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An advantageous variant of the Ozawa–Flynn–Wall analysis

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Abstract

An advantageous algorithm is proposed for correcting the Doyle approximation for the popular Ozawa–Flynn–Wall analysis to make a model-free evaluation of the activation energy from a series of non-isothermal measurements carried out at different heating rates. In this way a definite improvement in the corrective factor is reached by an approximation formula. The maximum approximation error is 3×10^{-4}. Evidence concerning this new variant is provided by means of simulated data.

INTRODUCTION

The attraction of both isoconversion methods, the Ozawa–Flynn–Wall analysis [1–3] and the Friedman analysis [4], stems from the possibility of being able to determine the activation energy for certain prerequisites, without knowing the kinetic model of the reaction mechanism. In contrast to the above, the traditional single-curve analyses such as those of Borchardt and Daniels [5] or Coats and Redfern [6] also supply totally inaccurate values of the activation energy when a false model has been chosen, even when the quality of fitting is very high [7,8]. This shortcoming is caused by the lack of information content of a single non-isothermal experiment so that the simultaneous determination of the correct kinetic model and the parameters is not possible.

In the Ozawa–Flynn–Wall analysis a direct evaluation of the activation energy becomes possible using the Doyle approximation of the exponential integral [9]; however, the resulting errors are often greater than generally expected. Flynn [10] has already referred to this fact and has indicated a simple method of correction. An effective routine is described as follows, through which the Flynn correction table is substituted by an approxima-

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday.

tion, so that in the end the correction appears as a simple computer routine.

THE OZAWA–FLYNN–WALL ANALYSIS

The separation of the variables α and T is possible in single-step reactions according to the basic kinetic equation:

$$\mathrm{d}\alpha/\mathrm{d}t = f(\alpha)k(T) \tag{1}$$

$$k(T) = A\ \exp(-E/RT) \tag{2}$$

where α is the degree of conversion, T the temperature in kelvins, $f(\alpha)$ the type of reaction, $k(T)$ the rate constant, E the activation energy, A the pre-exponential factor, and R the gas constant.

The following equation is given for measurements with a constant heating rate ($T = T_0 + \beta t$), assuming the validity of the Arrhenius equation (eqn. (2)) for the temperature dependence of the reaction rate:

$$G(\alpha) = \int_0^{\alpha} \mathrm{d}\alpha/f(\alpha) = A/\beta \int_{T_0}^{T} \exp(-E/RT)\ \mathrm{d}t \tag{3}$$

If T_0 lies below the temperature at which the reaction is noticeable, then one can set the lower limit of integration to $T_0 = 0$, so that eqn. (4) is obtained after integration and taking logarithms:

$$\ln G(\alpha) = \ln(AE/T) - \ln \beta + \ln p(x) \tag{4}$$

where

$$p(x) = \exp(-x)/x - \int_{\infty}^{x} \exp(-x)/x\ \mathrm{d}x$$

and $x = E/RT$.

By using the approximation given by Doyle, $\ln p(x) \approx -5.3305 + 1.052x$ in eqn. (4) and transposing, one obtains

$$\ln \beta = \ln(AE/R) - \ln G(\alpha) - 5.3305 + 1.052x \tag{5}$$

It can now be seen from eqn. (5) that the graph $\ln \beta_j = f(1/T_{jk})$ shows straight lines with a slope $m = -1.052E/R$ during a series of measurements with a heating rate of $\beta_1 \ldots \beta_j$ at a fixed degree of conversion of $\alpha = \alpha_k$. The temperatures T_{jk} are those at which the conversion α_k is reached at a heating rate of β_j.

The slope of the straight lines is directly proportional to the activation energy. If the determined activation energy is the same for various values of α_k, then one can conclude with certainty that a single-step reaction exists. However, a change in E with an increasing degree of conversion indicates a complex reaction mechanism, so that in fact the separation of the variables as in the Ozawa–Flynn–Wall analysis (eqn. (1)) is not allowed. The discrepancies are especially serious when the total reaction mechanism consists of competitive individual reactions.

