

Fast method for reaction kinetics determination under linear heating of reacting substance

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Abstract

A method has been developed for simultaneous evaluation of activation energy and kinetic function using rather small amounts of non-isothermal experimental data.

INTRODUCTION

Let us assume that heating is linear and has a heating rate ω , and the degree of conversion may be calculated from the available experimental data, e.g. from mass losses. Therefore, the degree of conversion η is determined experimentally as a function of time. Our approach gives an answer to the question as to whether or not the process under investigation may be represented as a single-stage one with a kinetic function $\varphi(\eta)$; in other words, whether it may be described by

$$\dot{\eta} = k \exp(-E/RT)\varphi(\eta) \quad \eta(0) = 0 \quad T = T_n + \omega t$$

If the answer is positive then the parameters k and E could be estimated and the kinetic function could be determined. Because $\varphi(\eta)$ is supposed to be within a class of functions

$$\varphi(\eta) = (\eta + \alpha)^k(1 - \eta)^n$$

where $n = 1, 2, 3$; $k = 0.1$; $\alpha \ll 1$, the method provides a possibility of evaluating k , E , n , and k simultaneously. It should be noted that the same approach may also be applied in the case of more complicated kinetic functions, e.g. for $k > 1$ or $k < 0$ and fractional n .

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DESCRIPTION OF THE METHOD

Our method is based on the well known approximation [1–4, 6] for the integral

$$\int_0^t k \exp(-E/RT(\tau)) d\tau \approx RT^2(t)k \exp(-E/RT(t))(1 - 2RT(t)/E)/\omega E \quad (1)$$

where $T = T_n + \omega t$.

Neglecting the term $2RT/E$, we shall obtain a less precise but more convenient approximation

$$\int_0^t k \exp(-E/RT(\tau)) d\tau \approx k \exp(-E/RT(t))RT^2(t)/\omega E \quad (2)$$

The relative error of eqn. (2) does not exceed $2RT(t)/E$. It is simple to see that this value does not exceed the accuracy of thermoanalytical experiment, and hence the use of eqn. (2) seems to be mathematically correct. Let us exploit eqn. (2) to study the reverse problem.

Assume the process studied to be a single-stage one, then the reaction is described by the differential equation

$$\dot{\eta} = K(t)\varphi(\eta) \quad \eta(0) = 0 \quad (3)$$

where $K(t) = k \exp(-E/RT)$. Now let us perform separation of variables in eqn. (3); denoting $\int_0^\eta \varphi(u)^{-1} du$ by $\chi(\eta)$, we rewrite eqn. (3) in the form $\dot{\chi}(\eta) = K(T(t))$. Using the definition of $\chi(\eta)$, from eqn. (2) we obtain

$$\chi(\eta) \approx K(t)RT^2/\omega E = \dot{\chi}(\eta)RT^2/\omega E \quad (4)$$

Integration of eqn. (4) over the interval (η_0, η) gives

$$\ln(\chi(\eta)/\chi(\eta_0)) \approx E(T - T_0)/TT_0R \quad (5)$$

where T_0 is the temperature corresponding to the degree of conversion η_0 . The relative error in eqn. (5) does not exceed $2RT(t)/E$, while η_0 may have any non-zeroth value. We may write eqn. (5) in the form

$$TT_0R \ln(\chi(\eta)/\chi(\eta_0))/(T - T_0) \approx E \quad (6)$$

Values of T , T_0 , η_0 and η from the left-hand side of eqn. (6) are known from experiment. Hence, further study of the reverse problem is reduced to searching for a kinetic function $\varphi(\eta)$ within the given class that provides the relationship

$$TT_0R \ln(\chi(\eta)/\chi(\eta_0))/(T - T_0) \approx \text{const} \quad (7)$$

It should be outlined that there is an analogy with isothermal data treatment in the case when the differential curve $\dot{\eta}(t)$ could not be obtained. Indeed, in this case, $\dot{T} = 0$, and we arrive at $\chi(\eta) = t \text{ const}$. Thus to solve the reverse problem one needs to find a kinetic function for $\chi(\eta)/t = \text{const}$. The possibility of this analogy has been mentioned in ref.

