\hat{T}_v}\right)\exp\left(-\frac{E_j}{RT}\right)\mathrm{f}_j(\alpha) \tag{4}$$

where $T_v = 1/2.3Rl_v$; v being the number of the heating rate β_v, in which $\hat{T}_v$ for the substance characterizes the experimental conditions, and E_j characterizes the kinetic function and the calculation method. With the proper choice of $\mathrm{f}_j(\alpha)$, the terms including $\hat{T}_v$ are cancelled and eqn. (4) becomes eqn. (3). As will be shown later, these terms decrease the ambiguity of the inverse problem solution.

The $\mathrm{f}_j(\alpha)$ models may be discriminated using the $\log \hat{A}$ and $\hat{E}$ values and using eqn. (3) to find the predicted values of $\mathrm{d}\alpha/\mathrm{d}t$. Having n of the i-th experimental values of $(\mathrm{d}\alpha/\mathrm{d}t)_i$, the residual sum of squares for each $\mathrm{f}_j(\alpha)$ can be found

$$(n-1)S_{jv}^2 = \sum_i^n \left[\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_i - \frac{\hat{A}}{\beta_v}\exp\left(-\frac{\hat{E}}{RT}\right)\mathrm{f}_j(\alpha_i)\right]^2$$

The most probable function $\hat{f}(\alpha)$ is then chosen by the minimum mean value of the heating rate approximate error, $\bar{S}$, for all v values

$$\bar{S} = \sum_{v} S_{jv}/v$$

Careful consideration shows that the method of $\hat{E}$ and $\hat{A}$ estimation under study is an adaptation of a more general approach to the description of multiparametric relations by polynomials and to the decrease of interdependence of the mathematic model parameters by introducing a transformed independent variable resulting in smaller values of non-diagonal elements of the information matrix [8]. The efficiency of the general approach to decreasing parameter inter-dependence relies on the correct choice of transformation. The method of $\hat{E}$ and $\hat{A}$ estimation corresponds to a polynomial model and allows the above transformation of the variable to improve conditionality of the problem. To show this, we consider the general form of the function under study, f(log k in this case), vs. three variables, x_1, x_2 and x_3, the first one specifically being T^{-1}, i.e., the Arrhenius variable

$$\log k = \log A - E/2.3RT \tag{5}$$

the second, the variable changing A and E in accordance with (1) and the third, changing B and l as in eqn. (2). Following ref. 9, the function of x_1, x_2 and x_3 arguments may be represented as

$$f(x_1, x_2, x_3) = f(x_1^0, x_2^0, x_3^0) + \sum_{i=1}^{i=3} a_i x_i + \sum\sum_{i<j} a_{ij} x_i x_j + a_{123} x_1 x_2 x_3$$

The interdependent equations of types (1), (2) and (5) being satisfied, the polylinear function simplifies to become

$$f(x_1, x_2, x_3) = f(x_1^0, x_2^0, x_3^0) + a_1 x_1 + a_2 x_2 + a_{12} x_1 x_2 + a_{23} x_2 x_3 + a_{123} x_1 x_2 x_3 \tag{6}$$

where x_i^0 are the values of the variables regarded as standard. The conformity of polynomial (6) to the set of equations (1), (2) and (5) may be followed from geometric interpretation eqn. (6) in the plane $f(x_1, x_2, x_3) - x_1$. Similar to the set of equations (1), (2) and (5) [7], polynomial (6) provides a set of line pencils of type (5)

$$f(x_1) = b_0 + b_1 x_1 \tag{7}$$

whose centres are located on the straight line of type (2). The Arrhenius equation (7) is, however, obtained from eqn. (6) provided x_2 and x_3 are fixed, hence

$$b_0 = f(x_1^0, x_2^0, x_3^0) + a_2 x_{2c} + a_{23} x_{2c} x_{3c} \qquad b_1 = a_1 + a_{12} x_{2c} + a_{123} x_{2c} x_{3c} \tag{8}$$

where subscript c means a fixed variable. If x_3 alone is fixed, then linear interdependence of b_0 and b_1 is seen from eqn. (8), since each of these quantities is a linear function of x_2. Eliminating x_2 from eqn. (8), the interdependence of b_0 and b_1 is obtained

$$b_0 = \mathrm{f}\left(x_1^0, x_2^0, x_3^0\right) - \frac{a_2 + a_{23}x_{3\mathrm{c}}}{a_{12} + a_{123}x_{3\mathrm{c}}}(a_1 - b_1) \tag{9}$$

