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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA, III

IMPROVEMENT OF DOYLE'S ISOTHERMAL METHOD

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Doyle's isothermal method is analysed by using it for deriving activation energies from theoretical curves. Empirical formulae are given for the time correction t_c, as well as for the factor r in the following equation: $E_a = -rm$ cal/mole. An iterative procedure is suggested, which eliminates the inaccuracy of Doyle's method and permits the derivation of activation energies with an accuracy of ± 0.1 kcal/mole in ideal cases.

In order to derive apparent activation energies, E_a, for thermal decompositions of solids, Doyle [1] has worked out a method based on the comparison of thermogravimetric curves, obtained at constant heating rate q, with thermogravimetric curves recorded under isothermal conditions.

By presuming the validity of a kinetic equation of the type:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where α stands for the reacted fraction of the initial compound, and by presuming further the rate constant k to obey Arrhenius' equation

$$k = Z \exp\left\{-\frac{E_a}{RT}\right\} \tag{2}$$

for the conditions of thermogravimetric analysis at constant heating rate, Doyle's equation of the thermogravimetric curves can be obtained [2]

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{ZE_a}{Rq}\,p(x) \tag{3}$$

In this relation $p(x)$ stands for the integral

$$p(x) = \int_x^\infty \frac{e^{-x}}{x^2}\,dx \quad \text{with} \quad x = \frac{E_a}{RT} \tag{4}$$

Under isothermal conditions, relations (1) and (2) give

$$g(\alpha) = Z \exp\left\{-\frac{E_a}{RT}\right\} t \tag{5}$$

The basic idea of Doyle's method is to take experimental points on thermogravimetric curves, obtained both under isothermal conditions and at a constant heating rate, corresponding to the same α value. In this case, irrespective of the analytical shape of the function $f(\alpha)$, we have the same $g(\alpha)$ value and Eqs (3) and (5) give

$$\exp\left\{-\frac{E_a}{RT_0}\right\} t_i = \frac{E_a}{Rq} p(x)$$

Taking logarithms

$$\lg t_i = \frac{E_a}{4.574\, T_0} + \lg \frac{E_a}{Rq} + \lg p(x) \tag{6}$$

If x is sufficiently large, $\lg p(x)$ is to a first approximation a linear function of $1/T_i$, where T_i stands for the absolute temperature at which α reaches the considered value at constant heating rate. Taking different α values and performing a graphical plot of $\lg t_i$ vs. $10^3/T_i$, a straight line is obtained. As shown by Doyle [1] the slope m of this straight line gives the apparent activation energy, according to the approximate formula:

$$E_a = -4351\ m \text{ cal/mole} \tag{7}$$

If the isothermal time is measured from the moment at which the sample reaches the isothermal working temperature T_0, this time t_{ia} must be corrected, since some decomposition occurs in the heat-up period too, i.e. $t_i = t_{ia} + t_c$. For the calculation of this equivalent isothermal time t_c, Doyle proposed the approximate formula

$$t_c = 0.03\ \frac{T_0}{q} \tag{8}$$

In Doyle's method there are two rough approximations, relation (8) and the constant factor in (7). In order to see the errors due to these approximations, the above method was used in the present paper to derive activation energy values from theoretical curves. By using the $\lg p(x)$ values listed in our earlier paper [3] for various E_a and T values, this theoretical verification can be carried out easily. With the $\lg p(x)$ value corresponding to T_0 and the considered E_a, Eq. (6) gives the equivalent isothermal time t_c of the heat-up period. The same equation gives the isothermal time t_i for higher temperatures $T > T_0$, by taking the corresponding $\lg p(x)$ values. The difference between the obtained t_i and t_c values will be the "observed" isothermal time t_{ia}. From these values the apparent activation energy was derived by means of Doyle's method in the following way: To the obtained t_{ia} value was added the correction t_c calculated by Doyle's approximate formula (8).

A plot of the resulting lg t_i values vs. $10^3/T_i$ was performed, and gave indeed a straight line. Its slope was calculated by means of the least squares method and E_a was obtained according to formula (7). Some examples of the results obtained are given in Table 1 for two hypothetical reactions, with $E_a = 24$ and 40 kcal/mole, respectively, for different isothermal ageing temperatures T_0, by presuming a constant heating rate of $q = 10°/\text{min}$ (for both the non-isothermal thermogravimetric curve and in the heat-up period of the isothermal analysis).

Table 1

Activation energy of two hypothetical reactions, derived by means of Doyle's method, $q = 10°/\text{min}$

$E_a = 24$ kcal/mole		$E_a = 40$ kcal/mole	
T_0, °C	E_a derived kcal/mole	T_0, °C	E_a derived, kcal/mole
120	24.5	170	38.0
130	24.6	180	37.7
140	24.9	190	37.2
150	25.2	200	36.5
160	25.6	210	35.6
170	26.4	220	34.4
180	27.6	230	32.9

As seen from Table 1, a systematic variation of the results obtained can be observed with the variation of the isothermal ageing temperature and the errors can be considerable, up to 20%.

In order to eliminate the inaccuracy of Doyle's method (due to the two rough approximations mentioned above) even in ideal cases, a systematic study of the equivalent isothermal time t_c and of the ratio E_a/m was performed. From Eq. (6) it is obvious that these values cannot be influenced either by the analytical shape of the function $f(\alpha)$ or by the value of the pre-exponential factor Z, which is a particular advantage of Doyle's method.

A great number of values of the equivalent isothermal time t_c were calculated by means of Eq. (6), for different activation energies between 10 and 66 kcal/mole, and for different temperatures between 100 and 430°. The analysis of these values led to an empirical formula which gives t_c with considerable accuracy. The empirical formula is the following:

$$t_c = \frac{1.191}{q} E_a^{-0.957} T_0^2 \tag{9}$$

At a given heating rate q and isothermal ageing time T_0, the equivalent isothermal time of the heat-up period is a function of the activation energy.