5. However, isothermal experiment does not provide information on the temperature dependence of reaction rate; but in the case of linear heating, by using similar procedures we are able to obtain the activation energy E together with a kinetic function

An algorithm of $\varphi(\eta)$ construction is very simple when $\varphi(\eta) = (1 - \eta)^n$, i.e. $k = 0$. Taking an arbitrary value of n_0 , we obtain that function $F_{k,n}(\eta)$ for $k = 0$

$$F_{0,n} = TT_0 \ln \left(\int_0^\eta (1-u)^{-n_0} du / \int_0^1 (1-u)^{-n_0} du \right) / (T - T_0)$$

increases at $n > n_0$, decreases at $n < n_0$, and remains constant at $n = n_0$ (Fig. 1).

The solution to the direct problem

$$\dot{\eta} = k \exp(-E/RT)(1 - \eta)^{n_0}$$

where $T = T_n + \omega t$, $E = 20$ kcal, $n_0 = 2$, $\omega = 0.04$ K s⁻¹, $k = 10$ s⁻¹, $T_n = 280$ K were taken as experimental data in Fig. 1.

Therefore, condition (7) (in our notation $F_{0,n}(\eta) = \text{const}$) holds true only for $n = n_0 = 2$ (see Fig. 2). Moreover the value of the constant 21.65 kcal gives an estimate for activation energy E . Note that upon substitution of eqn. (1) by eqn. (2), a value of E from eqn. (7) shows some surplus, the value of which may be estimated, e.g. from $\max(1 - 2RT(t)/E)$ at the temperatures under consideration. Multiplying the constant obtained by this correction factor (which is equal to 0.95 for the

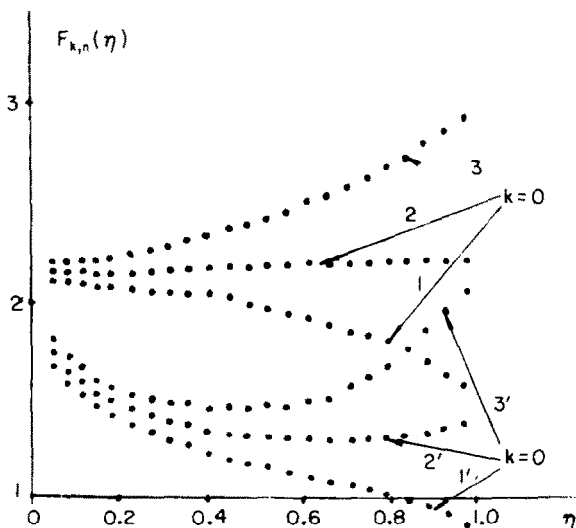


Fig. 1. Data treatment in the case of a single-stage reaction ($k = 0$, $n_0 = 2$): curve 1, plot of $F_{0,1}(\eta)$ ($n < n_0$); curve 1', plot of $F_{1,1}(\eta)$; curve 2, plot of $F_{0,2}(\eta)$ ($n = n_0$); curve 2', plot of $F_{1,2}(\eta)$; curve 3, plot of $F_{0,3}(\eta)$ ($n > n_0$); curve 3', plot of $F_{1,3}(\eta)$.

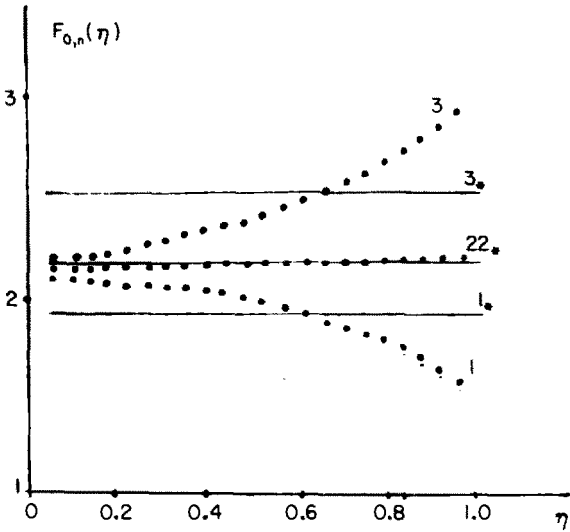


Fig. 2. Curves $F_{0,n}(\eta)$ for $n = 1, 2, 3$ and straight lines 1_* , 2_* , 3_* parallel to the η axis and approximating $F_{0,n}(\eta)$ in the best way.

