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Note

NON-ISOTHERMAL KINETICS AND THERMOGRAVIMETRIC ANALYSIS OF COMPLEX REACTIONS. I. FORMAL AND APPROXIMATE SOLUTION OF THE KINETICS OF HOMOGENEOUS SYSTEMS

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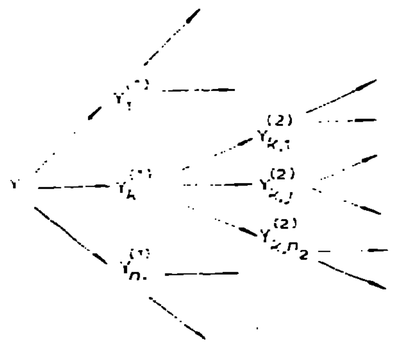
The dependence of the sample weight on temperature as recorded in the TG measurement results frequently form a quite complex system of competing and consecutive reactions, especially in the case of organic compounds and polymers. In spite of its demonstration by several authors [1—4], the substantial dependence of the TG curve on the overall reaction mechanism has been mostly ignored in practical TG analyses. If, however, the curve analysis is based on an oversimplified mathematical model, mere description parameters of questionable value rather than true activation energies and frequency factors are obtained [4].

It is well known that the major obstacle of a rigorous curve analysis in this case is the mathematical intractability of the complex non-isothermal kinetics. Therefore, the aim of this study is to find feasible approximations to the kinetics of the most common types of complex reactions (Part I) and to suggest an efficient procedure for the extraction of kinetic constants from the respective TG curves (Part II).

THE FORMAL SOLUTION OF THE NON-ISOTHERMAL KINETICS OF A GENERAL REACTION TREE

In this study, only a homogeneous reaction system without intervening effects of material and energy transport is considered. Furthermore, all possible cross-reactions of reaction intermediates are ignored in our model so that on the basic level there are only first-order reactions and the overall reaction scheme is a reaction tree rather than a reaction net, viz.



(I)

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Here, Y is the parent compound under TG analysis and, for the general reaction intermediate or product $Y^{(p)}_{..j,k,l}$, the upper index denotes its hierarchy level and the ordered set of lower indices denotes its ancestry.

Assuming (i) the separability of temperature and concentration functions (see, for example, refs 5 and 6), (ii) the applicability of the quasi-isothermal approximation [7—9], and (iii) the Arrhenius approximation for the elementary reactions, the chemical dynamics of the system is described by the set

$$
\begin{aligned}
\frac{\mathrm{d}[Y^{(p)}_{..j,k,l}]}{\mathrm{d}T} &= \frac{Z^{(p)}_{..j,k,l}}{q} \exp(-E^{(p)}_{..j,k,l}/RT)\,[Y^{(p-1)}_{..j,k}] \\
&\quad - \left\{ \sum_{i=1}^{n_{p+1}} \frac{Z^{(p+1)}_{..j,k,l,i}}{q} \exp(-E^{(p+1)}_{..j,k,l,i}/RT) \right\} [Y^{(p)}_{..j,k,l}]
\end{aligned}
\tag{1}
$$

with the formal solution

$$
\begin{aligned}
[Y^{(p)}_{..j,k,l}] &= \left\{ \prod_{i=1}^{p} Z^{(i)}_{..j,k} \right\} q^{-p} \left\{ \prod_{i=1}^{n_{p+1}} \eta\binom{p+1}{..j,\,k,\,l,\,i} \right\} \\
&\quad \times \int_0^T \chi\binom{p}{p+1} \int_0^T \chi\binom{p-1}{p} \int_0^T \cdots \int_0^T \chi\binom{1}{2}\, \mathrm{d}T^{(p-1)}
\end{aligned}
\tag{2}
$$

where q is the linear heating rate, $Z^{(i)}_{..j,k,l}$ is the frequency factor and $E^{(i)}_{..j,k,l}$ the activation energy of the corresponding reaction. The symbols χ and η have the meaning

$$
\chi\binom{r}{r+1} = \frac{\displaystyle\prod_{i=1}^{n_r} \eta\binom{r}{..l,\,m,\,i}}{\displaystyle\prod_{i=1}^{n_{r+1}} \eta\binom{r+1}{..m,\,i}} \exp(-E^{(r)}_{..l,m,n}/RT)
\tag{3}
$$

and

$$
\eta\binom{r}{..l,\,m,\,i} = \exp\left[-\frac{Z^{(r)}_{..l,m,i}}{q} \int_0^T \exp(-E^{(r)}_{..l,m,i}/RT)\,\mathrm{d}T \right]
\tag{4}
$$

