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New Approach in Treating Kinetic Data

GEORGI BLIZNAKOV, IVAN BAKARDJIEV, AND
OGNYAN PESHEV

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

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A new method of determining the activation energy (ϵ) throughout the whole range of experimentally accessible temperatures and degrees of transformation (α) has been proposed. No knowledge of the analytical form of the kinetic isotherms is required. A series of iso-α sections of these isotherms is used. The logarithm of time ($\ln t$) necessary for reaching a given degree of transformation is plotted as a function of the reciprocal of the absolute temperature (τ) at which the corresponding kinetic isotherm is recorded. From the shape of the curves $\ln t - \tau$, the character of the dependence of ϵ on α and τ may be determined. A matrix scheme for the calculation of ϵ without graphic differentiation is given.

INTRODUCTION

Finding the kinetic equation is usually regarded as the first step in studying the kinetics of a chemical process. The second step which depends on the successful solution of the first one is the determination of the activation energy of the process. There are methods requiring no knowledge of the analytical form of the kinetic equation [(*1*) p. 552; (*2–7*)] which has the following general form:

$$\left(\frac{\partial\alpha}{\partial t}\right)_\tau = \varphi(\alpha,\tau). \qquad (1)$$

Here, α denotes the quantity whose derivative with respect to time (t) is a measure of the rate of the process, and $\tau = 1/T$ is the reciprocal of the absolute temperature. Function $\varphi(\alpha,\tau)$ is according to (1), the isothermal ($\tau = \text{const}$) rate of the process and does not explicitly depend on time since the external conditions are supposed to be constant. Proceeding from the Mass Action Law, it is assumed that

$$\varphi(\alpha,\tau) = k(\tau)f(\alpha), \qquad (2)$$

while an Arrhenius type is attributed to the rate constant,

$$k(\tau) = k_0 \exp(-\epsilon\tau), \qquad (3)$$

k_0 and ϵ being constant. The ϵ has a dimension of temperature and is the activation energy, E, experimentally determined in R units (R, gas constant).

Some of the available methods of determining the energy of activation without knowing the analytical form of function $\varphi(\alpha,\tau)$ are associated with differentiation of the experimental kinetic isotherms $\alpha = \alpha_T(t)$ (*2–5*). However, with all methods, except (*2*), function $\varphi(\alpha,\tau)$ ought to have the form (2), e.g., the relatively more general coincident curves method [(*1*) p. 552] is based on the possibility of finding a time scale for each kinetic isotherm so as to make the isotherms coincide:

$$\frac{\partial\alpha}{\partial[k(\tau)t]} = f(\alpha), \qquad (4a)$$

$$\int_0^\alpha \frac{dx}{f(x)} = k(\tau_1)t_1 = k(\tau_2)t_2 = \ldots . \qquad (4b)$$

It is evident that this is possible only when $\varphi(\alpha,\tau)$ is in the form (2). In this case, each iso-α section of the family of kinetic isotherms will necessarily give the same value for the activation energy. Otherwise, the method would be inapplicable to this case. In other words, the coincident curves method cannot be used when the energy of activation depends on α. Its application is also impossible when the activation energy depends on temperature: as is evident from Eqs. (4b) and (3), the number of unknown $\epsilon(\tau_1)$, $\epsilon(\tau_2)$, ... in this case will always exceed the number of available equations by 1.

Thus, the most general method of determining the energy of activation without knowing the analytical form of the rate equation and without graphic differentiation of the kinetic isotherms is applicable only to the classical Arrhenius case of constant activation energy.

In studying reactions with heterogeneous systems, cases are often encountered with, in which the mechanism of the process is different for the various intervals of temperatures ($T = 1/\tau$) and degrees of transformation of the reactants (α). Thus, the effect of temperature on the reaction rate is not uniform over the whole range of temperatures and degrees of transformation studied experimentally, so that the activation energy should be regarded as a function of these parameters. In these cases, function $\varphi(\alpha,\tau)$ is not in form (2). Its determination on the basis of the experimental data is a study with its own difficulties [(*1*) Chap. 13].

