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SOME VARIANTS OF THE FREEMAN–CARROLL METHOD

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Two difference-differential methods for the evaluation of kinetic parameters from non-isothermal data are analysed.

In order to determine kinetic parameters from non-isothermal data, the difference-differential method proposed by Freeman and Carroll [1] is widely used [2, 3]. The main relationship on which the Freeman – Carroll method is based as follows:

$$\Delta \log \frac{\mathrm{d}\alpha}{\mathrm{d}t} = n \Delta \log (1-\alpha) - \frac{E}{2.303\,R} \Delta \left(\frac{1}{T}\right) \tag{1}$$

where

Δ = difference operator,
α = conversion degree,
t = time,
n = reaction order,
E = activation energy,
R = gas constant = 1.987 cal mole^{-1} K^{-1},
T = temperature in K.

This can be applied on one of the following particular forms:

$$\frac{\Delta \log \frac{\mathrm{d}\alpha}{\mathrm{d}t}}{\Delta \log (1-\alpha)} = n - \frac{E}{2.303\,R} \frac{\Delta \left(\frac{1}{T}\right)}{\Delta \log (1-\alpha)} \tag{2}$$

$$\frac{\Delta \log \frac{\mathrm{d}\alpha}{\mathrm{d}t}}{\Delta \left(\frac{1}{T}\right)} = n \frac{\Delta \log (1-\alpha)}{\Delta \left(\frac{1}{T}\right)} - \frac{E}{2.303\,R} \tag{3}$$

$$\frac{\Delta \left(\frac{1}{T}\right)}{\Delta \log \frac{\mathrm{d}\alpha}{\mathrm{d}t}} = \frac{2.303\,Rn}{E} \frac{\Delta \log (1-\alpha)}{\Delta \log \frac{\mathrm{d}\alpha}{\mathrm{d}t}} - \frac{2.303\,R}{E} \tag{4}$$

This allows to obtain the activation energy E and the reaction order n, from the slope and the intercept of a straight line.

The present work aims at establishing some of the more simple ways of using Eq. (1) to get the kinetic parameter values, involving less calculation. To accomplish this, we shall keep constant one of the three differences in Eq. (1).

1. By keeping the term $\Delta \log \frac{\mathrm{d}\alpha}{\mathrm{d}t}$ constant, i.e.

$$\Delta \log \frac{\mathrm{d}\alpha}{\mathrm{d}t} = \log K \tag{5}$$

we get:

$$\Delta \log (1-\alpha) = \frac{E}{4.575\, n} \Delta \left(\frac{1}{T}\right) + \frac{\log K}{n} \tag{6}$$

By plotting $\Delta \log (1-\alpha)$ against $\Delta \left(\frac{1}{T}\right)$, a straight line is obtained whose slope and intercept allow calculation of both the activation energy E and the reaction order n.

The use of Eq. (6) does not require difference ratios, so that the accuracy of the results is increased.

Relationship (5) can be written in the form:

$$\frac{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{m+1}}{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{m}} = K \tag{7}$$

which shows the necessity of taking the differences Δ only between pairs of points ($m+1$ and m), chosen in such a way as to fulfil condition (7) .

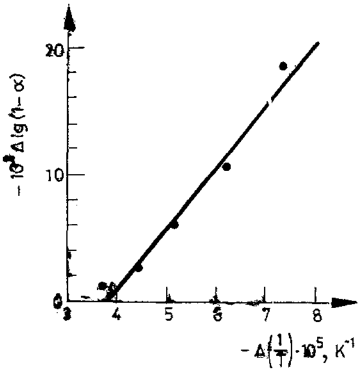

Fig. 1. Graph of $-10^2 \Delta \log (1-\alpha)$ values, *vs.* $-\Delta\left(\frac{1}{T}\right) 10^5 (\mathrm{K})^{-1}$ values for the dehydration of $CaC_2O_4 \cdot H_2O$

To check its validity, formula (6) was applied to determine the kinetic parameters for calcium oxalate monohydrate dehydration as a test reaction. The value chosen for the constant K was 1.5. The results have been plotted in Fig. 1. By treating the experimental results in the above described way, one finds: $E = 21.8$ kcal mole^{-1} and $n = 1.2$, which are in good agreement with the data reported in the literature [1, 4, 5].