The influence of the activation energy and temperature upon the ratio E_a/m was studied in a similar way. Plots of lg t_i vs. $10^3/T_i$ were made for different activation energies between 10 and 66 kcal/mole and for isothermal ageing temperatures between 100 and 400°. The corresponding lg t_i values were calculated by means of Eq. (6), by using the table of lg $p(x)$ values [3]. The slope of the straight lines was determined by means of the least squares method. The analysis of the data obtained led to the following empirical formula:

$$r = -\frac{E_a}{m} = 4076 + 995(\lg E_a - 4) - 610(\lg E_a - 4)^2 - (4.92 - 0.976 \lg E_a)t \quad (10)$$

In this formula E_a must be expressed in cal/mole, and t stands for the isothermal ageing temperature given in degrees centigrade ($t = T_0 - 273$). Thus, at a given isothermal ageing temperature also the ratio r is a function of the activation energy and can differ from the Doyle value ($r = 4351$) by up to 10 %.

On the basis of the above results Doyle's isothermal method can be improved considerably. The errors due to the two approximations can be removed by means of the following iterative procedure:

In the first iterative cycle E_a is determined according to the Doyle method, i.e. t_c is calculated by means of formula (8), and the slope of the straight line obtained by plotting lg t_i vs. $10^3/T_i$ is multiplied by the factor $r = 4351$.

In the second iterative cycle t_c is calculated according to Eq. (9), by using the E_a value obtained in the first cycle. In order to facilitate these calculations, we give in Table 2 the $-\lg t_c\, q/T_0^2$ values for sixty activation energies between 10 and 69 kcal/mole. If E_a has a fractional value, a linear interpolation can be made.

Table 2

Numerical values of $-\lg t_c\, q/T_0^2$ for different activation energies

$E_a \cdot 10^{-4}$ cal/mole	$-\lg t_c\, q/T_0^2$									
	0	1	2	3	4	5	6	7	8	9
1	3.752	3.791	3.828	3.861	3.892	3.920	3.947	3.972	3.996	4.019
2	4.040	4.060	4.079	4.098	4.116	4.133	4.149	4.164	4.180	4.194
3	4.208	4.222	4.235	4.249	4.260	4.273	4.284	4.296	4.307	4.318
4	4.328	4.339	4.348	4.358	4.367	4.377	4.386	4.395	4.404	4.412
5	4.421	4.430	4.437	4.445	4.453	4.460	4.468	4.475	4.482	4.490
6	4.497	4.503	4.510	4.517	4.523	4.530	4.537	4.542	4.549	4.555

By using these new t_c values and the experimental data, a new plot of lg t_i vs. $10^3/T_i$ is made and the second approximation of E_a is obtained by means of the following formula:

$$E_a = -rm \text{ cal/mole} \quad (11)$$

The factor r is calculated now according to Eq. (10), by using the E_a value obtained in the first cycle.

In the third iterative cycle the E_a obtained in the second one is used to derive t_c, r and a new E_a value. This procedure is continued till the t_c, r and E_a values become self-consistent.

Efficiency of the suggested method is illustrated by Table 3. The values presented refer to hypothetical reactions.

Table 3

Determination of E_a by means of the suggested method. Hypothetical reactions, $q = 10°/\text{min}$

E_a = 22 kcal/mole, t = 150°C				E_a = 46 kcal/mole, t = 300°C			
Iterative cycle	t_c, s	r	E_a kcal/mole	Iterative cycle	t_c, s	r	E_a kcal/mole
1	76	4351	23.33	1	103	4351	44.18
2	85	4261	22.35	2	84	4348	45.79
3	88	4248	22.13	3	81	4356	46.11
4	89	4244	22.07	4	81	4358	46.13
5	89	4244	22.07				

The "observed" isothermal ageing times, t_{ia}, were calculated by means of formula (6), using the corresponding lg $p(x)$ values (by taking the difference between the t_i values obtained for T_i and T_0).

As seen, the procedure is a rather quickly converging one and in ideal cases it gives the apparent activation energy with an accuracy of about ±0.1 kcal/mole.

References

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RÉSUMÉ — On analyse la méthode isotherme de Doyle en l'employant pour le calcul des énergies d'activation sur des courbes théoriques. On donne des formules empiriques pour la correction du temps t_c, ainsi que pour le facteur r dans l'équation $E_a = -rm$ cal/mole. On propose un procédé itératif éliminant l'incertitude de la méthode de Doyle et permettant le calcul des énergies d'activation à ± 0.1 kcal/mole dans les cas idéals.

ZUSAMMENFASSUNG — Die Doylesche isothermische Methode wurde analysiert, indem man sie zur Ableitung der Aktivierungsenergiewerte aus theoretischen Kurven heranzog. Empirische Formeln für die Zeitkorrektur t_c und für den Faktor r in der Gleichung $E_a = -rm$ cal/Mol wurden gegeben. Eine Iterationsmethode durch welche die Ungenauigkeit der Doyleschen Methode beseitigt und die Werte der Aktivierungsenergien auf ±0.1 Kcal/Mol Genauigkeit für den Idealfall bestimmt werden können, wurde vorgeschlagen.

Резюме — Проанализирован изотермический метод Дойля при его использовании для расчета энергии активации по теоретической кривой. Приведены эмпирические формулы для коррекции времени t_c и для фактора r в следующем уравнении: $E_a = -rm$ кал/мол. Предлагается приближенный метод, исключающий неточность метода Дойля и дающий возможность расчитать энергию активации с точностью ± 0,1 ккал/мол в идеальном случае.