In eqn. (3), the upper η belong to the parallel reactions on the rth level, the lower η to the family of parallel reactions on the $(r+1)$th level which stem from the rth level ancestor of the product $Y^{(p)}_{..j,k,l}$.

It is clear that the $(p-1)$-fold integral in eqn. (2) has no closed solution even for the simplest reaction trees. But given a sufficiently accurate approximation of it, the analysis of the reaction kinetics would be much less time-consuming than the tedious numerical integration of the equation set (1) (which has a tendency to get "stiff" in some cases and thus calls for special procedures). Examples of such approximations for the simplest cases are given below.

The approximate solution for the simple systems of competing and consecutive reactions

The simplest non-trivial sections of the reaction tree (I) are the systems of two competing (II) or two consecutive (III) reactions

$$\begin{tikzcd}[row sep=small] & Y_M \\ Y \arrow[ur] \arrow[dr] & \\ & Y_N \end{tikzcd} \qquad \text{(II)}$$

$$Y \rightarrow Y_M \rightarrow Y_N \qquad \text{(III)}$$

For brevity, let us introduce three additional symbols

$$\pi(\mathrm{M}) = \int_0^T \exp(-E_\mathrm{M}/RT)\,\mathrm{d}T \qquad (5)$$

$$\omega(\mathrm{M}, \mathrm{N}^a) = Z_\mathrm{M} \exp(-E_\mathrm{M}/RT)/[Z_\mathrm{M} \exp(-E_\mathrm{M}/RT) + aZ_\mathrm{N} \exp(-E_\mathrm{N}/RT)] \qquad (6)$$

$$\zeta(\mathrm{M}, \mathrm{N}^a; \mathrm{M}) = \int_0^T \eta(\mathrm{M})\, \eta^a(\mathrm{N}) \exp(-E_\mathrm{M}/RT)\,\mathrm{d}T \qquad (7)$$

where M, N stand for the sets of appropriate upper and lower indices and a has two values only, i.e. +1 for the system (II) and −1 for (III). Now, it holds for (II) that

$$[\mathrm{Y}] = [\mathrm{Y}]_0 \eta(\mathrm{M})\, \eta(\mathrm{N}) \qquad (8)$$

$$[\mathrm{Y}_\mathrm{M}] = \mathrm{Z}_\mathrm{M} q^{-1} [\mathrm{Y}]_0 \zeta(\mathrm{M}, \mathrm{N}; \mathrm{M}) \qquad (9)$$

and for (III)

$$[\mathrm{Y}] = [\mathrm{Y}]_0 \eta(\mathrm{M}) \qquad (10)$$

$$[\mathrm{Y}_\mathrm{M}] = Z_\mathrm{M} q^{-1} [\mathrm{Y}]_0 \eta(\mathrm{N})\, \zeta(\mathrm{M}, \mathrm{N}^{-1}; \mathrm{M}) \qquad (11)$$

The expressions for $[\mathrm{Y}_\mathrm{N}]$ are obvious. The explicit forms of eqns. (8)—(11) need the solution of the integrals $\pi(\mathrm{M})$ and $\zeta(\mathrm{M}, \mathrm{N}^a; \mathrm{M})$. It is well known than $\pi(\mathrm{M})$ cannot be solved in a closed form but numerous fairly good approximations are available. As for $\zeta(\mathrm{M}, \mathrm{N}^a; \mathrm{M})$, it clearly holds that

