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MEANINGFUL ACTIVATION ENERGIES FOR COMPLEX SYSTEMS

I. The application of the Ozawa–Flynn–Wall method to multiple reactions

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It is known that the application of an inappropriate kinetic method to the thermal analysis of complex systems can lead to misleading results. To avoid this problem, the new parameter 'instantaneous mean activation energy' is introduced and the Ozawa–Flynn–Wall method is assessed as a means of obtaining it. It is concluded that good results can generally be obtained by this method, provided that the various reactions occurring in the complex system are of the same type. The pyrolysis of coal is considered as a possible application of the method.

During thermal decomposition a variety of reactions can be occurring simultaneously. This is seen in the case of coal pyrolysis, for example, due to its inherent complexity and inhomogeneity. However, even pure polymers may decompose *via* oligomers of various sizes, and the different pathways may well have different kinetic parameters. Analogous situations can be found in other branches of thermal analysis, such as TPD from heterogeneous surfaces [1, 2]. A full kinetic analysis of such complex systems is generally not feasible, but some kind of 'effective' or 'average' kinetic description is still needed. It is important that these effective kinetic parameters are 'fundamental' enough to be invariant over a range of conditions. In this paper the parameter 'instantaneous mean activation energy' is recommended, and it is shown that the Ozawa–Flynn–Wall method [3–5] provides a useful way of obtaining it.

Single-run methods

Methods which involve a single non-isothermal thermal decomposition experiment are attractive because of their speed [6]. However, numerical examples [7, 8] have shown that if several reactions are occurring together then the observed

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activation energy can be substantially less than that of any of the component reactions. This result is the probable explanation of the anomalously low activation energies obtained for coal pyrolysis [9, 12]. This effect can be understood readily because a low activation energy results in broad TG, DTG *etc* traces, as shown in Fig. 1. A broad trace is also obtained when several different processes occur with overlapping temperature ranges [7, 8].

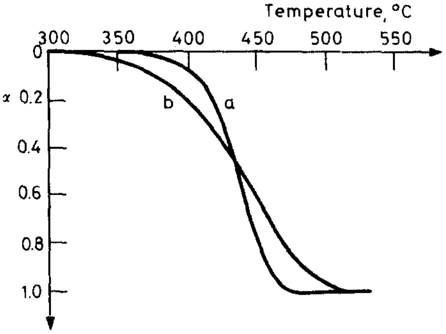

Fig. 1 The effect of activation energy on calculated TG curves.
a: $f(\alpha) = 1-\alpha$, $A = 1 \times 10^{14}\ \mathrm{s}^{-1}$, $E = 220\ \mathrm{kJ\ mol}^{-1}$
b: $f(\alpha) = 1-\alpha$, $A = 3.93 \times 10^{6}\ \mathrm{s}^{-1}$, $E = 110\ \mathrm{kJ\ mol}^{-1}$
Heating rate = 10 deg min^{-1}

There are, therefore, good reasons for rejecting single-experiment methods on fundamental grounds. In addition, it has been shown that the parameters usually obtained by such methods are dependent on the experimental conditions employed [11, 13, 14], making them of little practical value.

Description of the Ozawa–Flynn–Wall (OFW) method

The OFW method, proposed independently by Ozawa [3] and by Flynn and Wall [4], is sometimes known as the isoconversional method [5]. The major advantage of this method is that it does not require any assumptions concerning the form of the kinetic equation, other than that there is an Arrhenius-type temperature dependence, as in Eq. (1). If the heating rate is constant, then the integral form of this equation is Eq. (2).

$$\frac{d\alpha}{dt} = f(\alpha)A\exp(-E/RT) \tag{1}$$

$$\int_0^T \frac{d\alpha}{f(\alpha)} = F(\alpha) = \frac{A}{\beta}\int_0^T \exp(-E/RT)\,dT \tag{2}$$

$$F(\alpha) = \frac{AE}{R\beta} \exp\left(a - bE/RT\right) \tag{3}$$

The integral on the right hand side of Eq. (2) can be represented by the Doyle approximation [15], Eq. (3). In this equation, the parameters a and b are not strictly constant but depend slightly on the value of E/RT. However, b is almost always close to 1 and a value of 1.05 is a good initial guess. Using this value of b, a good first estimate of E can be determined, as described below, and a more appropriate value of b can then be obtained from tables [5]. This is normally sufficient, but iteration can be continued until the desired degree of self-consistency is achieved.