In the present paper, a method of determining the activation energy is proposed. No knowledge of $\varphi(\alpha,\tau)$ is required. A series of iso-α sections of the experimental kinetic isotherms, $\alpha = \alpha_\tau(t)$, is made (Fig. 1). The logarithm of the time for reaching a given α value is plotted as a function of the reciprocal of the absolute temperature, τ, at which the isotherm is obtained. The character of the dependence of the activation energy on α and τ may be judged by the shape of the curves $\ln t - \tau$. In the regions where this dependence is uniform, a relatively simple approximation for $\varphi(\alpha,\tau)$ could be sought. Preliminary determination of the character of this dependence facilitates the revealing of the mechanism of the process in the respective regions. Thus, omitting the step of finding the kinetic equation, i.e., function $\varphi(\alpha,\tau)$, the study begins with elucidating the temperature dependence of the process rate. Using the experimental kinetic isotherms and without differentiation, a classification of the experimental data can be made according to the manner in which the activation energy depends on the temperature and degree of transformation. Determining the kinetic equation and elucidating the mechanism of the process are the following steps. They are based on information obtained by the method proposed. For this reason, the latter may also be considered as a new approach in treating kinetic data. In what follows, this method will be discussed in detail and will simultaneously be applied to an example.

1. Theoretical

The relationship between the shape of the curves $\ln t - \tau$ and the dependence of the activation energy on the temperature and degree of transformation is deduced on the basis of the following consideration. We write function $\varphi(\alpha,\tau)$ in the form

$$\varphi(\alpha,\tau) = \varphi(\alpha,\tau_0) \exp\left[-\int_{\tau_0}^{\tau} \epsilon(\alpha,y)\,dy\right]. \quad (5)$$

The quantity $\epsilon(\alpha,\tau)$ will be called heat of activation (*8*). It actually represents a generalization of the apparent activation energy measured experimentally. In fact, from (5) it follows

$$\epsilon(\alpha,\tau) = -\frac{\partial \ln \varphi(\alpha,\tau)}{\partial\tau}. \quad (6)$$

This coincides with the usual definition of the energy of activation. When ϵ is a constant, a classical Arrhenius case is obtained (*3*). If ϵ depends only on α, a temperature dependence of the type given in Eq. (3) is again observed, the activation energy, $\epsilon(\alpha)$, being a function of the degree of transformation. The advantage of Eq. (5) consists in the fact that the whole temperature dependence of the rate is expressed by one function, $\epsilon(\alpha,\tau)$, which describes both the Arrhenius type dependencies and those differing from this type.

We integrate Eq. (1) under the initial condition $\alpha = 0$ at $t = 0$ for each τ. Taking into account Eq. (5), we obtain

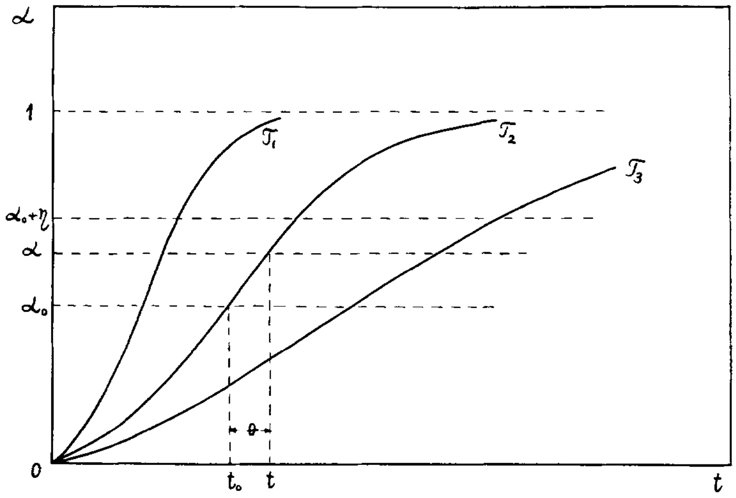

FIG. 1. A model type of kinetic isotherms obtained at various temperatures.

$$t = \int_0^\alpha \frac{\exp\left[\int_{\tau_0}^{\tau} \epsilon(x,y)\,dy\right]}{\varphi(x,\tau_0)}\,dx, \quad (7)$$

and using (5) again, from (7), we get the logarithmic derivative

$$\left(\frac{\partial \ln t}{\partial\tau}\right)_\alpha = \int_0^\alpha \frac{\epsilon(x,\tau)}{\varphi(x,\tau)}\,dx \bigg/ \int_0^\alpha \frac{dx}{\varphi(x,\tau)}, \quad (8)$$

which gives indications about the shape of the curves $\ln t - \tau$. Each curve is plotted on the basis of an iso-α section of the family of kinetic isotherms $[\alpha = \alpha_\tau(t)]$ and corresponds, therefore, to a given value of α.

