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MEANINGFUL ACTIVATION ENERGIES FOR COMPLEX SYSTEMS II

Evaluation of the Friedman method when applied to multiple reactions, and comparison with the Ozawa–Flynn–Wall method

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The validity of the Friedman method is assessed for systems of overlapping reactions. By means of mathematical analysis and numerical examples it is shown that, in the case of competitive reactions, the method gives the true value of the instantaneous mean activation energy. However, some error may be incurred if this method is applied to systems of independent reactions. The relative accuracy of the Friedman and Ozawa–Flynn–Wall methods is discussed in respect of complex systems of reactions.

The kinetic methods commonly used in thermal analysis have been derived for single reactions. For systems involving multiple reactions, the inappropriate application of such methods can lead to misleading results [1–4]. However, it has been shown that the Ozawa–Flynn–Wall (OFW) method [5–7] can give meaningful values of the activation energy in a wide range of circumstances [1]. The Friedman method is related to the OFW method inasmuch as they both rely on the use of several different heating rates; both provide separate values for the activation energy at different levels of conversion; and both are independent of the form of the kinetic equation. It is therefore of interest to find out whether the Friedman method is also appropriate to the analysis of complex systems of reactions. The method is already being used for such systems *e.g.* to demonstrate the variation in activation energy during the course of lignin pyrolysis [8].

The Friedman method has been tested against computer-generated data for multiple reactions (both independent and competitive), and the activation energies obtained were of comparable magnitude to those used to generate the data [3]. It is the purpose of this paper to establish the extent to which such results can be generalized. The reference point used as the "correct" activation energy is the instantaneous mean [1], as given by Eq. (1).

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This is the average of those reactions occurring at a given

$$E_{\text{inst}} = \frac{\Sigma v_i E_i}{\Sigma v_i} \tag{1}$$

instant in time, weighted according to their respective rates, v_i. E_{inst} will, in general, vary with the extent of conversion and, to a lesser extent, will also vary with the heating rate.

Application of the Friedman method to multiple reactions

The basic Friedman method

The Friedman method [9] is based on the Arrhenius plot, but the logarithm of the reaction rate (at constant degree of conversion, α) is used in place of the logarithm of the rate constant. A series of runs is performed at different heating rates to provide data at a range of temperatures. The basic equation used is Eq. (2).

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln(Af(\alpha)) \tag{2}$$

At constant α the last term in Eq. (2) is constant, and so a plot of $\ln(d\alpha/dt)$ against $1/T$, gives a straight line of slope $(-E/R)$.

For complex systems the activation energy, E, will vary slightly with temperature because, at a given α, the importance of the various component reactions varies with heating rate [10]. Thus a Friedman plot will not be an exact straight line, although the use of this method [3, 8] indicates that in practice satisfactory linearity is generally obtained. In general, a Friedman plot will yield a gradient, m_F, which is given by Eq. (3). The value of the activation energy, E_F, is then given by Eq. (4), where v is the total rate of reaction.

$$m_F = \left(\frac{\partial \ln(d\alpha/dt)}{\partial(1/T)}\right)_\alpha \tag{3}$$

$$\begin{aligned} E_F = -Rm_F &= -R\left(\frac{\partial \ln(d\alpha/dt)}{\partial(1/T)}\right)_\alpha \\ &= \frac{RT^2}{v}\left(\frac{\partial v}{\partial T}\right)_\alpha \end{aligned} \tag{4}$$

Application to competitive reactions

For a system of competitive reactions the rate of a single reaction is given by Eq. (5), and the total rate is given by Eq. (6).

$$v_i = A_i \exp(-E_i/RT) f_i(\alpha) \tag{5}$$

$$v = \Sigma v_i = \Sigma A_i \exp(-E_i/RT) f_i(\alpha) \tag{6}$$

$$\begin{aligned}\left(\frac{\partial v}{\partial T}\right)_\alpha &= \Sigma A_i \exp(-E_i/RT) \cdot \frac{E_i}{RT^2} \cdot f_i(\alpha) \\ &= \frac{1}{RT^2} \Sigma v_i E_i\end{aligned} \tag{7}$$

Differentiation of Eq. (6) with respect to T, at constant α, gives the differential which is required in Eq. (4). In this way Eq. (8) is obtained, which is identical in form to Eq. (1).

$$E_F = \frac{1}{v} \Sigma v_i E_i = \frac{\Sigma v_i E_i}{\Sigma v_i} \tag{8}$$

Thus we have the important result that, for competitive reactions, the Friedman method gives the exact value of the average activation energy.