CORRECTION OF THE DOYLE APPROXIMATION

The approximation of the exponential integral by Doyle allowed the direct estimation of the activation energy. The errors in this approximation are smaller than 1% for $31 < x < 47$, but the approximation error for values of $x < 25$ or $x > 100$ already exceeds 3% in the determination of the activation energy. Therefore Flynn [10] suggested that one should first estimate E by using eqn. (5). Then the mean temperature T_m for the temperature T_{jk} and the mean value $x_m = E/RT_m$ should be determined. Finally one should correct the activation energy with a recorded tabular correction factor $F = F(x_m)$.

It is favourable in the computer-aided analysis to use the approximation formula for the correction instead of the tables as recommended by Flynn. Equation (6) was found empirically and the optimal coefficients a_0 to a_3 were determined by a non-linear adjustment:

$$F(x) = a_0\left(1 + \frac{a_1 + x}{1 + a_2 x + a_3 x^2}\right) \tag{6}$$

where $a_0 = 0.94961$, $a_1 = 7.770439$, $a_2 = 4.56092$ and $a_3 = 0.48843$. The dependence of $F(x)$ on x is expressed by eqn. (6) with high precision ($r > 0.99999$, Fig. 1); the maximum deviation is below 3×10^{-4} in the range $4 < x < 200$.

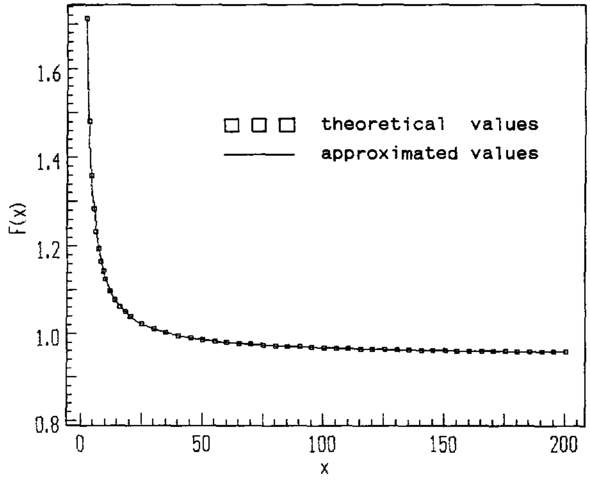

Fig. 1. Correction factor $F(x)$ vs. x.

The new algorithm for the correction is different from that suggested by Flynn.

(1) Determine E according to the Doyle approximation.

(2) Calculate the mean value $x_m = E/RT_m$.

(3) Determine the corrected activation energy E_{corr}: $E_{corr} = E/F(x_m)$.

The advantage of the Ozawa–Flynn–Wall analysis, where one can determine the activation energy without knowledge of the specific kinetic model, has to be weighed against the disadvantage that one obtains no information concerning the type $f(\alpha)$ or $G(\alpha)$ of the reaction. In order to obtain at least an indication about the reaction rate $d\alpha/dt$, one must determine the pre-exponential factor A for fixed degrees of conversion, $\alpha = \alpha_k$, as an average for all heating rates β_j on the basis of eqn. (4), assuming a reaction of first order (F1), $G(\alpha) = -\ln(1-\alpha)$. Many approximations are recommended in the literature [11] for the calculation of the required exponential integral $p(x)$. The approximation of fourth degree, given by Senum and Yang [12], has been proven sufficiently exact, with a maximum deviation of less than 0.03% for $5 < x < 100$:

$$p(x) = \frac{\exp(-x)}{x}\left(\frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}\right) \tag{7}$$

DISCUSSION AND APPLICATION

Both the Ozawa–Flynn–Wall analysis and the Friedman analysis will be discussed here. Taking logarithms, and assuming the validity of the Arrhenius equation (eqn. (1)), one obtains

$$\ln(d\alpha/dt) = \ln f(\alpha) + \ln A - E/RT \tag{8}$$

which serves as a basis for the Friedman analysis. For fixed degrees of conversion, $\alpha = \alpha_k$, the graph of $\ln(d\alpha/dt) = f(1/T_{jk})$ shows lines with the slope of $m = -E/R$.