Let $\epsilon = \text{const}$. From Eq. (8), we obtain

$$\left(\frac{\partial \ln t}{\partial\tau}\right)_\alpha = \epsilon = \text{const}. \quad (9)$$

This means that curves $\ln t - \tau$ are in this case a family of parallel straight lines. Their slope gives the constant energy of activation, ϵ. The same result is obtained as in the case when using the coincident curves method. This is the classical Arrhenius case, i.e., the only case when the mentioned method is applicable.

Let $\epsilon = \epsilon(\alpha)$. From Eq. (8), it is evident that here $(\partial \ln t/\partial\tau)_\alpha$ will depend, generally speaking, both on α and τ. In other words, each of the curves $\ln t - \tau$ will have its own course differing from that of the others. With small α, however, $(\partial \ln t/\partial\tau)_\alpha$ depends only on α but not on τ, i.e., the curves $\ln t - \tau$ corresponding to the narrow interval $(0,\alpha)$ where $\alpha \ll 1$, represent a family of nonparallel straight lines. In fact, when expanding function $\epsilon(x)$ in powers of x, we obtain from Eq. (8):

$$\left(\frac{\partial \ln t}{\partial\tau}\right)_\alpha = \sum_{n=0}^{\infty} \frac{1}{n!}\left[\frac{d^n\epsilon(x)}{dx^n}\right]_{x=0} \int_0^\alpha \frac{x^n\,dx}{\varphi(x,\tau)} \bigg/ \int_0^\alpha \frac{dx}{\varphi(x,\tau)}$$

$$= \sum_{n=0}^{\infty} \frac{1}{(n+1)!}\left[\frac{d^n\epsilon(x)}{dx^n}\right]_{x=0} \alpha^n = \xi(\alpha), \quad (10)$$

since at $\alpha \to 0$, the ratio of the integrals in Eq. (10) is equal to $\alpha^n/(n+1)$.

Let $\epsilon = \epsilon(\tau)$. From Eq. (8), it is evident that in this case

$$\left[\frac{\partial \ln t}{\partial\tau}\right]_\alpha = \epsilon(\tau), \quad (11)$$

and therefore,

$$\ln t = \int \epsilon(\tau)\,d\tau + u(\alpha) = u(\alpha) + v(\tau). \quad (12)$$

When plotting τ along the abscissa, and $\ln t$ along the ordinate we shall obtain, according to Eq. (11), a family of curves which will however be parallel since (12) shows that any two curves may be obtained one from another by translation along the ordinate over a distance $u(\alpha_2) - u(\alpha_1)$.

Finally, let $\epsilon = \epsilon(\alpha,\tau)$. From Eq. (8), we conclude that in this most general case $(\partial \ln t/\partial\tau)_\alpha$ is a function of both α and τ, the dependence on τ not disappearing even at low values of α. We obtain a family of nonparallel curves $\ln t - \tau$.

We shall point out that the value $\alpha = 0$ is not a privileged one, so that the above classification remains valid for any narrow interval of degrees of transformation (α_0, $\alpha_0 + \eta$). Indeed, when integrating Eq. (1) from 0 to α_0 (over α) and from 0 to t_0 (over t), and then between the limits 0 and $\alpha_0 + \eta$ for α, which correspond to 0 and $t_0 + \theta$ for t, we have

$$t_0(\alpha_0,\tau) = \int_0^{\alpha_0} \frac{d\alpha}{\varphi(\alpha,\tau)}, \qquad (13a)$$

$$t_0 + \theta = \int_{\alpha_0}^{\alpha_0+\eta} \frac{d\alpha}{\varphi(\alpha,\tau)}, \qquad (13b)$$