Application to independent reactions

For independent reactions the individual rates are given by Eq. (9), and the overall rate by Eq. (10).

$$v_i = c_i A_i \exp(-E_i/RT) f_i(\alpha_i) \tag{9}$$

$$v = \Sigma v_i = \Sigma c_i A_i \exp(-E_i/RT) f_i(\alpha_i) \tag{10}$$

In this case the partial differentiation with respect to T gives Eq. (11).

$$\left(\frac{\partial v}{\partial T}\right)_\alpha = \frac{1}{RT^2} \Sigma v_i E_i + \Sigma c_i k_i f'_i(\alpha_i) \left(\frac{\partial \alpha_i}{\partial T}\right)_\alpha \tag{11}$$

where

$$k_i = A_i \exp(-E_i/RT) \tag{12}$$

The second term on the right hand side of Eq. (11) arises because the composition of the mixture is not constant for constant α, but does vary slightly with heating rate (and hence with T). If Eq. (11) is used with Eq. (4), we obtain Eq. (13).

$$E_F = E_{\text{inst}} + \frac{RT^2}{v} \Sigma k_i f'_i(\alpha_i) c_i \left(\frac{\partial \alpha_i}{\partial T}\right)_\alpha \tag{13}$$

Eq. (13) indicates that a definite relationship exists between E_F and E_{inst}. The difference between the two is determined by the rate constants, k_i, of the individual reactions; by the variation in composition with temperature, $c_i(\partial\alpha_i/\partial T)_\alpha$; and by the differential of the individual rate equations $f'_i(\alpha_i)$. This rather complicated expression is difficult to quantify, but its qualitative behaviour can be readily ascertained.

The sum of the variation in composition is zero, as shown by differentiation of Eq. (14) to give Eq. (15).

$$\alpha = \Sigma c_i \alpha_i \tag{14}$$

$$0 = \Sigma c_i \left(\frac{\partial \alpha_i}{\partial T}\right)_\alpha \tag{15}$$

Thus the final term in Eq. (13) will disappear (and E_F will equal E_{inst}) if the values of $k_i f'_i(\alpha_i)$ are equal. The circumstances in which this can occur are described below, firstly for first-order reactions, and then for more general cases.

In the case of first-order reactions $f'_i(\alpha_i)$ is simply -1. Thus E_F becomes equal to E_{inst} if the rate constants, k_i, for the individual reactions are equal. This is equivalent to saying that a compensation relationship applies between E_i and A_i. Considering a situation where such compensation does not occur, i.e. the A_i are equal or undercompensating, then k_i will decrease with increasing E_i. Thus the contribution of reactions of low E_i to the sum in Eq. (13) will be exaggerated. Now, for these reactions α_i will decrease with T (or β), at constant α [10], i.e. $(\partial\alpha_i/\partial T)_\alpha$ is negative, and $f'_i(\alpha_i)\,(\partial\alpha_i/\partial T)_\alpha$ will be positive. Thus positive deviaton from E_{inst} will be expected for under-compensated systems, and conversely, negative deviations will occur for over-compensated systems. Computer-simulated examples of these situations are given below.

For reactions of higher order than first, $f'_i(\alpha_i)$ will still be negative, but will be proportional to some power of $(1-\alpha)$. In these circumstances the products $k_i f'_i(\alpha_i)$ are equal at some stage intermediate between equal rate constants and equal extents of conversion, i.e. slightly less compensation is required.