The reliability of both methods of analysis is demonstrated here by two simulated examples. The data set was simulated under the assumption of a reaction of first order with the parameters log A (s) = 11.0 and $E = 200$ kJ mol^{-1} (Fig. 2). Both the Ozawa–Flynn–Wall and the Friedman analyses (Figs. 3 and 4) reproduce the theoretical values of the activation energy and of the pre-exponential factor (Tables 1 and 2). The insignificant deviation from the theoretical values could result from the limited number of used data points ($n < 200$).

For the simulation of a two-step reaction

$$A \xrightarrow{F1} B \xrightarrow{F1} C$$

we assume a decomposition reaction of first order (F1) for both steps. These steps were set with parameters log A_1 (s) = 11.6 and $E_1 = 200$ kJ

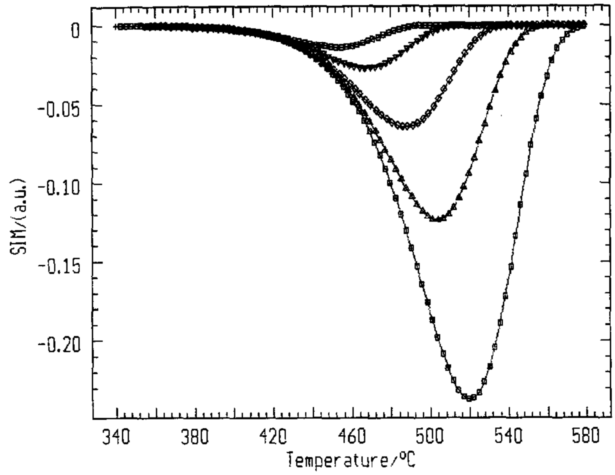

Fig. 2. Simulated curves of a single-step reaction. Heating rates: 0.5, 1.0, 2.5, 5.0 and 10 K min^{-1}. Parameters: log A (s) = 11.0 and $E = 200$ kJ mol^{-1}.

mol^{-1} for the first step and log A_2 (s) = 15.0 and $E_2 = 260$ kJ mol^{-1} for the second step, and both reactions contribute equally to the total area (Fig. 5).

The model-free evaluation of the activation energy (Figs. 6 and 7) results in a surprisingly good recapture of the original parameters only in the conversion ranges in which the single reactions are sufficiently isolated (i.e. $\alpha < 0.30$ or $0.80 < \alpha$) (Tables 3 and 4).

One should indicate, however (and this applies much more so far as real measurements are concerned) that the values for the activation energy are more reliable in the Ozawa–Flynn–Wall analysis than in the Friedman

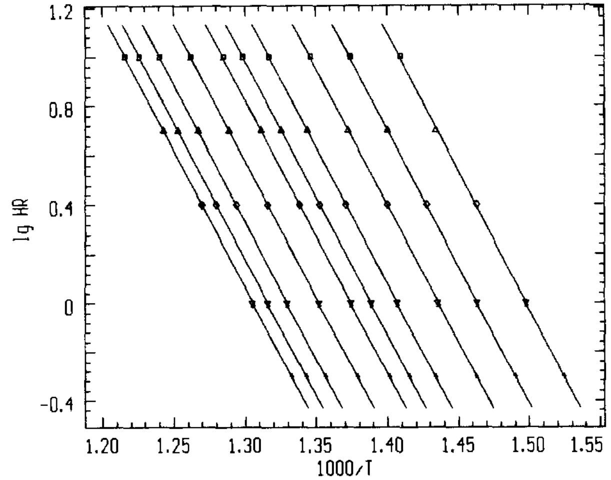

Fig. 3. Ozawa–Flynn–Wall analysis of a simulated single-step reaction.