whence, on substracting (13a) from (13b), and assuming $\alpha = \alpha_0 + z$, we obtain

$$\theta(\eta,\tau;\alpha_0) = \int_{\alpha_0}^{\alpha_0+\eta} \frac{d\alpha}{\varphi(\alpha,\tau)} = \int_0^{\eta} \frac{dz}{\varphi(\alpha_0 + z,\tau)}, \qquad (14)$$

and

$$\left(\frac{\partial \ln \theta}{\partial \tau}\right)_\eta = \int_0^{\eta} \frac{\epsilon(\alpha_0 + z,\tau)}{\varphi(\alpha_0 + z,\tau)}\, dz \Bigg/ \int_0^{\eta} \frac{dz}{\varphi(\alpha_0 + z,\tau)}. \qquad (15)$$

It is evident that a complete formal analogy exists between Eq. (15) and (8). This means that the part of the axis of abscissa can be played by an arbitrary iso-α section taken, say, at $\alpha = \alpha_0$. Thus, to any kinetic isotherm, a time-zero may be ascribed and on this basis, an individual time too, which we shall call reduced time, $\theta = t - t_0(\alpha_0,\tau)$ (Fig. 1). The shape of the curves $\ln \theta - \tau$ plotted on the basis of a series of iso-α sections of the kinetic isotherms within the range $(\alpha_0,\alpha_0 + \eta)$ characterizes the effect of temperature on the rate of the process over this range. Eq. (8) is a special case of (15) at $\alpha_0 = 0$ (i.e., $t_0 = 0$). Thus, the analysis of the curves $\ln \theta - \tau$ corresponding to a narrow interval degrees of transformation $(\alpha_0,\alpha_0 + \eta)$ shows that the following four cases are possible:

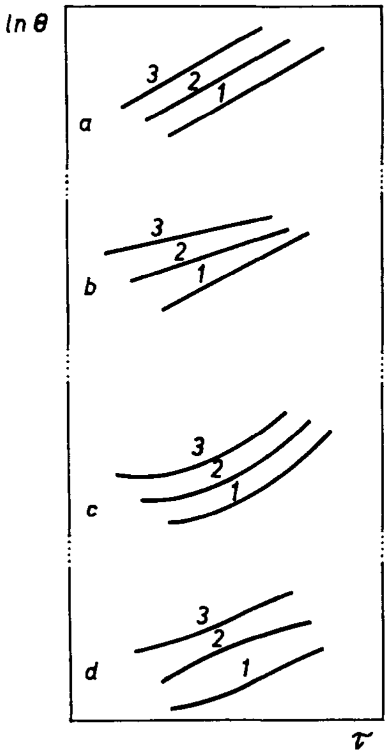

FIG. 2. Model type of the $\ln \theta - \tau$ curves; (a), constant heat of activation; (b), the heat of activation (HA) depends on the degree of transformation; (c), HA depends on temperature; (d), HA depends both on the degree of transformation and on temperature. Curves 1, 2, and 3, correspond to degrees of transformation α_1, α_2, and α_3, respectively, with $\alpha_1 < \alpha_2 < \alpha_3$, and in (b) $\alpha_3 \ll 1$.

1. A family of parallel straight lines (Fig. 2a). The heat of activation, ϵ, is independent of both the temperature and degree of transformation and is the activation energy in this classical Arrhenius case [Eq. (3)].

2. A family of nonparallel straight lines (Fig. 2b). The heat of activation, $\epsilon(\alpha)$, depends only on the degree of transformation, α. The dependence of the rate on temperature has an Arrhenius character, i.e., the logarithm of the rate depends linearly on τ [Eqs. (1)–(3)], the activation energy being a function of α and representing the heat of activation in this case.

3. A family of parallel curves (Fig. 2c). The heat of activation, $\epsilon(\tau)$, depends only on temperature ($T = 1/\tau$). The dependence

of the rate on temperature is not of an Arrhenius character but we may formally attribute the latter to this dependence on the basis of (5) by assuming that ϵ is a function of τ.