$$Z_\mathrm{M} \zeta(\mathrm{M}, \mathrm{N}^a; \mathrm{M}) + Z_\mathrm{N} \zeta(\mathrm{M}, \mathrm{N}^a; \mathrm{N}) = q[1 - \eta(\mathrm{M})\, \eta^a(\mathrm{N})] \qquad (12)$$

which indicates that this integral has no closed form even in terms of $\pi(\mathrm{M})$ and $\pi(\mathrm{N})$. Various series expansions converge too slowly or not at all. On the other hand, eqn. (12) gives a clue to an intuitively good approximation

$$\zeta(\mathrm{M}, \mathrm{N}^a; \mathrm{M}) \approx qZ_\mathrm{M}^{-1} [1 - \eta(\mathrm{M})\, \eta^a(\mathrm{N})]\, \omega(\mathrm{M}, \mathrm{N}^a) \qquad (13)$$

For $E_\mathrm{M} = E_\mathrm{N}$, eqn. (13) is the exact solution even for $Z_\mathrm{M} \neq Z_\mathrm{N}$. In the general case, the error of eqn. (13) increases with increasing T in absolute values (though not in the relative ones) but its first derivative converges to zero. The extensive comparison of the values of eqn. (13) with the results of the double precision Gaussian quadrature shows that the error of eqn. (13) does not exceed the order of 1 rel.% for practically interesting values of Z and E. The only serious failure of eqn. (13) is its relative disability to converge to a finite maximum as does the exact $\zeta(\mathrm{M}, \mathrm{N}; \mathrm{M})$. We found that eqn. (13) generally begins to behave badly if $\eta(\mathrm{M}) < 10^{-3}$. Therefore, the behaviour of eqn. (13) can be improved if the value of T_c is found from

$$\exp\left[-Z_{\mathrm{M}} q^{-1} \int_{T_0}^{T_c} \exp(-E_{\mathrm{M}}/RT)\, \mathrm{d}T\right] = 10^{-3}$$

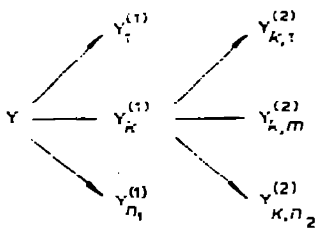
[which can be done, for example, by iteration using Gorbachev [10] or some other approximation for $\pi(\mathrm{M})$], and then the upper bound is set a priori to the integral

$$\zeta(\mathrm{M}, \mathrm{N}^a; \mathrm{M})_{T > T_c} = \zeta(\mathrm{M}, \mathrm{N}^a; \mathrm{M})_{T_c} \tag{14}$$

With the upper bound (14), eqn. (13) can be considered to be a fairly good approximation for use in TG curve analysis.

EXTENSION TO MORE COMPLICATED CASES

Various more complicated sections can be cut out from the general reaction tree (I). Let us consider the model (IV).



(IV)

From eqn. (2), the concentration of the knot product $\mathrm{Y}_k^{(1)}$ is given by

$$[\mathrm{Y}_k^{(1)}] = [\mathrm{Y}]_0 \frac{Z_k^{(1)}}{q} \prod_{i=1}^{n_2} \eta\binom{2}{k,\, i} \int_0^T \frac{\prod\limits_{i=1}^{n_1} \eta\binom{1}{i}}{\prod\limits_{j=1}^{n_2} \eta\binom{2}{k,\, j}} \exp[-E_k^{(1)}/RT]\, \mathrm{d}T \tag{15}$$

The integral in eqn. (15) denoted by $\zeta(n_1, n_2^{-1}; k)$ may, by analogy with eqn. (13), be approximated by

$$\zeta(n_1, n_2^{-1}; k) \approx \frac{q}{Z_k^{(1)}} \left[1 - \frac{\prod\limits_{i=1}^{n_1} \eta\binom{1}{i}}{\prod\limits_{j=1}^{n_2} \eta\binom{2}{k,\, j}}\right]$$

$$\times \frac{Z_k^{(1)} \exp[-E_k^{(1)}/RT]}{\sum\limits_{i=1}^{n_1} Z_i^{(1)} \exp[-E_i^{(1)}/RT] - \sum\limits_{j=1}^{n_2} Z_{k,j}^{(2)} \exp[-E_{k,j}^{(2)}/RT]} \tag{16}$$

With the upper bound analogous to eqn. (14), eqn. (19) is a somewhat poorer but still sufficient approximation. If some of the products $Y^{(2)}$ have to be expressed individually, some approximation to the double integral is needed. A possible way to it will be considered in connection with the next system.