By taking logarithms of both sides of Eq. (3) and rearranging, Eq. (4) is obtained.

$$\mathrm{lo}\,\alpha = \frac{-bE}{RT} + \ln\left(\frac{AE}{RF(\alpha)}\right) + a \tag{4}$$

This equation can be used to obtain E if several experimental runs are performed at different heating rates. A specific degree of conversion is considered, and the temperature required for this degree of conversion is determined for each heating rate. (The fact that the extent of conversion is kept constant means that the form of $F(\alpha)$ is irrelevant, making it possible to obtain the activation energy even when the kinetic equation is not known.) If $\log \beta$ is plotted against $1/T$ the gradient is $-bE/R$, and so E can be determined *for the particular degree of conversion being considered.* Separate calculations can then be carried out to obtain E for other degrees of conversion. The OFW method is therefore potentially suited for use in systems where many reactions are occurring, such that the average activation energy varies with time. However, the mathematical basis of the method [3–5] assumes a single reaction. It is therefore necessary to establish whether this method is indeed valid for complex systems, especially in the light of the misleading results given by certain other methods.

Application of the OFW method to multiple independent reactions

For complex systems there is no *a priori* reason to suppose that an OFW plot will give a straight line. However, even if the plot is curved it should be possible to obtain a good estimate of the gradient near the centre of the temperature range studied. In fact, unpublished experiments in this laboratory have shown that the plots for the pyrolysis of coal or paper are very close to being straight lines, and that the slope of the tangent can be determined quite easily. In mathematical terms, the gradient obtained in the way is $(\partial[\ln \beta]/\partial[1/T])_\alpha$, i.e. the rate of change of $\ln \beta$ with respect to $1/T$ at constant conversion. Application of the OFW method will then give an apparent activation energy, E_{OFW}, according to Eq. (5).

$$E_{\mathrm{OFW}} = \frac{-R}{b}\left(\frac{\partial \ln \beta}{\partial (1/T)}\right)_{\alpha} = \frac{RT^2}{b\beta}\left(\frac{\partial \beta}{\partial T}\right)_{\alpha} \tag{5}$$

In order to establish the physical significance of E_{OFW}, it is necessary to obtain an expression for the partial differential on the right hand side of Eq. (5).

Unfortunately, the required partial differential, $(\partial\beta/\partial T)_{\alpha}$, cannot be obtained directly. However, because α is a function of β and T alone it is possible to use Eq. (7) to express this partial differential in terms of two more easily accessible partial differentials.

$$\left(\frac{\partial \beta}{\partial T}\right)_{\alpha} = -\left(\frac{\partial \alpha}{\partial T}\right)_{\beta}\left(\frac{\partial \beta}{\partial \alpha}\right)_{T} \tag{6}$$

$$= -\left(\frac{\partial \alpha}{\partial T}\right)_{\beta}\Big/\left(\frac{\partial \alpha}{\partial \beta}\right)_{T} \tag{7}$$

These can be obtained by differentiation of Eq. (8), which is simply a statement of the fact that the total extent of conversion, α, is the sum of the contributions from the individual reactions, $c_i\alpha_i$.