4. A family of nonparallel curves (Fig. 2d). The heat of activation, $\epsilon(\alpha,\tau)$, depends on both the temperature and degree of transformation. In this case again, the temperature dependence of the rate is not of an Arrhenius type. If we describe it formally as an Arrhenius dependence, the heat of activation in Eq. (5) must be regarded as a function of both α and τ. Therefore, there exists an unique relationship between the shape of the curves $\ln \theta - \tau$ and the character of the dependence of ϵ on α and τ. In addition, the following should be pointed out:

(a) It is the temperature dependence of the heat of activation, ϵ, which causes the appearance of the curves $\ln \theta - \tau$, since in the cases in which no such dependence is present, a family of straight lines is obtained.

(b) The width, η, of the interval, $(\alpha_0,\alpha_0 + \eta)$, within which the iso-$\alpha$ sections are made, is of importance only in case 2. The peculiarities of the other three cases are independent of this width. For this reason, it is reasonable to begin with the curves $\ln t - \tau$ obtained as a result of iso-α sections covering, in equal intervals, the whole range of α between 0 and 1. When the heat of activation, ϵ, depends neither on α nor on τ (case 1), all the straight lines $\ln t - \tau$ will be parallel. If ϵ depends only on τ (case 3), parallel curves $\ln t - \tau$ will be obtained. The appearance of nonparallel lines $\ln t - \tau$ would indicate the presence of case 2 or case 4. It is difficult to differentiate both cases from each other when a broad interval of α is used, owing to which the interval (0,1) should be divided into a sum of narrow intervals $(\alpha_0,\alpha_0 + \eta)$, each having its own reduced time $\theta(\eta,\tau;\alpha_0)$. The results corresponding to the respective intervals will allow the differentiation of cases 2 and 4: with the former, the curves $\ln \theta - \tau$ become straight lines when the width of the interval, η, decreases; with the latter curves $\ln \theta - \tau$ remain curves.

(c) In case 2, the straight lines $\ln \theta - \tau$ in a zero approximation with respect to α are parallel when a narrow interval, $(\alpha_0,\alpha_0 + \eta)$, is used [Eq. (10)]. Their slope, $\epsilon(\alpha_0)$, gives the heat of activation at $\alpha = \alpha_0$. The straight lines become nonparallel in the higher approximations with respect to α. This may lead, in some cases, to a family of parallel straight lines in both case 1 and case 2. The differentiation will be possible when increasing the width of the intervals. When the presence of case 2 is established, the equal slope of the straight lines may be used for finding the heat of activation at $\alpha = \alpha_0$.

2. PRINCIPLE OF THE CALCULATIONS

Processing of the experimental data with a view to studying the iso-α sections corresponding to a given narrow interval of α-values may be carried out as follows: Let m kinetic isotherms (corresponding to the reciprocals of the absolute temperature, $\tau_1, \tau_2, \ldots\ldots\ldots, \tau_m$) be plotted and n iso-α sections of these isotherms be made in the interval $(\alpha_0,\alpha_0 + \eta)$ at $\alpha = \alpha_1, \alpha_2, \ldots, \alpha_n$, respectively. The logarithm of the reduced time for reaching the degree of transformation $\alpha = \alpha_i$ along the kinetic isotherm (for which $\tau = \tau_j$) will be denoted by ϕ_{ij}. We write down the matrix ϕ_{ij} having n rows and m columns. On subtracting each column from the preceding one (the first column remaining unchanged), we obtain the matrix ϕ':

$$\phi'_{ij} = \phi_{ij} - \phi_{i,j-1}(1 - \delta_{1j}), \quad \begin{array}{l} i = 1, 2, \ldots n, \\ j = 1, 2, \ldots m, \end{array} \tag{16}$$

therein, δ_{kl} is the Krokener symbol ($\delta_{kl} = 1$ when $k = l$ and $\delta_{kl} = 0$ when $k \neq l$).

