*Thermochimica Acta*, 225 (1993) 143–151
Elsevier Science Publishers B.V., Amsterdam

# Determination of chemical kinetics by DSC measurements.
## Part 1. Theoretical foundations

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(Received 31 March 1992; accepted 29 January 1993)

### Abstract

A new evaluation method for determining the kinetic parameters of a chemical reaction from DSC measurements is presented. This method evaluates a series of thermograms at different heating rates. The activation energy, the frequency factor and a general description of the concentration dependence of the reaction rate are obtained. Theorical DSC curves are also evaluated and the results obtained are compared with the prescribed parameters.

LIST OF SYMBOLS

| | |
|---|---|
| $c_{A0}/\mathrm{mol\,l^{-1}}$ | initial concentration of the reference component |
| $Da_\infty$ | Damköhler number defined in eqn. (16) |
| $Da(T)$ | temperature-dependent Damköhler number defined in eqn. (17) |
| $E\ /\mathrm{J\,mol^{-1}}$ | activation energy |
| $F(X)$ | function defined in eqn. (10) |
| $G(X)$ | function defined in eqn. (13) |
| $I(X)$ | function defined in eqn. (15) |
| $m/\mathrm{g}$ | initial sample weight |
| $\dot{Q}/\mathrm{W}$ | heat flow |
| $Q_{\mathrm{tot}}/\mathrm{J}$ | total evolved heat of reaction |
| $r/\mathrm{mol^{-1}\,s^{-1}}$ | reaction rate |
| $r_{0\infty}/\mathrm{mol\,l^{-1}\,s^{-1}}$ | initial reaction rate extrapolated to infinite temperature |
| $R/\mathrm{J\,mol^{-1}\,K^{-1}}$ | gas constant |
| $t/\mathrm{s}$ | time |
| $T/\mathrm{K}$ | temperature |
| $X$ | conversion |

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*Greek letters*

| | |
|---|---|
| $\beta/\mathrm{K\,s^{-1}}$ | heating rate |
| $\Delta h/\mathrm{J\,g^{-1}}$ | reaction enthalpy per gram |
| $\overline{\Delta h}/\mathrm{J\,g^{-1}}$ | mean reaction enthalpy per gram |
| $\Phi(X)$ | dimensionless description of the concentration dependence of the reaction rate |
| $\tau^0/\mathrm{s}$ | time unit (1 s) |
| $\nu_A$ | stoichiometric coefficient of the key component |

## 1. INTRODUCTION

The use of thermokinetic data to evaluate kinetic parameters of solid-state or liquid-state reactions has been previously investigated by several authors [1–5]. Well known evaluation methods have been developed by Borchardt and Daniels [1], Freeman and Carroll [2] and Coats and Redfern [3]. These methods calculate the activation energy, frequency factors and reaction order from a single thermogram.

As shown by Hentschel [6], there are several problems associated with the determination of reaction parameters from a single thermokinetic thermogram. From evaluations of theoretical thermograms, he confirmed that these evaluation methods are not suitable for determining real measurement reaction parameters, when one takes into account realistic errors. Another disadvantage of these evaluation methods is that, in general, real reaction cannot be adequately described by only one reaction order.

Based on these disadvantages a method is presented here which evaluates a series of thermograms at different heating rates but with the same initial composition. Furthermore a general description of the concentration dependence of the reaction rate, which may contain more than one parameter, is used.

## 2. THEORY

### 2.1. *Evaluation of an ideal DSC measurement*

The following assumptions form the basis of the evaluation.

1. There is only one exothermic, irreversible reaction. Other thermic effects do not exist.

2. The sample is heated at a constant heating rate of $\beta = \mathrm{d}T/\mathrm{d}t$.

3. The reaction rate equation can be separated into a temperature-dependent contribution, due to the Arrhenius equation, and into a concentration-dependent contribution. The type of concentration dependence is not specified but will be determined by the measurements.

For a general description, the conversion $X$ is used instead of the concentration. The heat developed by the reaction can be described by

$$\dot{Q}(t) = Q_{\mathrm{tot}} \frac{\mathrm{d}X}{\mathrm{d}t} \tag{1}$$

$Q_{\mathrm{tot}}$ is the total heat evolved by the reaction which can be determined by integration of $\dot{Q}(t)$. The heat of reaction per gram $\Delta h$ can be calculated from $Q_{\mathrm{tot}}$ and the initial amount of sample $m$

$$\Delta h = \frac{Q_{\mathrm{tot}}}{m} \tag{2}$$

The conversion and its derivation can be calculated from the measured data $\dot{Q}(t)$ by eqn. (1). From this derivation, the reaction rate $r$ for a closed system (batch-reactor) can be obtained by

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{(-\nu_{\mathrm{A}})r}{c_{\mathrm{A}_0}} \tag{3}$$

where $\nu_{\mathrm{A}}$ is the stoichiometric coefficient and $c_{\mathrm{A}_0}$ is the initial concentration of the key component A. If there is a two-component reaction mixture, the key component A has to be selected such that $X = 1$ at full conversion.