If one of the reactions occurring is "autocatalytic", i.e. $f'_i(\alpha_i)$ is positive, then the components of the sum in Eq. (13) will no longer tend to cancel, and quite large errors could occur.

Computer simulation

Competitive reactions (cases 1 and 2)

Two cases were considered. The first was Ozawa's example [4] of two reactions differing greatly in their activation energies (84 kJ mol^{-1}). The second is a more realistic example of two reactions with activation energies differing by 20 kJ mol^{-1}. In both cases substantial competition is only possible because the pre-exponential factors, A_i, were chosen to compensate for the difference in activation energies.

The results of these calculations are given in Tables 1 and 2. As predicted the Friedman method gave values for the activation energy which are identical with E_{inst}. For the second case the OFW method gave results in close agreement with E_{inst}, but in the first case the error was significant. In both cases the error in E_{OFW} was in good agreement with the expected error [1], which increases with μ_{2E}, the second moment of the individual activation energies Eq. (16).

$$\mu_{2E} = \Sigma v_i (E_i - E_{\text{inst}})^2 / \Sigma v_i \tag{16}$$

Table 1 Competitive reactions, case 1

E_1 = 167.36 kJ mol^{-1} (40 kcal mol^{-1}), $A_1 = 2 \times 10^{11}$ s^{-1}
E_2 = 251.04 kJ mol^{-1} (60 kcal mol^{-1}), $A_2 = 1 \times 10^{19}$ s^{-1}

Heating rates: 1.5 and 2.0 deg min^{-1}

α	E_{inst}, kJ mol^{-1}	μ_{2E}, kJ mol^{-1}	$E_F - E_{\text{inst}}$, kJ mol^{-1}	$E_{\text{OFW}} - E_{\text{inst}}$, kJ mol^{-1}
0.2	219.10	40.65	0.00	−7.92 (−3.6%)
0.5	226.91	37.90	0.00	−7.15 (−2.7%)
0.8	231.77	35.23	0.00	−6.33 (−2.7%)

Table 2 Competitive reactions, case 2

E_1 = 190 kJ mol^{-1} $A_1 = 1.28 \times 10^{13}$ s^{-1}
E_2 = 210 kJ mol^{-1} $A_2 = 3.21 \times 10^{14}$ s^{-1}

Heating rates 1.5 and 2.0 deg·min^{-1}

α	E_{inst}, kJ mol^{-1}	μ_{2E}, kJ mol^{-1}	$E_F - E_{\text{inst}}$, kJ mol^{-1}	$E_{\text{OFW}} - E_{\text{inst}}$, kJ mol^{-1}
0.2	198.00	9.80	0.00	−0.45 (−0.23%)
0.5	198.88	9.94	0.00	−4.47 (−0.24%)
0.8	199.28	9.97	0.00	−0.47 (−0.24%)

Under-compensated independent reactions (cases 3 and 4)

For reactions with under-compensating Arrhenius parameters the temperature at which reaction occurs increases with the activation energy. An example of this is when the pre-exponential factors are equal (case 3). In case 4 the pre-exponential factors, A_i, were adjusted so that when the E_i of two reactions differ by 10 kJ mol^{-1} then the reaction with the higher E_i should be 10% complete when the one with lower E_i was 90% complete.

The results from these two calculations are shown in Table 3. For brevity only the results for $\alpha = 0.5$ are included. For α in the range $0.3 \leqslant \alpha \leqslant 0.7$ deviations from E_{inst} were comparable to those for $\alpha = 0.5$ and deviations were less at the extremes of α. Calculations were also performed using sets of 5 and 17 reactions. The results (not shown) indicated that the only effect of increasing the number of component reactions was to make $E_F - E_{\mathrm{inst}}$ and $E_{\mathrm{OFW}} - E_{\mathrm{inst}}$ smoother functions of α, without changing the average values.

As expected E_F shows positive deviations from E_{inst}, but these deviations are barely significant. E_{OFW} shows negative deviations from E_{inst} for these, and all other cases [1].