We multiply ϕ' on the right-hand side by the diagonal matrix T

$$T_{sp} = [\tau_p - \tau_{p-1}(1 - \delta_{1p})]^{-1}\delta_{sp}, \tag{17}$$

and obtain the matrix $\phi'' = \phi'T$:

$$\phi''_{ij} = \frac{\phi_{ij} - \phi_{i,j-1}(1 - \delta_{1j})}{\tau_j - \tau_{j-1}(1 - \delta_{1j})}, \quad \begin{array}{l} i = 1, 2, \ldots n, \\ j = 1, 2, \ldots m. \end{array} \tag{18}$$

Elements ϕ''_{i1} will not be used further so that the first column of ϕ'' can be neglected. For the elements of the remaining columns we have

$$\phi''_{ij} = \frac{\phi_{ij} - \phi_{i,j-1}}{\tau_j - \tau_{j-1}}, \quad \begin{array}{l} i = 1, 2, \ldots n, \\ j = 1, 2, \ldots m. \end{array} \tag{19}$$

They represent the average value of expression (8) or (15), respectively, for the range (τ_j,τ_{j-1}).

In case 1 (a family of parallel straight lines $\ln\theta - \tau$, [Eq. (12) and (9)], we have:

$$\phi_{ij} = u(\alpha_i) + \epsilon\tau_j, \tag{20}$$

whence at $j \neq 1$ we get

$$\phi''_{ij} = \epsilon = \text{const}, \tag{21}$$

or

$$\phi'' = \begin{array}{c|c} & \xrightarrow{\tau} \\ \alpha\downarrow & \begin{array}{c|c|c|c|c} i \backslash j & 2 & 3 & \cdots & m \\ \hline 1 & \varepsilon & \varepsilon & \cdots & \varepsilon \\ \hline 2 & \varepsilon & \varepsilon & \cdots & \varepsilon \\ \hline \cdots & \cdots & \cdots & \cdots & \cdots \\ \hline n & \varepsilon & \varepsilon & \cdots & \varepsilon \end{array} \end{array} \tag{22}$$

The elements of ϕ'' are constant over both columns and rows. The columns correspond to different values of τ whereas the rows, to different values of α. Therefore, the constancy of the elements of a given row is associated with their being independent of τ (at a definite α) while the constancy of the elements of a given column means that they do not depend on α (at constant τ).

In case 2 [a family of nonparallel lines $\ln\theta - \tau$, Eq. (10)], we have

$$\phi_{ij} = u(\alpha_i) + \xi(\alpha_i)\tau_j, \tag{23}$$

and therefore, $\phi''_{ij} = \xi(\alpha_i) = \xi_i$ when $j \neq 1$, i.e.,

$$\phi'' = \begin{array}{c|c|c|c|c} i \backslash j & 2 & 3 & \cdots & m \\ \hline 1 & \xi_1 & \xi_1 & \cdots & \xi_1 \\ \hline 2 & \xi_2 & \xi_2 & \cdots & \xi_2 \\ \hline \cdots & \cdots & \cdots & \cdots & \cdots \\ \hline n & \xi_n & \xi_n & \cdots & \xi_n \end{array} \tag{24}$$

We obtain a constancy of the elements over the rows but not over the columns.

In case 3 (a family of parallel curves $\ln\theta - \tau$):

$$\phi_{ij} = u(\alpha_i) + v(\tau_j), \tag{25}$$

so that

$$\phi''_{ij} = \frac{v(\tau_j) - v(\tau_{j-1})}{\tau_j - \tau_{j-1}} = f_j, \quad j \neq 1, \tag{26}$$

or

$$\phi'' = \begin{array}{c|c|c|c|c} i \backslash j & 2 & 3 & \cdots & m \\ \hline 1 & f_2 & f_3 & \cdots & f_m \\ \hline 2 & f_2 & f_3 & \cdots & f_m \\ \hline \cdots & \cdots & \cdots & \cdots & \cdots \\ \hline n & f_2 & f_3 & \cdots & f_m \end{array} \tag{27}$$

A constancy of the elements in the columns but not in the rows is observed.