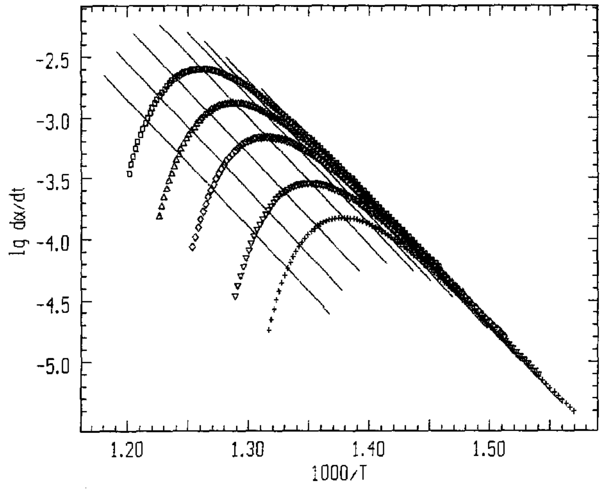

Fig. 4. Friedman analysis of a simulated single-step reaction.

TABLE 1

Calculated values of the activation energy and pre-exponential factor from the Ozawa–Flynn–Wall analysis of a simulated single-step reaction

α	E (kJ mol^{-1})	log A (s)
0.95	200.95 ± 0.15	11.06
0.90	200.96 ± 0.10	11.06
0.80	200.93 ± 0.08	11.06
0.60	200.96 ± 0.17	11.06
0.40	201.00 ± 0.06	11.06
0.30	201.04 ± 0.14	11.07
0.20	201.10 ± 0.15	11.07
0.10	201.31 ± 0.38	11.08
0.05	201.70 ± 0.78	11.10
0.02	202.32 ± 1.91	11.17

TABLE 2

Calculated values of the activation energy and pre-exponential factor from the Friedman analysis of a simulated single step reaction

α	E (kJ mol^{-1})	log A (s)
0.95	200.86 ± 0.64	11.03
0.90	200.82 ± 1.16	11.03
0.80	200.72 ± 0.84	11.02
0.60	200.73 ± 1.34	11.02
0.40	200.75 ± 0.56	11.03
0.30	200.76 ± 0.65	11.03
0.20	200.76 ± 0.91	11.03
0.10	200.80 ± 0.64	11.03
0.05	200.85 ± 1.11	11.03
0.02	200.88 ± 0.60	11.03

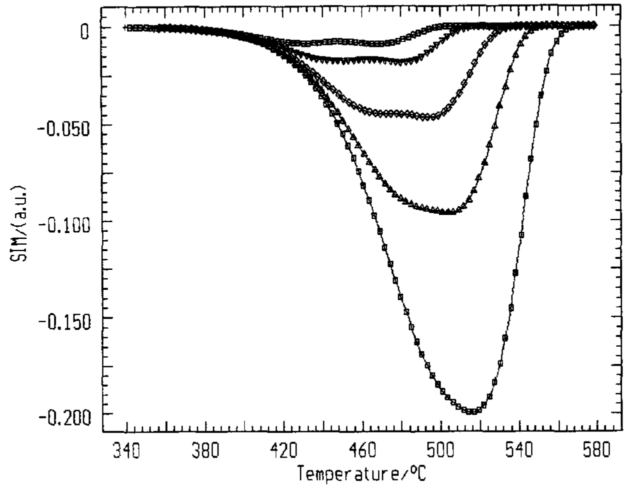

Fig. 5. Simulated data set of two-step consecutive reaction. Heating rates: 0.5, 1.0, 2.5, 5.0 and 10 K min^{-1}. Parameters: log A_1 (s) = 11.6 and E_1 = 200 kJ mol^{-1}; log A_2 (s) = 15.0 and E_2 = 260 kJ mol^{-1}.

analysis. Moreover, the Ozawa–Flynn–Wall analysis reacts with less sensitivity to noise, owing to its integrating character, than the Friedman analysis. The latter, however, provides a better visual separation of more reaction steps as well as information concerning the existence of an autocatalytically activated process.