Over-compensated independent reactions (case 5)

Situations in which reactions with high activation energies occur at lower temperatures than those with low activation energies are rare in practice, but the case has been considered here for completeness. The pre-exponential factors were adjusted so that the converse of case 4 was obtained.

The results for this case were similar to those for the preceding cases, except that E_F shows negative errors, as predicted by Eq. (13).

Compensated independent reactions (cases 6 and 7)

Equation (13) predicts that if the rate constants of the component first-order reactions are equal, then the Friedman method gives the exact value of E_{inst}. This is demonstrated by case 6 (Table 4). Here the give pre-exponential factors have been adjusted to satisfy this condition when $\alpha = 0.5$. Exact compensation can occur at one temperature only, and so at conversions lower than 0.5 the Arrhenius parameters are under-compensated, but above this point they are over-compensated. This is reflected by the deviations of E_F from E_{inst}.

Another calculation was performed using component reactions having maximum overlap of their α *vs.* T curves, using the condition that at $\alpha = 0.5$ then $\alpha_i = 0.5$ for all i (case 7). The required values of A_i were slightly different from those employed above, but the $E_F - E_{\mathrm{inst}}$ values still changed sign, this time at $\alpha = 0.2$.

Table 3 Summary of results for independent reactions, at $\alpha = 0.5$[h]

Case	Reaction set	E_{inst}, kJ mol^{-1}	μ_{2E}, kJ mol^{-1}	$E_F - E_{inst}$, kJ mol^{-1}	$E_{OFW} - E_{inst}$, kJ mol^{-1}
4	Under-compensated[a]	199.87	4.22	3.47 (1.7%)	−0.08 (−0.04%)
3	Uncompensated (equal A_i)[b]	200.02	6.33	4.89 (2.4%)	−0.18 (−0.09%)
8	Maximized $E_F - E_{inst}$[c]	198.81	9.88	7.60 (3.8%)	−0.46 (−0.23%)
6	Compensation based on rate constants[d]	200.66	14.10	0.00	−0.95 (−0.47%)
7	Compensation based on extent of reaction[e]	200.98	14.10	−0.72 (−0.4%)	−0.94 (−0.47%)
9	Maximised $-(E_F - E_{inst})$[f]	201.93	10.29	−8.76 (−4.3%)	−0.50 (−0.25%)
5	Over-compensated[g]	200.08	4.28	−3.84 (−1.9%)	−0.08 (−0.04%)

[a] 9 reactions; $E_i = 200 + 5(i-5)$ kJ mol^{-1}; $A_1 = 7.1 \times 10^{14}$, $A_2 = 4.5 \times 10^{14}$, $A_3 = 2.9 \times 10^{14}$, $A_4 = 1.7 \times 10^{14}$, $A_5 = 1 \times 10^{14}$, $A_6 = 5.3 \times 10^{13}$, $A_7 = 2.9 \times 10^{13}$, $A_8 = 1.6 \times 10^{13}$, $A_9 = 7.1 \times 10^{12}$; $c_i = 1/9$; $f_i(\alpha_i) = 1 - \alpha_i$.

[b] 9 reactions; E_i as note a; $A_i = 1 \times 10^{14}$; $c_i = 1/9$; $f_i(\alpha_i) = 1 - \alpha_i$.

[c] 9 reactions; E_i as note a; $A_1 = 1.47 \times 10^{13}$, $A_2 = 2.40 \times 10^{13}$, $A_3 = 3.94 \times 10^{13}$, $A_4 = 6.27 \times 10^{13}$, $A_5 = 1 \times 10^{14}$, $A_6 = 1.54 \times 10^{14}$, $A_7 = 2.40 \times 10^{14}$, $A_8 = 3.75 \times 10^{14}$, $A_9 = 5.46 \times 10^{14}$; $c_i = 1/9$; $f_i(\alpha_i) = 1 - \alpha_i$.