Using assumption no. 3, the reaction rate can be expressed as

$$r = r_{0\infty}\, \mathrm{e}^{-E/RT}\, \Phi(X) \tag{4}$$

In this equation, $r_{0\infty}$ is the initial reaction rate extrapolated to infinite temperature. $\Phi(X)$ is the dimensionless description of the concentration dependence of the reaction rate using the variable conversion $X$; when $X = 0$, $\Phi(0) = 1$; and when $X = 1$, $\Phi(1) = 0$. The aim of a series of measurements is to determine $(-\Delta h)$, $E/R$, $r_{0\infty}$ and the function $\Phi(X)$.

### 2.2. *Determination of the activation energy*

The determination of the activation energy is based on empirical results, which were obtained from a large number of simulated $\dot{Q}(t)$ curves using the above equations [4]. It was discovered that for a given set of data and a given type of function $\Phi(X)$, the conversion $X_{\mathrm{m}}$ at the maximum of heat production was practically independent of the heating rate $\beta$. Therefore, the corresponding temperature $T_{\mathrm{m}}$ at the maximum heat flow $\dot{Q}_{\mathrm{m}}(t)$ varies at different heating rates as a function of the activation energy. Thus the activation energy obtained from an Arrhenius diagram of $\ln(\dot{Q}_{\mathrm{m}}/Q_{\mathrm{tot}})$ vs. $1/T_{\mathrm{m}}$ corresponds to the equation

$$\ln \frac{\dot{Q}_{\mathrm{m}} \tau^{\circ}}{Q_{\mathrm{tot}}} = -\frac{E}{RT_{\mathrm{m}}} + \ln \frac{(-\nu_{\mathrm{A}}) r_{0\infty} \Phi(X_{\mathrm{m}}) \tau^{\circ}}{c_{\mathrm{A}_0}} \tag{5}$$

The time unit $\tau^0 = 1$ s was introduced to obtain dimensionless expressions within the logarithm. The determination of the activation energy with a similar diagram was first described by Kissinger [5].

The method presented here, which uses a full series of measurements at different heating rates, will lead to reliable values of $E$.

### 2.3. *Principles of the kinetics determination*

From a theoretical point of view, it should be possible to determine $\Phi(X)$, with the exception of the constant factor, from

$$\Phi(X) = \frac{\dot{Q}}{Q_{\text{tot}}} e^{E/RT} \frac{c_{A_0}}{(-\nu_A) r_{0\infty}} \tag{6}$$

because the activation energy has already been determined. In principle, the constant factor can be determined by extrapolation to the zero conversion where $\Phi(0) = 1$.

In practical cases, no meaningful data are obtained from this method. This is due to the dominant influence of the exponential term on this calculation method. A sufficiently accurate determination can only be obtained from the reaction rate law in an integrated manner.

From the mass balance eqn. (3), using eqn. (4) and a constant heating rate $\beta = dT/dt$, one obtains

$$\frac{dX}{dT} = \frac{(-\nu_A) r_{0\infty}}{c_{A_0} \beta} e^{-E/RT} \Phi(X) \tag{7}$$

By integration of the temperature-dependent contribution, one gets an exponential integral. If $E/RT > 10$, this exponential integral can be approximated by analytical function with sufficient accuracy [7]. The result is

$$\int_0^X \frac{dX}{\Phi(X)} = \frac{(-\nu_A) r_{0\infty} T}{c_{A_0} \beta} \frac{e^{-E/RT}}{(E/RT) + 2} \tag{8}$$

In this solution the exponential term can be substituted by eqn. (6)

$$\Phi(X) \int_0^X \frac{dX}{\Phi(X)} = \frac{\dot{Q}}{Q_{\text{tot}}} \frac{T}{\beta[(E/RT) + 2]} \tag{9}$$

In contrast to eqn. (6), this equation contains only a nearly-quadratic temperature dependence and is easier to evaluate. The right-hand-side of this equation contains only expressions which are already known ($E$, $Q_{\text{tot}}$) or are obtained from measurement ($T$, $\dot{Q}$). So the expression

$$F(X) = \Phi(X) \int_0^X \frac{dX}{\Phi(X)} \tag{10}$$

can be calculated. This function $F(X)$ should be the same for all measurements at different heating rates, provided that the measurements are carried out with a reaction mixture of the same initial composition. Therefore, from these measurements and from

$$X(t) = \frac{1}{Q_{\text{tot}}} \int_0^t \dot{Q}(t)\,\mathrm{d}t \tag{11}$$

a mean curve of the function $F(X)$ is obtained.