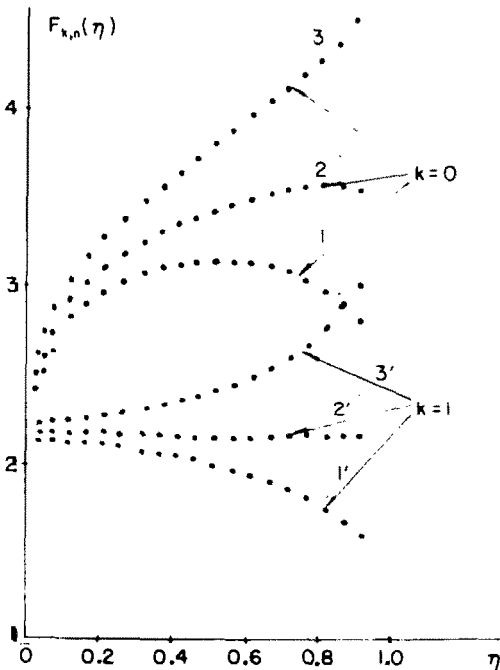


Fig. 3. Data treatment in the case of autocatalytic reaction ($k = 1$, $n_0 = 2$): curve 1, plot of $F_{0,1}(\eta)$; curve 1', plot of $F_{1,1}(\eta)$ ($n < n_0$); curve 2, plot of $F_{0,2}(\eta)$; curve 2', plot of $F_{1,2}(\eta)$ ($n = n_0$); curve 3, plot of $F_{0,3}(\eta)$; curve 3', plot of $F_{1,3}(\eta)$ ($n > n_0$).

data of Fig. 1), we finally obtain $E = 20.567$ kcal, which differs from the true value of 20 kcal by 2.8%. Figure 3 represents the procedure for the reverse problem studied in the case of an autocatalytic reaction. Here a solution to the direct problem

$$\dot{\eta} = k \exp(-E/RT)(\eta + \alpha)(1 - \eta)^{n_0}$$

where $E = 20$ kcal, $n_0 = 2$, $k = 10^7 \text{ s}^{-1}$, $\omega = 0.04 \text{ K s}^{-1}$ and $\alpha = 0.01$ was taken as the experimental data. In Fig. 3, these data (curves 1-3) are treated as a simple reaction, i.e. curves 1, 2 and 3 are the plots of $F_{k,n}(\eta)$ for $k = 0$ and $n = 1, 2, 3$ respectively. The shape of these curves is seen to differ markedly from that shown in Fig. 1. It implies that the process studied cannot be described as a simple reaction. In Fig. 3 (curves 1'-3'), the data are treated as an autocatalytic process with various values of n . For $k = 1$, we obtain

$$F_{1,n_0}(\eta) = TT_0 \ln \left[\int_0^\eta (1-u)^{-n_0}(u+\alpha)^{-1} du / \int_0^{n_0} (1-u)^{-n_0}(u+\alpha)^{-1} du \right] / (T - T_0)$$

Then condition (7) has the form $F_{1,n}(\eta) = \text{const}$. Curves 1', 2' and 3' in Fig. 3 represent the plots of functions $F_{1,n}(\eta)$ at $n = 1, 2, 3$; moreover condition (7) is fulfilled only for $n = n_0 = 2$.

As seen from Fig. 3, the plots of functions $F_{1,n}(\eta)$ for $k = 0, 1; n = 1, 2, 3$ form two fans: the upper one corresponds to simple functions (or $k = 0$) and for the lower fan $k = 1$. It may be shown that the fan of simple functions is always above the fan for autocatalytic functions.