[d] 5 reactions; $E_i = 200 + 10(i-3)$ kJ mol^{-1}; $A_i = 1 \times 10^{14} \times \exp(10{,}000(i-3)/646.6R)$; $c_i = 1/5$; $f_i(\alpha_i) = 1 - \alpha_i$.

[e] 5 reactions; E_i as note d; $A_1 = 2.17 \times 10^{12}$, $A_2 = 1.48 \times 10^{13}$, $A_3 = 1 \times 10^{14}$, $A_4 = 6.76 \times 10^{14}$, $A_5 = 4.56 \times 10^{15}$; $c_i = 1/5$; $f_i(\alpha_i) = 1 - \alpha_i$.

[f] 9 reactions; E_i as note a; $A_1 = 4.02 \times 10^{11}$, $A_2 = 1.57 \times 10^{12}$, $A_3 = 6.15 \times 10^{12}$, $A_4 = 2.48 \times 15^{13}$, $A_5 = 1 \times 10^{14}$, $A_6 = 4.14 \times 10^{14}$, $A_7 = 1.71 \times 10^{15}$, $A_8 = 7.15 \times 10^{15}$, $A_9 = 2.99 \times 10^{16}$; $c_i = 1/9$; $f_i(\alpha_i) = 1 - \alpha_i$.

[g] 9 reactions; E_i as note a; $A_1 = 6.4 \times 10^{9}$, $A_2 = 6.7 \times 10^{10}$, $A_3 = 7.2 \times 10^{11}$, $A_4 = 8.5 \times 10^{12}$, $A_5 = 1 \times 10^{14}$, $A_6 = 1.28 \times 10^{15}$, $A_7 = 1.64 \times 10^{16}$, $A_8 = 2.18 \times 10^{17}$, $A_9 = 2.9 \times 10^{18}$; $c_i = 1/9$; $f_i(\alpha_i) = 1 - \alpha_i$.

[h] Heating rates .316228 and 3.16228 deg min^{-1}

Table 4 Independent reactions obeying a compensation law

Parameters as Table 3 notes *d* and *h*

α	E_{inst}, kJ mol^{-1}	$\sqrt{\mu_{2E}}$, kJ mol^{-1}	$E_F - E_{inst}$, kJ mol^{-1}	$E_{OFW} - E_{inst}$, kJ mol^{-1}
0.1	198.49	14.05	0.18 (0.09%)	−0.94 (−0.48%)
0.2	199.37	14.10	0.24 (0.12%)	−0.95 (−0.48%)
0.3	199.93	14.11	0.23 (0.11%)	−0.95 (−0.47%)
0.4	200.35	14.11	0.15 (0.07%)	−0.95 (−0.47%)
0.5	200.66	14.10	0.00	−0.95 (−0.47%)
0.6	200.90	14.09	−0.24 (−0.12%)	−0.95 (−0.47%)
0.7	201.04	14.08	−0.63 (−0.31%)	−0.95 (−0.47%)
0.8	201.04	14.07	−1.29 (−0.64%)	−0.94 (−0.47%)
0.9	200.69	14.02	−2.62 (−1.30%)	−0.93 (−0.46%)

Condition for maximum error (cases 8 and 9)

As shown above compensated reactions result in E_F being close to E_{inst}. However, for extremes of under- and over-compensation E_F is also close to E_{inst} because overlap is greatly reduced.

The pre-exponential factors were varied on a logarithmic scale, between extreme under-compensation (case 4) and exact compensation (case 6), and the case which resulted in the greatest positive deviation is given in Table 3 as case 8. Similarly on the over-compensation side the greatest negative deviation is given by case 9.

Discussion

The numerical examples given here demonstrate that both the Friedman and OFW methods are valid for systems of multiple reactions, when the component reactions are of the same general type (*i.e.* have similar kinetic parameters). However, this validity can break down if the activation energies of the component reactions differ widely. For the Friedman method this occurs in the case of independent reactions only, but for the OFW method this applies to both independent and competitive reactions [1]. Other limitations to the use of isoconversional methods have been discussed elsewhere [1].