$$\alpha = \sum c_i\alpha_i \tag{8}$$

$$\left(\frac{\partial \alpha}{\partial \beta}\right)_{T} = \sum c_i\left(\frac{\partial \alpha_i}{\partial \beta}\right)_{T} \tag{9}$$

$$\left(\frac{\partial \alpha}{\partial \beta}\right)_{T} = \frac{-1}{R\beta^2}\sum c_iA_iE_if_i(\alpha_i)\exp\left(a - bE_i/RT\right) \tag{9a}$$

$$\left(\frac{\partial \alpha}{\partial T}\right)_{\beta} = \sum c_i\left(\frac{\partial \alpha_i}{\partial T}\right)_{\beta} \tag{10}$$

$$\left(\frac{\partial \alpha}{\partial T}\right)_{\beta} = \frac{b}{R^2T^2\beta}\sum c_iA_iE_i^2f_i(\alpha_i)\exp\left(a - bE_i/RT\right) \tag{10a}$$

Thus Eqs (9) and (10) are obtained, which give the two partial differentials in terms of the corresponding partial differentials for the individual reactions. The latter are readily obtained by differentiation of Eq. (3), so that Eqs (9) and (10) become Eqs (9a) and (10a).

Putting these expressions into Eq. (5) *via* Eq. (7) gives the apparent activation energy in terms of the kinetic parameters of the component reactions, Eq. (11).

$$E_{\mathrm{OFW}} = \frac{\Sigma[c_if_i(\alpha_i)A_i\exp\left(-bE_i/RT\right)E_i^2]}{\Sigma[c_if_i(\alpha_i)A_i\exp\left(-bE_i/RT\right)E_i]} \tag{11}$$

This equation can be simplified by noting that the expressions are similar to the rate equations for the individual reactions, Eq. (12),

$$v_i = c_i \frac{\mathrm{d}\alpha_i}{\mathrm{d}t} = c_i f_i(\alpha_i) A_i \exp(-E_i/RT) \tag{12}$$

and by introducing a new parameter, the 'instantaneous mean activation energy', E_{inst}, as defined by Eq. (13).

$$E_{\text{inst}} = \frac{\Sigma v_i E_i}{\Sigma v_i} \tag{13}$$

It should be noted that this is an average activation energy for the reactions occurring at a given instant, and not an average for the overall reaction, as used elsewhere [16]. By substituting Eqs (12) and (13) into Eq. (11), the relationship between E_{OFW} and $E^{\text{n}}_{\text{inst}}$ can be obtained, Eq. (14).

$$E_{\text{OFW}} = E_{\text{inst}} + \frac{\Sigma\{v_i \exp[-(b-1)\Delta E_i/RT](E_{\text{inst}} + \Delta E_i)\Delta E_i\}}{\Sigma\{v_i \exp[-(b-1)\Delta E_i/RT](E_{\text{inst}} + \Delta E_i)\}} \tag{14}$$

where

$$\Delta E_i = E_i - E_{\text{inst}} \tag{15}$$

The difference between the two 'activation energies' is the rather complicated expression on the right hand side of Eq. (14). This can be simplified by applying Eqs (16) to (18), and by neglecting terms in ΔE^3 in the numerator or ΔE^2 in the denominator.

$$\exp[-(b-1)\Delta E_i/RT] \approx 1 - \frac{(b-1)\Delta E_i}{RT} \tag{16}$$

$$\Sigma v_i \Delta E_i = 0 \tag{17}$$

$$\frac{\Sigma v_i \Delta E_i^2}{\Sigma v_i} = \mu_{2E} \tag{18}$$

Thus the relationship between E_{OFW} and E_{inst} reduces to Eq. (19).

$$E_{\text{OFW}} = E_{\text{inst}} - \frac{(b-1)E_{\text{inst}}/RT - 1}{E_{\text{inst}}} \mu_{2E} \tag{19}$$

Eq. (19) makes use of the instantaneous second moment of the component activation energies, μ_{2E}. This is a measure of the spread of activation energies of the reactions occurring at the specified degree of conversion. For a large number of discrete reactions this will be the same as the statistical variance. However, as defined by Eq. (18), the second moment also exists for small numbers of reactions, or for a continuum of reactions (but in this latter case the summations in Eq. (18) should be replaced by integrals).