Finally, in case 4 (a familyof nonparallel curves $\ln\theta - \tau$):

$$\phi_{ij} = \phi(\alpha_i,\tau_j), \tag{28}$$

whence, at $j \neq 1$,

$$\phi''_{ij} = \frac{\phi(\alpha_i,\tau_j) - \phi(\alpha_i,\tau_{j-1})}{\tau_j - \tau_{j-1}} = f_{ij}. \tag{29}$$

or

$$\phi'' = \begin{array}{c|c|c|c|c} i \backslash j & 2 & 3 & \cdots & m \\ \hline 1 & f_{12} & f_{13} & \cdots & f_{1m} \\ \hline 2 & f_{22} & f_{23} & \cdots & f_{2m} \\ \hline \cdots & \cdots & \cdots & \cdots & \cdots \\ \hline n & f_{n2} & f_{n3} & \cdots & f_{nm} \end{array} \tag{30}$$

There is no constancy of the elements in both columns and rows. The quantity ϵ in Eq. (22) represents the constant heat of activation characteristic of case (i). ξ_i in (24) depends linearly on α [as first approximation, Eq. (10)] so that the intercept of the straight line $\xi_i - \alpha_i$ gives the value of the heat of activation, $\epsilon(\alpha_0)$, at $\alpha = \alpha_0$, when the narrow interval investigated is $(\alpha_0,\alpha_0 + \eta)$ (case 2). The f_j in (27) is the mean value of the heat of activation over the range (τ_j, τ_{j-1}) (case 3). f_{ij} in (30) gives the mean value of the heat of activation in the rectangular region $\alpha_0 \leqslant \alpha \leqslant \alpha_i \leqslant \alpha_0 + \eta$, $\tau_{j-1} \leqslant \tau \leqslant \tau_j$ [Eq. (15) at $\eta \to 0$]. Thus, the heat of activation is determined in the course of identification of the separate cases.

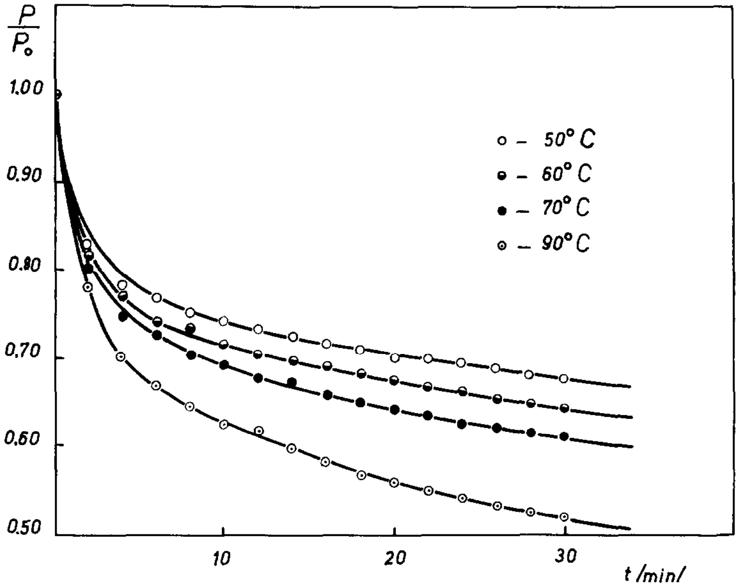

FIG. 3. Kinetic isotherms of catalytical oxidation of CO on chromium oxide.

If the number of the kinetic isotherms is not large, the matrices $\phi''(k)$ may be used in addition to ϕ'':

$$\phi''_{ij}(k) = (\phi_{ij} - \phi_{i,j-k})(\tau_j - \tau_{j-k})^{-1} \quad \begin{aligned} k &= 2, 3, \ldots m-1, \\ i &= 1, 2, \ldots n, \\ j &= k+1, k+2, \ldots m. \end{aligned} \tag{31}$$

Each of them has n rows and $m - k$ columns and has the same characteristic features as matrix ϕ'' ensuring the differentiation of cases 1, 2, 3, and 4. In fact, ϕ'' represents $\phi''(k = 1)$. Joining successively $\phi''(2)$, $\phi''(3)$, . . . , $\phi''(m - 1)$ to ϕ'', we obtain an overall Table with n rows and $[m(m - 1)]/2$ columns. The constancy of its elements may be judged with a greater certainty than when using only ϕ''.