On the other hand, linearity of the b_0 and b_1 interdependence means that lines (7) form a pencil. The formation of a pencil by lines (7) may be written in the form corresponding to the CE

$$b_0 = B - \hat{x}_1 b_1 \tag{10}$$

where $(B, \hat{x}_1)$ are the coordinates of the pencil centre in the $\mathrm{f}(x_1) - x_1$ plane. From eqns. (9) and (10) we have

$$\hat{x}_1 = -\frac{a_2 + a_{23}x_{3\mathrm{c}}}{a_{12} + a_{123}x_{3\mathrm{c}}} \tag{11}$$

$$B = \mathrm{f}\left(x_1^0, x_2^0, x_3^0\right) + a_1\hat{x}_1 \tag{12}$$

Following the terminology of ref. 9 $\hat{x}_1$ may be defined as an isoparametric value of x_1. Substituting $\hat{x}_1$ into eqn. (6) immediately gives eqn. (12), which is completely consistent with the meaning of B as the ordinate of the pencil centre.

Finally, cancelling the conditions of fixed x_3 variable gives eqn. (11) without subscripts c and eqn. (12) with the meaning of the function linear relative to $\hat{x}_1$, i.e., of the x_3 function. Line (12) includes the centres of line pencils (7). Thus, we have obtained the consistency of the set of particular equations (1), (2) and (5) to the set of eqns. (7), (10) and (12) obtained for the general case governed by polynomial (6).

Now consider how the validity of eqns. (7), (10) and (12) affects the conditionality of the problem of reconstructing parameters (of E and A type) from experimental data. For brevity, the above equalities are written as

$$f = f_0 + a_1x_1 \qquad f_0 = \hat{f} - \hat{x}_1a_1 \qquad \hat{f} = \hat{f}_0 + \hat{a}_1\hat{x}_1 \tag{13}$$

The successive substitution of relations (13), which corresponds to the algorithm of $\hat{E}$ and $\hat{A}$ estimation in an inverse order, results in

$$f = \hat{f}_0 + \hat{a}_1\hat{x}_1 - a_1\hat{x}_1 + a_1x_1 \qquad \text{or} \qquad f = \hat{f}_0 + a_1\hat{x}_1\frac{x_1 - \hat{x}_1}{\hat{x}_1} + \hat{a}_1\hat{x}_1$$

i.e., allows transformation of the x_1 variable by introducing the dimensionless variable $x_1^* = (x_1 - \hat{x}_1)/\hat{x}_1$. The use of x_1^* leads the first of eqns. (13) to become

$$f = a_0^* + a_1^*x_1^* \tag{14}$$

where $a_0^* = f_0 + a_1^*$; $a_1^* = a_1\hat{x}_1$. If the information matrix of a transformed model (14) is denoted as $\mathbf{M}^*$, while the matrix of the nontransformed model, i.e., $f = f_0 + a_1 x_1$ is denoted as **M**, comparing the determinants of these matrices

$$\det \mathbf{M} = n \sum_{i}^{n} x_{1i}^2 - \left(\sum_{i}^{n} x_{1i} \right)^2$$

$$\det \mathbf{M}^* = n \sum_{i}^{n} x_{1i}^{*2} - \left(\sum_{i}^{n} x_{1i}^* \right)^2$$

where n is the number of the experimental points, easily shows that in the above range of x_{1i} the matrix **M** becomes degenerated (det **M** is close to zero). In det **M***, the second term alone is close to zero as x_{1i}^* may attain both positive and negative values; therefore, det $\mathbf{M}^* \gg 0$ and matrix **M*** will not degenerate and the worst estimates of the model parameters will be less shifted. Moreover, as $\hat{x}_1$, in the final analysis, is a variable (eqn. 12) dependent on x_3 (eqn. 11), we may state that a transformation to x_1^*, compared to suggested transformations [8], has specific features indicating the dependence of x_1^* on x_3

$$x_1^* = -\frac{x_1(a_{12} + a_{123}x_3)}{a_2 + a_{23}x_3} - 1 \qquad (15)$$

Substitution of eqn. (15) into det **M*** shows that due to x_3 variation ($x_3 = x_{31}, x_{32} \ldots, x_{3j}$), the first term in det **M*** increases (as a set of x_{3j} corresponds to each x_{1i}^*), the second one vanishing more rapidly (as x_3 variation may add both positive and negative values to x_{1i}^*), i.e., conditionality of the problem improves, as was set out to be proved.