For $K = 1$, Eq. (6) becomes

$$\Delta \log (1-\alpha) = \frac{E}{2.303\,R} \Delta \left(\frac{1}{T}\right) \tag{8}$$

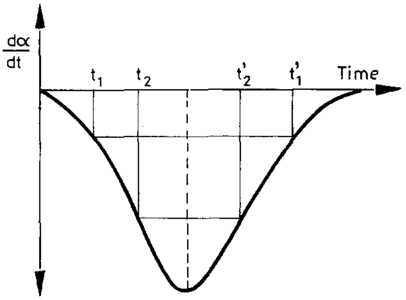

Fig. 2. Symmetrical points with respect to the maximum rate values on the rate (DTG) curve

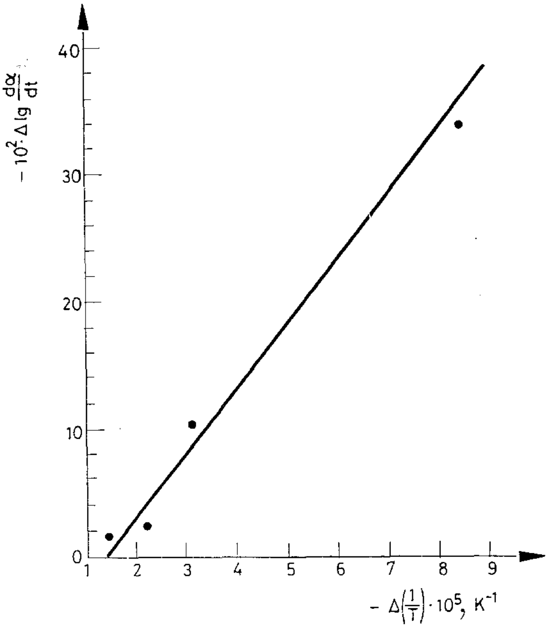

Fig. 3. Graph of $-10^2 \Delta \log \frac{d\alpha}{dt}$ values, *vs.* $-\Delta\left(\frac{1}{T}\right) 10^5$ (K)$^{-1}$ values for the dehydration of $CaC_2O_4 \cdot H_2O$

which allows very easy calculation of the activation energy. To fulfil the condition $K = 1$, one should take the differences between points located symmetrically with respect to the maximum rate value points on the curve of reaction rate *vs.* temperature or time (Fig. 2).

2. One can keep constant the term $\Delta \log(1-\alpha)$ in Eq. (1), i.e.

$$\Delta \log(1-\alpha) = \log K' \tag{9}$$

which may be written in the equivalent form:

$$\frac{(1-\alpha)_{m'+1}}{(1-\alpha)_{m'}} = K' \tag{10}$$

This shows how to choose the pair of points $(m'+1,\ m')$ between which the differences Δ should be taken.

From Eq. (1), taking into account condition (9), we obtain:

$$\Delta \log \frac{d\alpha}{dt} = n \log K' - \frac{E}{2.303\,R}\,\Delta\left(\frac{1}{T}\right) \tag{11}$$

By plotting $\Delta \log \frac{d\alpha}{dt}$ against $\Delta\left(\frac{1}{T}\right)$, one gets a straight line whose slope and intercept allow calculation of the activation energy and reaction order. Such a straight line for $K' = 0.8$ and the same test reaction, the dehydration of calcium oxalate monohydrate, is shown in Fig. 3.

The values obtained for the activation energy and the reaction order are $E = 23$ kcal mole^{-1} and $n = 1.1$, also in good agreement with those reported previously [1, 4, 5].

3. Finally, by keeping constant the term $\Delta\left(\frac{1}{T}\right)$ in Eq. (1), one gets another variant of the Freeman–Carroll method, which was proposed by Anderson and Freeman [6].

Once the activation energy and the reaction order are known, the preexponential factor can be evaluated from the general rate equation for non-isothermal conditions in the logarithmic form:

$$\log \frac{d\alpha}{dt} = \log \frac{Z}{a} + n \log(1-\alpha) - \frac{E}{RT}$$

where Z is the preexponential factor and a is the heating rate.

Conclusions

The two difference-differential methods, proposed as variants of the Freeman–Carroll method for the evaluation of kinetic parameters from non-isothermal data, are advantageous due to their simplicity and the reduction in the calculation work.

References

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RÉSUMÉ — L'article présente deux méthodes pour l'évaluation des paramètres cinétiques à partir des données non-isothermes, par différence de différentielles.

ZUSAMMENFASSUNG — Es werden zwei Differenz-Differentialmethoden zur Bewertung kinetischer Parameter aus nicht-isothermen Daten analysiert.

Резюме — В статье проанализированы различные дифференциальные методы для выделения кинетических параметров из неизотермических данных.