As shown below, the final term in Eq. (19) is normally quite small and so E_{OFW} is a close approximation to E_{inst}. It should be noted that, in keeping with the aim of the OFW method, no assumptions have been made about the form of the rate equations of the individual reactions.

Application of the OFW method to multiple competitive reactions

For competitive reactions, the overall rate equation is given by Eq. (20). This equation cannot be integrated as it stands because the $f_i(\alpha)$ are unknown.

$$\frac{d\alpha}{dt} = \Sigma f_i(\alpha) A_i \exp(E_i/RT) \tag{20}$$

However, if it is assumed that each component reaction follows the same kinetic function, then, after application of the Doyle approximation, Eq. (20) can be integrated to give Eq. (21). This equation can be differentiated at constant α to give Eq. (22).

$$F(\alpha) = \frac{1}{\beta R} \Sigma A_i E_i^2 \exp(a - E_i/RT) \tag{21}$$

$$\left(\frac{\partial \beta}{\partial T}\right)_\alpha = \frac{b\beta}{RT^2} \frac{\Sigma[A_i E_i^2 \exp(a - E_i/RT)]}{\Sigma[A_i E_i \exp(a - E_i/RT)]} \tag{22}$$

This expression is identical to the one obtained for the case of multiple parallel reactions (e.g. by substitution of Eqs (9a) and (10a) into Eq. (7)).

Thus, in the specific case where each component obeys the same kinetic law the relationship between E_{OFW} and E_{inst} will be the same as has been derived for parallel reactions. Mathematical intractability prohibits the assessment of E_{OFW} for competing reactions obeying different kinetic laws.

Accuracy of the OFW method when applied to multiple reactions

Equation (19) shows that the difference between the observed activation energy, E_{OFW}, and the mean activation energy, E_{inst}, depends on the spread of activation energies, as given by σ_E. In practice this spread will be limited by the nature of the reactions occurring. Two cases will be considered here: firstly, a situation in which the pre-exponential factors of the component reactions are equal; and secondly, a situation in which a compensation effect occurs.

If the Arrhenius pre-exponential factors are constant, then variation in the activation energies will result in the component reactions occurring in different temperature regions. Thus the spread of activation energies at any given temperature is quite small. The results from a numerical example are given in Table

1. For this example, the value of the activation energies, although differing by only 14 kJ mol^{-1}, were chosen so as to maximise the instantaneous standard deviation (i.e. the worst possible case). It can be seen that E_{OFW} is always close to E_{inst} (0.1% error), and that the errors are predicted quite well by Eq. (19).

If the pre-exponential factors vary in such a way as to compensate for the change in the activation energy, then a much greater spread of activation energies can be found at a given temperature. However, choosing realistic ranges for the pre-exponential factor still results in E_{OFW} being close to E_{inst}, as shown in Tables 2 and 3 (0.6% error). In these examples, the values of A_i and E_i were chosen so as to give maximum overlap of the reactions. At these moderate error levels, excellent agreement was obtained with Eq. (19).

Table 1 Application of the OFW method to a pair of first-order independent reactions with equal pre-exponential factors
$A_1 = 1\times10^{13}$ s^{-1}; $E_1 = 193$ kJ mol^{-1}
$A_2 = 1\times10^{13}$ s^{-1}; $E_2 = 207$ kJ mol^{-1}
Heating rates: 0.316 deg min^{-1} and 3.16 deg min^{-1}

α	E_{inst}, kJ mol^{-1}	μ_{2E}, kJ mol^{-1}	E_{OFW}, kJ mol^{-1}	$E_{\mathrm{OFW}}-E_{\mathrm{inst}}$, kJ mol^{-1}	Calculated error^a, kJ mol^{-1}
0.1	193.986	3.579	193.922	−.064	−.063
0.2	193.293	4.051	194.214	−.079	−.080
0.3	194.765	4.664	194.666	−.098	−.105
0.4	195.627	5.464	195.495	−.132	−.145
0.5	197.591	6.572	197.395	−.195	−.208
0.6	202.649	6.468	202.440	−.209	−.197
0.7	206.697	1.992	206.692	−.005	−.018
0.8	206.996	0.211	207.006	.009	.000
0.9	207.000	0.004	207.000	.000	.000

^{a}: calculated according to Eq. 19.