The OFW method is predicted to always result in small negative deviations from E_{inst} [1], whereas the Friedman method will normally be expected to give positive deviations. For this reason a comparison of the results from the two methods is a useful check on their accuracy. In favourable circumstances the difference in the values for the activation energy obtained by the two methods may give useful information concerning the nature of the reactions occurring.

Systems of competitive reactions

For competitive reactions the Friedman method gives the true value of the instantaneous mean activation energy, and for this reason is to be favoured when it is suspected that such a situation exists. However, both the Friedman and OFW methods require the degree of conversion to be a well-defined observable. This condition is not always satisfied if the competing reactions give different products. The validity of the OFW method has not been proved when the competing reactions obey different kinetic equations.

Systems of independent reactions

For truly independent reactions the question of variable products does not arise. However, care needs to be taken to prevent the occurrence of competitive side reactions; e.g. oxidation during organic pyrolysis.

For realistic systems both methods are predicted to give reasonable results, but the maximum possible error of the OFW method is substantially less than that of the Friedman method. In addition, the OFW method requires integral (e.g. TG) data only, whereas the Friedman method also requires differential (e.g. DTG) data. For this reason the former method is particularly favoured for those thermal analysis techniques which give integral data, due to the errors involved in the differentiation step.

A possible source of error for the OFW method, which is absent from the Friedman method is uncertainty in the actual heating rate, due to the tendency of the sample temperature to lag behind that of the furnace. This effect is particularly strong at low temperatures because of poor radiative heat transfer. Thus the true sample heating rate can be greater than the furnace heating rate. However, determination of the true heating rate, for the preceding 50–100 K, can easily be incorporated into a computerised analysis of thermal analysis data.

For purely independent reactions, the OFW method places no constraints on the forms taken by the kinetic equations of the component reactions [1]. However, the Friedman method is normally slightly affected by the kinetic equations, as shown by Eq. (13). This effect is likely to become significant if the individual reactions have very different kinetic equations, and especially if an autocatalytic process is occurring.

* * *

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Glossary of symbols

A	Arrhenius pre-exponential factor.
c_i	Contribution of individual independent reactions to the overall reaction (dimensionless).
E	Arrhenius activation energy.
E_{inst}	Instantaneous mean activation energy, as defined by Eq. (1).
E_F	Activation energy as calculated by the Friedman method.
E_{OFW}	Activation energy as calculated by the Ozawa–Flynn–Wall method.
$f(\alpha)$	Function describing the dependence of the rate constant on the degree of conversion.
$f'(\alpha)$	First derivative with respgct to α of $f(\alpha)$.
i	(subscript) Denotes a component reaction.
k	Rate constant.
t	Time.
T	Temperature (K).
v	Reaction rate.
α	Degree of conversion (dimensionless).
β	Heating rate.
μ_{2E}	Instantaneous second moment of individual activation energies, as defined by Eq. (16].

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Zusammenfassung — Die Gültigkeit der Friedman-Methode wird für Systeme von überlappenden Reaktionen einer Betrachtung unterzogen. Durch mathematische Analyse und numerische Beispiele wird gezeigt, daß im Falle kompetitiver Reaktionen die Methode den richtigen Wert der jeweiligen mittleren Aktivierungsenergie ergibt. Fehler können jedoch auftreten, wenn diese Methode auf Systeme voneinander unabhängiger Reaktionen angewandt wird. Die relative Genauigkeit der Methoden von Friedman und Ozawa–Flynn–Wall wird mit Hinsicht auf komplexe Reaktionssysteme diskutiert.

Резюме — Показана применимость метода Фридмена для систем с перекрывающимися реакциями. С помощью математического анализа и числовых примеров показано, что в случае конкурирующих реакций метод дает истинное значение мгновенной средней энергии активации. Однако, некоторые ошибки могут вноситься, если этот метод применен к системам с независимыми реакциями. Обсуждена относительная точность методов Фридмена и Озавы–Флинна–Уолла по отношению к сложным системам реакций.