EXPERIMENTAL

K_3CrO_8 was synthesized in accordance with ref. 10 and crushed to particles less than 50 μm. Thermolysis was studied using an OD-103 derivatograph in the air atmosphere at $v = 1, \ldots, 6$; temperature rise rates, β, of 0.6, 1.25, 2.5, 5, 10 and 20 K min^{-1} were used as well as under isothermal conditions (± 3 K) identical to those in the derivatograph in other respects. In all of the runs, the K_3CrO_8 sample (50 mg) was diluted with a 20-fold amount of calcinated aluminium oxide.

Based on the data of non-isothermal experiments, E and log A were found for $\alpha \leqslant 0.6$ (as in the general case for large α the process mechanism changes, they are not recommended [11]) by the Coats–Redfern method [12] using $j = 1, \ldots, 20$ of different kinetic functions including ones differing in their order as presented in ref. 13. Treating data by the above method is rather tedious. We have, therefore, developed a complex including the OD-103 derivatograph operating on-line with a microcomputer. In this complex, a thermocouple and thermobalance signal is applied via a commutator to the

15-bit analog-to-digital converter and then introduced into the microcomputer through the interface. The analog-to-digital converter and the commutator are controlled by a timer. Data may be fed to the microcomputer at 5-s intervals. The thermocouple EMF is converted into temperature following the calibration chart stored in the computer, while the thermobalance signal is used for α computation. If a solvent is used as in our experiments, its phon has been loaded in the microcomputer memory and subtracted automatically. As the process terminates, which is signalled by the DTG curve, the computer starts to compute kinetic parameters by the Coats–Redfern method using $j = 20$ functions $f_j(\alpha)$. The procedure is repeated with different heating rates.

RESULTS AND DISCUSSION

As K_3CrO_8 was diluted with 20-fold Al_2O_3 for a derivatographic study, even an insignificant generation of adsorbed gases per unit solvent surface may have affected the kinetic results. In all the tests, therefore, the phon TG curve was subtracted. The check of the Al_2O_3 effects on the kinetics of isothermal K_3CrO_8 decomposition shows that this is described by the first-order autocatalysis (Prout–Thompkins) equation just as in the case of K_3CrO_8 without Al_2O_3. The Arrhenius parameters of thermolysis (Fig. 1) $\log(A/s^{-1}) = 5.5 \pm 0.8$; E (kJ mol^{-1}) $= 58.6 \pm 6.7$ agree with the data for

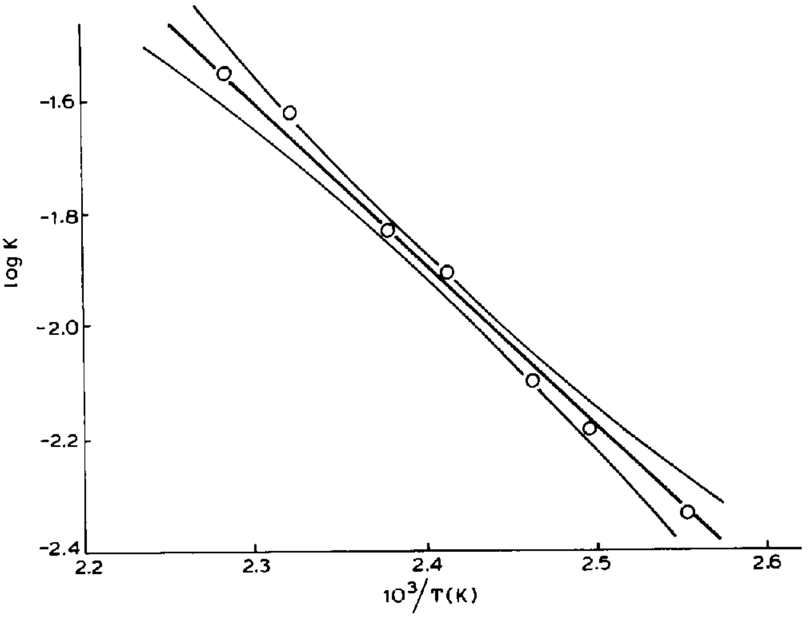

Fig. 1. Arrhenius dependence of rate constants of isothermal decomposition of K_3CrO_8 diluted with 20-fold Al_2O_3.

pure K_3CrO_8 [1]. Hence, the Al_2O_3 admixture does not change the kinetics of K_3CrO_8 decomposition. Following our data, this conclusion is also valid for ZnO diluant.

