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Note

# ON THE TEMPERATURE INTEGRAL IN NON-ISOTHERMAL KINETICS WITH LINEAR HEATING RATE. PART II

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Most methods of working non-isothermal kinetic data are based on the integral form of the rate equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(1-\alpha)} = \frac{A}{b} \exp(-E/RT)\, \mathrm{d}T \tag{1}$$

where the symbols have their usual meanings.

Let us denote the left- and right-hand sides of the integral equation as follows:

$$F(1-\alpha) = \int \frac{\mathrm{d}\alpha}{\mathrm{f}(1-\alpha)} \tag{2}$$

$$I(T) = \int \exp(-E/RT)\, \mathrm{d}T \tag{3}$$

Equation (3) defines the so-called "temperature integral" and a lot of work has been performed to obtain a better approximation of it. A previous paper [1] deals with a method to solve the integral, and the present paper aims to develop some more possibilities of the method.

Let us suppose, according the quoted paper [1]:

$$I(T) = q(T) \exp(-E/RT) \tag{4}$$

$q(T)$ being an unknown $T$ function which has to satisfy the following differential equation:

$$\frac{\mathrm{d}q}{\mathrm{d}T} + \frac{E}{RT^2} q = 1 \tag{4a}$$

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## THE FUNCTION $q(T)$

(a) We have proposed [1] the following form of $q(T)$:

$$q(T) = hT^{i} \qquad i \in R \tag{5}$$

and it was found that:

$$I^{(i)}_{(T)} = \frac{RT^2}{E + iRT} \exp(-E/RT) \tag{6}$$

The condition of having an exact solution for the temperature integral leads to the following equation for $i$:

$$i^2 - (1 - E/RT)i - 2E/RT = 0 \tag{7}$$

which has two roots:

$$i_{1,2} = \frac{1 - E/RT \pm \sqrt{\left[(1 - E/RT)^2 + 8E/RT\right]}}{2} \tag{7a}$$

The quoted paper discussed only the best positive $i$-integer value approximation, and proved it for $i = 2$, i.e. the Doyle–Gorbachev solution [2]:

$$I^{(2)} = \frac{RT^2}{E + 2RT} \exp(-E/RT) \tag{8}$$

Let us now write:

$$i_{1,2} = \frac{1 - E/RT \pm (1 - E/RT + 2l)}{2}$$

where $l$ is an adjusting parameter. For $i = i_1 = -l$ it turns out that:

$$I^{(i_1)} = \frac{RT^2}{E - lRT} \exp(-E/RT) \tag{8a}$$

which is basically identical to eqn. (8). For $i = i_2 = 1 + l - E/RT$ we obtain:

$$I^{(i_2)} = \frac{T}{1 + l} \exp(-E/RT) \tag{8b}$$

Equation (8b), together with eqns. (1) and (2), allows us to write:

$$F(1 - \alpha) = \frac{A}{b} \frac{T}{1 + l} \exp(-E/RT)$$

and taking the logarithms and rearranging the terms one obtains:

$$\ln \frac{F}{T} = -\frac{E}{RT} + \ln \frac{A}{b} - \ln(1 + l) \tag{9}$$

(b) Another form which we suggest to be used for $q(T)$ is the following:

$$q(T) = c \exp(jT) \tag{10}$$

Equation (4a) becomes:

$$cj \exp(jT) + \frac{E}{RT^2} c \exp(jT) = 1$$

which gives:

$$c = \frac{1}{j + E/RT^2} \exp(-jT)$$

The temperature integral has, therefore, the following solutions:

$$I^{(j)} = \frac{1}{j + E/RT^2} \exp(-E/RT) \tag{11}$$

The condition to obtain an exact solution for the integral leads to:

$$j^2 + \frac{E}{RT^2} j + \frac{2E}{RT^3} = 0$$

with two roots:

$$j_{1,2} = \frac{-E/RT^2 \pm \sqrt{\left[(E/RT^2)^2 - 8E/RT^3\right]}}{2} = \frac{-E/RT^2 \pm (E/RT^2 - 2m)}{2}$$

$$= -m \text{ or } m - E/RT^2 \tag{12}$$

where $m$ is an adjusting parameter. The corresponding forms of the temperature integral are:

$$\left.\begin{aligned} I^{j_1} &= \frac{RT^2}{E - mRT^2} \exp(-E/RT) \\ I^{j_2} &= \frac{1}{m} \exp(-E/RT) \end{aligned}\right. \tag{13}$$

Subsequently, two other integral equations will be obtained:

$$\left.\begin{aligned} \ln \frac{F}{T^2} &= -\frac{E}{RT} + \ln \frac{A}{b} + \ln \frac{R}{E - mRT^2} \\ \ln F &= -\frac{E}{RT} + \ln \frac{A}{b} - \ln m \end{aligned}\right. \tag{13a}$$

Summing up, the approach proposed leads to three different approximations of the temperature integral and subsequently to three integral equations, viz.:

$$\ln F = -\frac{E}{RT} + \ln A - \ln b - \ln m \tag{A}$$

$$\ln F - \ln T = -\frac{E}{RT} + \ln A - \ln b - \ln(1 + l) \tag{B}$$

$$\ln F - 2 \ln T = -\frac{E}{RT} + \ln A - \ln b + \begin{cases} \ln \dfrac{R}{E - lRT} \\ \ln \dfrac{R}{E - mRT^2} \end{cases} \tag{C}$$

The first and the third equations are mathematically identical to those of Flynn–Wall [3], Ozawa [4] and Doyle–Gorbachev [2] and Coats–Redfern [5] and all three are particular forms of a general equation which can be written as follows:

$$\ln F - r \ln T = -\frac{E}{RT} + \ln A - \ln b + L \tag{14}$$

where $r = 0$, 1 or 2, and $L$ is an adjusting parameter. Higher values of $r$ (or even rational values in the range 0–2) would probably be obtained within the frame of other approaches.