The algorithm for the determination of $\varphi(\eta)$ (parameters k and n) and the activation energy E is generally as follows: for experimental data η , find $F_{k,n}(\eta)$ for all n and k values under consideration, and then determine those n and k values for which $F_{k,n}(\eta) = \text{const}$. This constant gives a value of the activation energy E . The process could easily be formalized, as may be illustrated (see Fig. 2) with curves 1-3 in Fig. 1 taken as an example. Comparison of curves 1-3 may be reduced to a comparison of straight lines 1*-3*, obtained upon linearization of appropriate curves. Then the problem is reduced to choice of such k and n values that the function $F_{k,n}(\eta)$ is approximated by a straight line parallel to the η axis. Note that some sets of points $\{a_i\}$ may be approximated by a straight line parallel to the η axis by using the zeroth order approximation $c = 0.5(\max_i a_i + \min_i a_i)$. As a measure of deviation of points $\{a_i\}$ from the straight line, let us use an average deviation of the points from the line or dispersion

$$DC = \sqrt{\sum_i (a_i - c)^2 / (m - 1)}$$

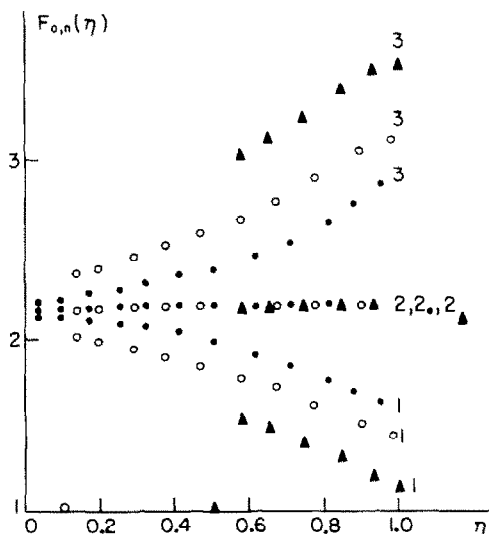


Fig. 4. Values of $F_{0,n}(\eta)$ for different values of η_0 : $\eta_0 = 0.01$ (●), $\eta_0 = 0.1$ (○), $\eta_0 = 0.5$ (▲).

where m is a number of experimental points. For curve 2_* in Fig. 2, this separation is considerably smaller (by two orders of value) than that for 1_* and 3_* .

There exists an additional opportunity to prove or deny the result obtained for some certain η_0 values. As it followed from eqn. (5) relation $F_{k,n}(\eta) \approx \text{const}$ is stable with respect to η_0 (see Fig. 4).

The values of $F_{k,n}(\eta)$ for the data of Fig. 1 (curves 1-3) calculated for various η_0 values are presented in Fig. 4, where curves 1-3 are the plots of $F_{0,n}(\eta)$ for $\eta_0 = 0.01$; curves 1_{\circ} - 3_{\circ} are of $F_{0,n}(\eta)$ for $\eta_0 = 0.01$; and curves 1_{\blacktriangle} - 3_{\blacktriangle} are of $F_{0,n}(\eta)$ for $\eta_0 = 0.5$, the constant value is seen to remain unchanged (curves 2_{\circ} , and 2_{\blacktriangle} are coincident); the remaining curves are shifted proportionally to η_0 .

TREATMENT OF EXPERIMENTAL DATA

The method was tested for calcium oxalate dehydration at varied heating rates. The experimental data were taken from ref. 7. Nine values of $\eta = 0.1, 0.2, \dots, 0.9$ were treated. The results of treatment for $\omega = 2.353 \text{ K min}^{-1}$ are collected in Table 1. Here n is an assumed power of kinetic function $\varphi(\eta) = (1 - \eta)^n$. The straight line equation approximating $F_{k,n}(\eta)$ is given by $C_n = C_n(\eta)$; DC_n denotes a dispersion of points $F_{k,n}(\eta)$ with respect to the straight line C_n . From a comparison between DC_n values calculated for $\eta_0 = 0.5$, we see that condition (5) holds true for $n = 0.5$ and $n = 0.4$. Increase in η_0 ($\eta_0 = 0.6$) shows that $C_{0.4}$ undergoes no shift, while dispersion of points with respect to $C_{0.5}$ is