Limitations of the method

The derivation of the OFW method is strictly independent of the property being observed, whether weight (TG), evolved/absorbed heat (DSC), or cumulative yield of gas (EGA, TPD). However, the last three methods normally give rates of reaction, from which cumulative yields must be obtained by summation/integration. This process may introduce significant errors, which would limit the application of the method to those situations where very accurate data is available.

A consequence of the requirement for a well-defined degree of conversion is that

Table 2 Application of the OFW method to two independent reactions with compensating Arrhenius parameters

$A_1 = 1 \times 10^{13}\ \mathrm{s}^{-1}$; $E_1 = 200$ kJ mol^{-1}
$A_2 = 4.5 \times 10^{14}\ \mathrm{s}^{-1}$; $E_2 = 220$ kJ mol^{-1}
Heating rates: 0.316 deg min^{-1} and 3.16 deg min^{-1}

α	E_{inst}, kJ mol^{-1}	μ_{2E}, kJ mol^{-1}	E_{OFW}, kJ mol^{-1}	$E_{\mathrm{OFW}} - E_{\mathrm{inst}}$, kJ mol^{-1}	Calculated error, kJ mol^{-1}
0.1	209.67	9.98	209.21	−0.46	−0.46
0.3	210.25	9.99	209.79	−0.46	−0.46
0.5	210.45	9.99	209.99	−0.46	−0.45
0.7	210.41	9.99	209.95	−0.46	−0.45
0.9	209.76	9.97	209.31	−0.45	−0.45

Table 3 Application of the OFW method to three independent reactions with compensating Arrhenius parameters

$A_1 = 2.22 \times 10^{12}\ \mathrm{s}^{-1}$; $E_1 = 180$ kJ mol^{-1}
$A_2 = 1 \times 10^{13}\ \mathrm{s}^{-1}$; $E_2 = 200$ kJ mol^{-1}
$A_3 = 4.5 \times 10^{14}\ \mathrm{s}^{-1}$; $E_3 = 220$ kJ mol^{-1}
Heating rates: 0.316 deg min^{-1} and 3.16 deg min^{-1}

α	E_{inst}, kJ mol^{-1}	μ_{2E}, kJ mol^{-1}	E_{OFW}, kJ mol^{-1}	$E_{\mathrm{OFW}} - E_{\mathrm{inst}}$, kJ mol^{-1}	Calculated error, kJ mol^{-1}
0.1	199.02	16.26	197.74	−.1.27	−.1.28
0.3	200.65	16.29	199.38	−.1.27	−.1.27
0.5	201.23	16.27	199.97	−.1.26	−.1.26
0.7	201.14	16.26	199.88	−.1.26	−.1.26
0.9	199.36	16.13	199.88	−.1.23	−.1.24

the initial and final states must be the same for each heating rate. For a set of truly independent reactions this condition will always be satisfied, but competitive reactions may cause problems, as described below for coal pyrolysis.

In the numerical examples given above it was assumed that the pre-exponential factors had values which were reasonable for non-catalytic chemical reactions. This meant that the activation energies were constrained to certain limits, if the reactions were to be truly overlapping. However, if the component reactions are of very different types, e.g. catalytic and non-catalytic, then this constraint is removed, and a much larger spread of activation energies is possible. In these circumstances Eq. (19) indicates that the OFW method could yield a value for the activation energy which is considerably less than the instantaneous mean. In such extreme cases the use of several different heating rates is still valuable for separating independent reactions [17], and for highlighting the presence of competitive reactions [17, 18].