It is not possible to establish a priori which of the forms of eqn. (14) allows the most accurate value of the activation energy to be obtained. However, it seems that an increased $r$ value will make the left-hand side of eqn. (14) less sensitive to the variation of $\alpha$.

## APPLICATION OF EQN. (14)

Equation (14), for $r = 0$, 1 and 2 has been applied to evaluate the non-isothermal kinetic parameters of decomposition of calcium oxalate using the data from ref. 6, obtained for three different heating rates, i.e. $b = 2.3$, 7.4 and 14.8 K min$^{-1}$.

The form of the conversion integral has been chosen as

$F(1-\alpha) = -\ln(1-\alpha)$

but the right choice of the function can be proved by the slope value of $-1$ when $\ln F(1-\alpha)$ is plotted vs. $\ln b$, at constant temperature for eqn. (14).

The plot of the left-hand side of each of the three equations vs. $1/T$ should give the activation energy. The results are given in Table 1. Equation (A) also offers this value from the slope of the plot $\ln b$ vs. $1/T$, at constant conversion. The results obtained for $\alpha$ within the 0.1–0.9 range are given in Table 2.

From Table 1 the following hierarchies are obtained:

For the same heating rate: $E^{\mathrm{A}} > E^{\mathrm{B}} > E^{\mathrm{C}}$

For the same equation: $E_{b1} > E_{b2} > E_{b3}$

TABLE 1

Activation energy and correlation coefficients for the plot ($\ln F - r \ln T$) vs. $1/T$ with $r = 0$, 1 and 2

| $B$ (K min$^{-1}$) | $E$ (kcal mol$^{-1}$) | | | Correlation coefficient | | |
|---|---|---|---|---|---|---|
| | $r = 0$ (A) | $r = 1$ (B) | $r = 2$ (C) | $r = 0$ (A) | $r = 1$ (B) | $r = 2$ (C) |
| 2.3 | 23.0 | 22.1 | 21.2 | 0.99676 | 0.99655 | 0.99631 |
| 7.4 | 22.3 | 21.4 | 20.5 | 0.99642 | 0.99618 | 0.99589 |
| 14.8 | 21.5 | 20.6 | 19.6 | 0.99486 | 0.99446 | 0.99400 |

TABLE 2

Activation energy and correlation coefficients for the plot (ln $b$) vs. $1/T$

| $\alpha$ | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|---|---|---|---|---|---|---|---|---|---|
| $E$ (kcal mol$^{-1}$) | 26.81 | 26.33 | 25.88 | 24.75 | 24.50 | 24.03 | 24.76 | 24.78 | 24.51 |
| Corr. coef. | 0.978 | 0.981 | 0.954 | 0.963 | 0.986 | 0.987 | 0.989 | 0.988 | 0.983 |

TABLE 3

Pre-exponential factor computed from eqn. (14) for $L = 0$

| $b$ (K min$^{-1}$) | $A$ (s$^{-1}$) | | |
|---|---|---|---|
| | $r = 0$ (A) | $r = 1$ (B) | $r = 2$ (C) |
| 2.3 | $1.4 \times 10^{11}$ | $1.1 \times 10^{10}$ | $9.0 \times 10^{10}$ |
| 7.4 | $6.3 \times 10^{10}$ | $4.9 \times 10^{10}$ | $3.8 \times 10^{10}$ |
| 14.8 | $3.9 \times 10^{10}$ | $3.0 \times 10^{10}$ | $2.3 \times 10^{10}$ |

Comparing the value of activation energy given by ref. 6 it appears that $E_{b1}^{A}$ is the best result and $E_{b3}^{C}$ the worst. The correlation coefficients seem to indicate the same tendency, their values decreasing from $E_{b1}^{A}$ to $E_{b3}^{C}$, even if only at the third and fourth figures. The results seem to support our suggestion of the role of $r$ value, its increase leading to a decrease of the energy values. The influence of increasing heating rate has already been discussed in the literature [7] and the results of Table 1 agree with ref. 7. The values obtained in Table 2 are higher than those of Table 1, and the correlation coefficients are lower than the others. An explanation of these differences can be suggested by the different number of data for computation which is used in the two methods. Another possible reason is the differences which lie in the method themselves, Table 1 using the $F$ function and Table 2 using the $b$ function. However, the results of both tables are close enough.

Another fact to be pointed out is the small influence of $L$ on the intercepts which, at least for this reaction, seems to be negligible. The values of pre-exponential factor computed for $L = 0$ are given in Table 3. All nine values of the pre-exponential factor are close enough to the literature values [7].

## CONCLUSION

A general integral equation to be used in non-isothermal kinetics was derived. Particular forms of this equation, for $r = 0$, 1 and 2 (eqn. A, B and C) were used in order to compute the kinetic parameters of the calcium oxalate decomposition reaction and the results, given in the Tables 1, 2 and 3 are in good agreement with literature values.

A small heating rate and use of the $r = 0$ equation seem to be the best conditions for good agreement with reality.

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