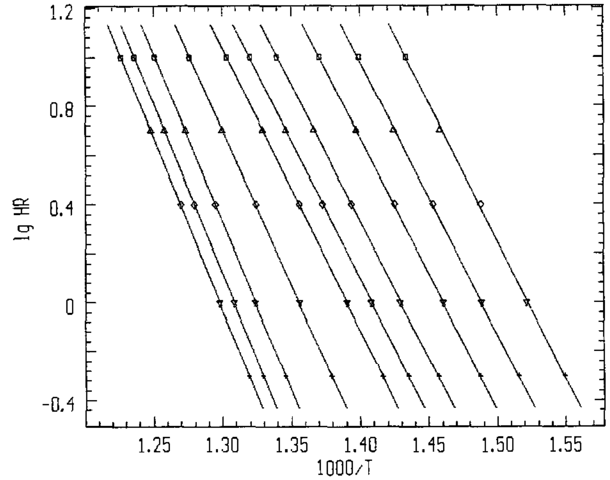

Fig. 6. Ozawa–Flynn–Wall analysis of a simulated two-step reaction.

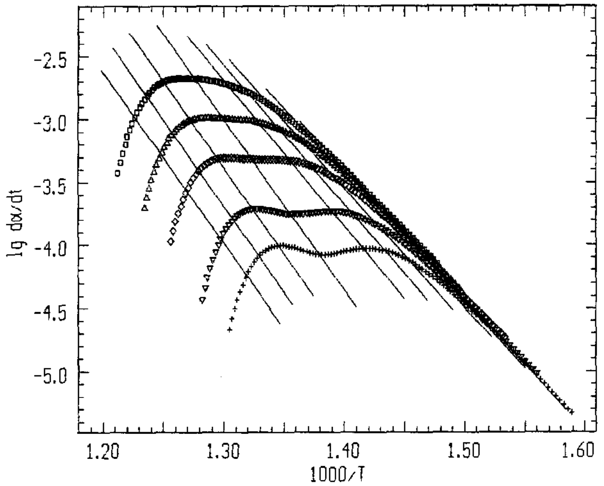

Fig. 7. Friedman analysis of a simulated two-step reaction.

TABLE 3

Calculated values of the activation energy and pre-exponential factor from the Ozawa–Flynn–Wall analysis of a simulated two-step reaction

α	E (kJ mol^{-1})	log A (s)
0.95	256.44 ± 0.27	14.83
0.90	254.59 ± 0.47	14.73
0.80	249.93 ± 0.75	14.47
0.60	229.22 ± 0.54	13.16
0.40	209.03 ± 0.39	11.84
0.30	204.99 ± 0.33	11.58
0.20	202.94 ± 0.37	11.46
0.10	202.16 ± 0.76	11.42
0.05	202.59 ± 1.49	11.45
0.02	204.37 ± 3.63	11.57

TABLE 4

Calculated values of the activation energy and pre-exponential factor from the Friedman analysis of a simulated two-step reaction

α	E (kJ mol^{-1})	log A (s)
0.95	261.03 ± 1.68	15.04
0.90	261.37 ± 0.93	15.06
0.80	263.07 ± 2.31	15.18
0.60	259.74 ± 1.30	15.04
0.40	221.63 ± 0.36	12.59
0.30	210.81 ± 0.48	11.90
0.20	205.05 ± 0.42	11.55
0.10	202.11 ± 0.81	11.39
0.05	201.33 ± 1.35	11.35
0.02	200.98 ± 0.75	11.33

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