In practical TG, however, a sequence of three different reactions, i.e. system (V), is of a much greater interest.

$$Y \rightarrow Y_1 \rightarrow Y_2 \rightarrow Y_3 \tag{V}$$

Here, for brevity, we drop the obvious upper indices for hierarchy levels. As indicated by eqn. (2), the concentrations of Y_1 and Y_2 are given by eqns. (17) and (18), respectively.

$$[Y_1] = Z_1 q^{-1} [Y]_0 \, \eta(2) \, \zeta(1, 2^{-1}; 1) \tag{17}$$

$$[Y_2] = Z_1 Z_2 q^{-2} [Y]_0 \, \eta(3) \int_0^T \frac{\eta(2)}{\eta(3)} \exp(-E_2/RT) \, \zeta(1, 2^{-1}; 1) \, \mathrm{d}T \tag{18}$$

The integral $\zeta(1, 2^{-1}; 1)$ in eqn. (17) can be calculated by the approximation (13). For the double integral in eqn. (18), denoted further by ζ, let us suppose than eqn. (13) is the exact solution of $\zeta(1, 2^{-1}; 1)$ and may be integrated accordingly. Then, by the repeated use of eqn. (13), the following approximation is found.

$$\xi \approx \frac{q^2}{Z_1 Z_2} \left\{ \left[1 - \frac{\eta(2)}{\eta(3)}\right] \omega(1, 2^{-1}) \, \omega(2, 3^{-1}) - \left[1 - \frac{\eta(1)}{\eta(2)}\right] [1 - \omega(1, 2^{-1})] \, \omega(1, 3^{-1}) \right\} \tag{19}$$

The repeated use of the same approximation, as used in the derivation of eqn. (19), may be somewhat risky. Nevertheless, with the use of the upper bounds corresponding to $\eta(2)$, $\eta(1) = 10^{-6}$ for the first and the second term, respectively, the approximation (19) gives, according to the first results, an error of several rel. %. Rough TG analyses, at least, are thus possible by means of the model (V).

CONCLUSIONS

The systems (II)—(V) and their obvious combinations cover all cases of complex "tree" reactions practically analysable by TGA. With the equations given in this paper, especially with the approximations (13) and (19), the quantitative TG curve analysis can be performed on a computer yielding sufficiently precise true activation energies and frequency factors. One has to bear in mind, however, the limitations of the statistical reliability of any curve analysis in the more complicated cases caused by the uncertainties of the experimental points and by their finite number. Such cases have thus to be considered critically.

The formal solution of the complex kinetics given here applies to the specified homogeneous systems only. Reactions in heterogeneous systems or, generally, of non-linear kinetics, give rise to additional mathematical difficulties even in the cases of moderate complexity and are under investigation.

ADDENDUM

After this study had been finished, the author obtained access to the book by Koch [11] containing an approximation of some likeness to eqn. (13), namely, in our notation

$$\zeta(\mathrm{M}, \mathrm{N}^{-1}; \mathrm{M}) \approx qZ_{\mathrm{M}}^{-1}[1 - \eta(\mathrm{M})/\eta(\mathrm{N})] \qquad (20)$$

As indicated in [11], eqn. (20) gives good results only for $Z_{\mathrm{N}}\pi(\mathrm{N}) << Z_{\mathrm{M}}\,\pi(\mathrm{M})$, i.e. for the very early stages providing that $E_{\mathrm{N}} >> E_{\mathrm{M}}$. If, however, $(E_{\mathrm{N}} - E_{\mathrm{M}}) \leqslant 20$ kJ mole^{-1}, the error of eqn. (20) is of the order of at least 10 rel. %, even for the early stages and for $Z_{\mathrm{N}} = Z_{\mathrm{M}}$.

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