3. APPLICATION

The following example will be given to illustrate the above method. Figure 3 shows the isotherms of catalytical oxidation of CO (in a stoichiometric ratio with O_2) on chromium oxide (*9*). The initial pressures

TABLE 1

	$\tau \cdot 10^3$ (°K)$^{-1}$: 2.7533	2.9137	3.0012	3.0941
α		t Time (min)		
0.20	1.7	2.3	2.8	3.7
0.22	2.1	2.9	3.4	5.0
0.24	2.3	3.6	4.5	6.8
0.26	2.8	4.8	6.3	9.6
0.28	3.3	6.6	9.0	14.5
0.30	4.0	8.4	12.9	20.0
0.32	5.0	11.5	18.2	29.0
0.34	6.3	15.2	24.0	36.4
0.36	8.3	19.7	30.3	—
0.38	10.6	25.2	36.6	—
0.40	13.2	32.2	—	—

TABLE 2[a]

α	ϕ''			$\phi''(2)$		$\phi''(3)$	$\bar{\epsilon}R$	$\rho(\%)$
0.20	3.73	4.46	5.94	3.99	5.22	4.52	4.643	22.6
0.22	3.99	3.60	8.27	3.85	5.98	5.04	5.122	14.2
0.24	5.53	5.05	8.80	5.36	6.99	6.30	6.338	21.6
0.26	6.08	6.16	8.98	6.48	7.61	7.16	7.162	6.2
0.28	8.56	7.02	10.17	8.01	8.83	8.60	8.530	4.9
0.30	9.16	9.71	10.39	9.35	10.06	9.64	9.718	1.9
0.32	10.29	10.39	9.48	10.32	9.93	10.09	10.083	1.4
0.34	10.87	10.34	8.88	10.68	9.59	10.19	10.092	3.0
0.36	10.67	9.74	—	10.34	—	—	10.250	1.2
0.38	10.69	8.45	—	9.90	—	—	9.680	2.9
0.40	11.01	—	—	—	—	—	11.01	—

[a] $\alpha_0 = 0$.

of the mixture, P_0, are practically equal and the degree of transformation is $\alpha = 1 - P/P_0$. The initial data concerning the iso-α sections made at α-values ranging between 0.20 and 0.40 (each section differing from the other by 0.02) are given in Table 1. On taking the logarithm of the values of time in Table 1, we process them as described above [Eq. (16)–(19) and (31)] and obtain Table 2. Here, the heat of activation is given in kcal/mole. In the next to last column of Table 2, the mean values with respect to the rows are given, whereas the last column contains the corresponding variance coefficients, ρ (percentage of standard deviations). It is evident that the elements in the first rows cannot be considered constant due to the great differences between them, but at $\alpha \geqslant 0.28$, the variance coefficients considerably decrease and the mean values over the rows become equal (with a statistical security of 95%). It may be assumed that the process takes place under nonstationary conditions due possibly to the fact that high reactivity states of the reagents are formed on the surface of the catalyst simultaneously with the oxidation of CO. Subsequently, the process becomes uniform, i.e., the separate intervals of time and degrees of transformation become equivalent. The constant values obtained at $\alpha \geqslant 0.28$ enable us to estimate the heat of activation which can also be made by the known method using the time to half-reaction. This estimation will, however, be influenced to some extent by the initial period which introduces some systematical error. To eliminate this error, $\alpha_0 = 0.28$ was assumed to be the initial value. The matrices $\phi''(k)$ corresponding to $\alpha_0 = 0.28$ and obtained using the corresponding reduced times [Eqs. (13) and (15)] are shown in Table 3. It is evident that there is a constancy of the elements, i.e., the process (in the given interval) may be related to case 1. The heat of activation amounts to 11.95 kcal/mole, the variance coefficients being ~3%.

TABLE 3[a]

α	ϕ''			$\phi''(2)$		$\phi''(3)$	$\bar{\epsilon}R$	$\rho(\%)$
0.30	11.60	17.49	7.33	13.72	12.27	11.98	12.41	6.7
0.32	13.07	14.26	9.71	13.49	11.92	12.46	12.49	5.7
0.34	13.00	12.59	8.06	12.85	10.27	11.55	11.40	6.5
0.36	11.89	11.00	—	11.57	—	—	11.49	7.1
0.40	11.73	—	—	—	—	—	11.73	—

[a] $\alpha_0 = 0.28$.

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