The Coats–Redfern discrimination of kinetic functions is usually realized by verifying the linearity of the expression

$$\log\frac{g_j(\alpha)}{T^2} = \log\frac{A_j R}{\beta E_j} - \frac{E_j}{2.3RT} \tag{16}$$

for different $g_j(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$. Close linear correlation coefficients (± 0.02) for all the 20 functions did not allow the choice of the kinetic model from eqn. (16). This resulted in the uncertainty of the Arrhenius parameters corresponding to eqn. (1), the maximum and minimum E values being more than an order of magnitude different. To eliminate this uncertainty, as mentioned above, pencil (1) must be obtained. The latter is achieved by changing the heating rate: each β_v has its own line (1) as the variation of β causes the thermoanalytical curve to shift, and the coefficient l in eqn. (2) correlates with the position of this peak [14]. As elementary analysis shows, correlation of parameters B and l of eqn. (2) consists with line pencil (1). This correlation can be conveniently used for checking the pencil formed by lines (1) and for computation of $\log \hat{A}$ and $\hat{E}$, as well as for simplified estimation of the error of $\log \hat{A}$ and $\hat{E}$ values, whose correct calculation requires a special analysis. The values of $\log \hat{A}$ and $\hat{E}$ found from eqn. (2) were 6 ± 2 and 60.7 ± 12.5, respectively (Fig. 2). A maximum error was

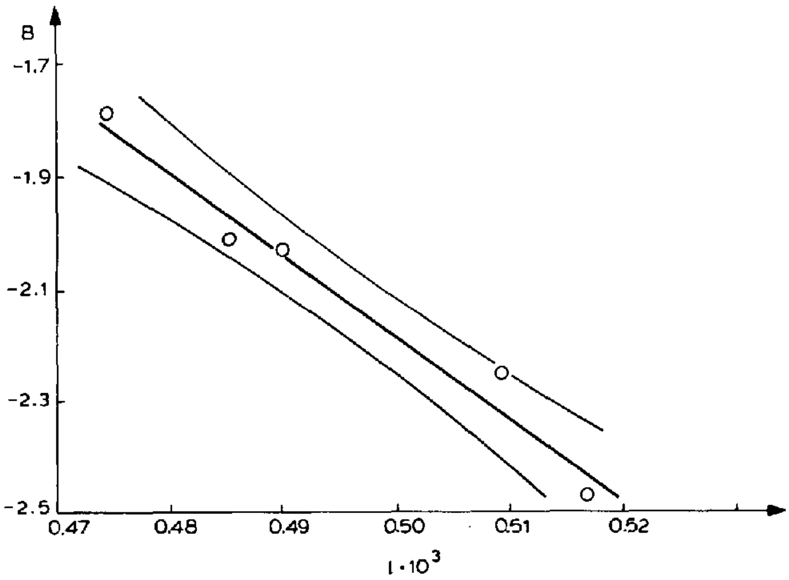

Fig. 2. Dependence of B on l, determined by treating with data of the non-isothermal decomposition of K_3CrO_8.

estimated through simple regression analysis eqn. (2) exposing the occurrence of the point for $\beta = 20$ K min^{-1} beyond the confidence domain of the function. An absolute error in the estimation of E is within an ordinary value but due to the smallness of E values its relative value amounts to 20%. Note, for more typical E values of the order of 120 kJ mol^{-1} and $\log(A/\mathrm{s}^{-1}) = 10$, it does not exceed 10% for both values [6]. Accuracy also increases for the substances and conditions with the greatest shift of the thermoanalytical curve with changing heating rates. A minimum mean approximation error $\bar{S}$ corresponds to the first-order autocatalysis equation $\hat{f}(\alpha) = \alpha(1-\alpha)$. The results indicate that the kinetics of K_3CrO_8 thermolysis is the same under isothermal and non-isothermal conditions.

The agreement between the results of isothermal and non-isothermal studies evidences the reliability of $\hat{A}$ and $\hat{E}$ values obtained by the suggested technique. It is also significant that $\hat{A}$ and $\hat{E}$ values allow the most probable function $\hat{f}(\alpha)$ to be found. Thus, adhering to the framework of the non-isothermal kinetics approaches to the analysis of the results and using the practically simple algorithm considered above and suggested in refs. 6 and 7, the inverse kinetic problem may be solved unambiguously and kinetic characteristics may be obtained with satisfactory, following pessimistic estimates, accuracy.

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