TABLE 1

Dependence of dispersion on reaction order n at degree of conversion $\eta_0 = 0.5$ and 0.6

η_0		n				
		1	2	0.5	0.4	0.25
0.5	C_n	3.756	6.22	2.839	2.680	2.457
	DC_n	0.452	1.835	0.045	0.037	0.108
0.6	C_n	3.946	7.01	2.83	2.64	2.37
	DC_n	0.425	1.684	0.065	0.022	0.06

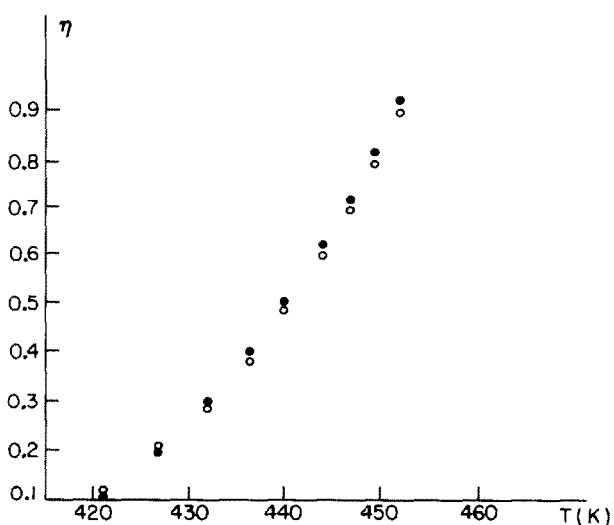


Fig. 5. Conversion curves for calcium oxalate dehydration: ●, experimental; ○, calculated.

increased. Thus we obtain finally $n = 0.4$, i.e. $\varphi(\eta) = (1 - \eta)^{0.4}$, $C_{0.4} = 2.64 \times 10^4$, and upon correction $(1 - 2RT/E) = 0.93$, we arrive at $E = 24920$. Comparison with the reported [7] data $n = 0.4$ and $E = 23 \times 10^3$ shows that inaccuracy of the E determination is about 7%. Figure 5 presents the experimentally obtained and calculated degrees of conversion which are seen to be in excellent agreement.

In conclusion it should be noted that a computer program has been compiled for $F_{k,n}(\eta)$ determinations by using the experimentally obtained points for degree of conversion. The scheme of computation procedure has been presented merely for the sake of illustration.

CONCLUSIONS

The method suggested provides a means for (i) obtaining kinetic information by using a small number of experimentally obtained points

(i.e. it is a fast method), (ii) using only some fraction of an experimentally obtained curve, (iii) determining both kinetic function and activation energy simultaneously, (iv) taking into consideration kinetic functions of any type and thus extending the range of parameters n and k (fractional n , $k > 1$, $k < 0$).

REFERENCES

- 1 A.G. Merzhanov, V.T. Abramov and L.T. Abramova. *J. Phys. Chem.* 41(1) (1967) 179.
- 2 V.G. Gorskii, *planning of Kinetic Experiments*, Nauka, Moscow, 1984.
- 3 G.T. Piloyan, *Introduction to the Theory of Thermal Analysis*, Nauka, Moscow, 1964.
- 4 G. Kramer, *Mathematical Method of Statistics*, Mir, Moscow, 1975.
- 5 S.V. Pestrikov, A.N. Peregudov and V.T. Gontkovskaya, *Solutions for direct and reverse problems on linear heating of reacting substance. Double-stage reactions*, Preprint, Institute of Structural Macrokinetics, USSR Academy of Sciences, Chernogolovka, 1988, pp. 19.
- 6 S.-S.A. Pavlova, I.V. Zhuravleva, Yu.I. Tolchinskii, *Thermal Analysis of Organic and Highmolecular Combinations*, Chimiya, Moscow, 1983.
- 7 E. Urbanovici and E. Segal, *Thermochim. Acta*, 107 (1986) 339.