Application of the OFW method to coal pyrolysis

Weight loss during coal pyrolysis has been successfully modelled using multiple independent reactions with a gaussian spread of activation energies [9, 14, 19, 20]. However, it has been noted that the assignment of a value to the overall mean activation energy can be ambiguous [14]. Application of the OFW method could provide a suitable way of fixing this parameter at a realistic value. The fact that the model can involve a broad spread of activation energies is in no way inconsistent with this suggestion, because at any given degree of conversion only a limited range of reactions are actually proceeding at a significant rate.

A potential problem associated with the application of multiple heating rate methods to coal pyrolysis is the presence of competition between pyrolysis and either gasification or combustion. This means that the pyrolysis must be carried out in an inert atmosphere and, in particular, it is necessary to rigorously exclude oxygen. In the presence of reactive gases, the weight loss at low heating rates can be greater than that for high heating rates, due to the increased time available for gasification. In such circumstances it would be impossible to define an 'extent of reaction' which was independent of heating rate.

The discussion here is primarily concerned with the overall modelling of coal pyrolysis. A more complete understanding of the pyrolysis process requires a study of individual volatile species. The pattern of evolution of coal volatiles strongly suggests that many different reactions contribute to the production of any given species [21, 22]. Use of the OFW method in such a situation is theoretically possible, but may be restricted by the nature of EGA data, as described above.

Conclusions

The new parameter 'instantaneous mean activation energy', E_{inst}, has been introduced for systems of overlapping reactions.

For independent reactions, a mathematical analysis of the Ozawa–Flynn–Wall method indicates that it is suitable for obtaining E_{inst} from thermogravimetry, subject to the limitations given below. The applicability of the method is not affected by the form of the individual kinetic equations. Numerical examples are given which illustrate these results for 2 or 3 independent overlapping reactions having a moderate spread of activation energies and pre-exponential factors.

The method has also been shown to be applicable to multiple competitive reactions in the specific case where the component reactions have the same kinetic form.

The method is predicted to fail if reactions of widely differing type (and hence having very different activation energies) are occurring simultaneously. Competitive reactions which have different products also render the method inapplicable.

* * *

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Table of symbols

a	Parameter used in the Doyle approximation (Eq. (3)).
A	Arrhenius pre-exponential factor.
b	Parameter used in the Doyle approximation (Eq. (3)).
c_i	Contribution of an individual reaction to the overall reaction.
E_{inst}	Instantaneous mean activation energy (Eq. (13)).
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.
$F(\alpha)$	Integral of $1/f(\alpha)$ (Eq. (2)).
i (subscript)	Denotes a component reaction.
R	Gas constant.
t	Time.
T	Temperature.
v	Reaction rate.
α	Degree of conversion.
β	Heating rate.
μ_{2E}	Instantaneous second moment of activation energies (Eq. (18)).

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Zusammenfassung — Es ist bekannt, daß die Anwendung einer ungeeigneten kinetischen Methode bei der thermischen Analyse komplexer Systeme zu falschen Ergebnissen führen kann. Um dieses Problem zu vermeiden, wird der neue Parameter „momentane mittlere Aktivierungsenergie“ eingeführt. Die Ozawa–Flynn–Wall-Methode wird als zur Bestimmung dieses Parameters geeignet angesehen. Es wird der Schluß gezogen, daß mit dieser Methode im allgemeinen gute Ergebnisse zu erhalten sein sollten, vorausgesetzt, daß die in komplexen Systemen verlaufenden verschiedenen Reaktionen vom gleichen Typ sind. Die Pyrolyse von Kohle wird als mögliche Anwendung dieser Methode angesehen.

Резюме — Применение несоответствующего кинетического метода к термическому анализу сложных систем может привести к ошибочным результатам. Для решения этой проблемы вводится новый параметр «мгновенная средняя энергия активации» и метод Озава–Флинна–Валла использован для получения этого параметра. Сделано заключение, что в общем, этим методом могут быть получены хорошие результаты, но при условии, что протекающие в сложной системе реакции являются одного и того же типа. Считается, что этот метод может быть применен для пиролиза угля.