The problem to be solved is to recalculate $\Phi(X)$ from eqn. (10). This, however, is a mathematical problem. Differentiating eqn. (10)

$$\frac{1}{\Phi(X)}\frac{\mathrm{d}\Phi(X)}{\mathrm{d}X} = \frac{1}{F(X)}\left[\frac{\mathrm{d}F(X)}{\mathrm{d}X} - 1\right] \tag{12}$$

The boundary conditions are at $X = 0$: $\Phi(0) = 1$, $F(0) = 0$, $(\mathrm{d}F(X)/\mathrm{d}X)_{X=0} = 1$; at $X = 1$: $\Phi(1) = 0$, $F(1) = 0$. Thus, if $F(X)$ can be approximated by a proper function, $\Phi(X)$ can be calculated by numerical integration. In order to approximate $F(X)$, it is useful to first look at the common practical case of a second-order reaction, i.e. $\Phi_1(X) = (1 - X)^2$ or, from eqn. (10), $F_1(X) = X(1 - X)$.

From several practical calculations, it was found that the best way of calculating $\Phi(X)$ is not from $F(X)$ but its a deviation from the case of second-order reaction

$$G(X) = \frac{F(X) - X(1 - X)}{X^2(1 - X)} \tag{13}$$

is approximated by a third-degree polynomial. This is sufficient when the actual reaction is nearly second-order. But for other kinetics $G(X)$ is generally curved in such a manner that it is more useful to approximate $1/G(X)$ by a polynomial. If $G(X)$ is known, $\Phi(X)$ can be calculated from eqn. (12) (see Appendix) by

$$\Phi(X) = (1 - X)^2(1 + XG(X))\,\mathrm{e}^{I(X)} \tag{14}$$

where

$$I(X) = \int_0^X \frac{G(X)}{(1 - X)(1 + XG(X))}\,\mathrm{d}X \tag{15}$$

is calculated by a numerical (Runge-Kutta fourth-order). If $G(X) = 0$, one obtains a second-order reaction type.

With the already known intercept of the Arrhenius diagram and the value of $\Phi(X_m)$, one obtains the dimensionless Damköhler number

$$Da_\infty = \frac{(-\nu_A) r_{0\infty} \tau^0}{c_{A_0}} \tag{16}$$

## 3. EVALUATION OF SIMULATED DSC CURVES BY A COMPUTER PROGRAM

Based on the above derivation of the evaluation method, the computer program TherKin 2.0 was developed. For the evaluation, the DSC curves are needed as ASCII data with the initial sample weight, heating rate, number of measured points and the measured values of $T$ and $\dot{Q}$.

In order to check the precision of the computer program, simulated DSC curves were evaluated. The fixed values of the kinetic parameters are $Da_\infty = 10^{10}$, $E/R = 10\,000$ K, $\Delta h = -100$ J g$^{-1}$, $m = 30$ mg, and the function $\Phi(X)$ is $\Phi_1(X) = (1-X)^2$ or $\Phi_2(X) = (1+10X)(1-X)^2$ where $\Phi_1(X)$

TABLE 1

Characteristic thermogram data of the kinetic type with $\Phi_1(X) = (1-X)^2$

| $\beta$/K min$^{-1}$ | $T_m$/°C | $\dot{Q}_m/Q_{tot}/10^{-3}$ s$^{-1}$ | $X_m$ | $Q_{tot}$/mJ | $\Delta h$/J g$^{-1}$ |
|---|---|---|---|---|---|
| 1 | 64.5 | 0.3878 | 0.468 | −3005.4 | −100.18 |
| 2 | 72.1 | 0.7429 | 0.469 | −3005.9 | −100.19 |
| 3 | 76.6 | 1.0863 | 0.467 | −3005.6 | −100.19 |
| 4 | 80.0 | 1.4223 | 0.468 | −3005.3 | −100.18 |
| 5 | 82.6 | 1.7527 | 0.468 | −3005.0 | −100.17 |
| 6 | 84.7 | 2.0790 | 0.469 | −3004.4 | −100.15 |
| 7 | 86.6 | 2.4017 | 0.468 | −3003.9 | −100.13 |
| 8 | 88.2 | 2.7214 | 0.468 | −3003.4 | −100.11 |
| 9 | 89.6 | 3.0385 | 0.467 | −3002.9 | −100.10 |

TABLE 2

Characteristic thermogram data of the kinetic type with $\Phi_2(X) = (1+10X)(1-X)^2$

| $\beta$/K min$^{-1}$ | $T_m$/°C | $\dot{Q}_m/Q_{tot}/10^{-3}$ s$^{-1}$ | $X_m$ | $Q_{tot}$/mJ | $\Delta h$/J g$^{-1}$ |
|---|---|---|---|---|---|
| 1 | 52.8 | 0.7461 | 0.481 | −2981.6 | −99.39 |
| 2 | 59.9 | 1.4264 | 0.482 | −2991.3 | −99.71 |
| 3 | 64.1 | 2.0847 | 0.479 | −2994.6 | −99.82 |
| 4 | 67.2 | 2.7291 | 0.480 | −2996.3 | −99.88 |
| 5 | 69.7 | 3.3631 | 0.482 | −2997.3 | −99.91 |
| 6 | 71.7 | 3.9890 | 0.481 | −2998.1 | −99.94 |
| 7 | 73.4 | 4.6082 | 0.480 | −2998.4 | −99.95 |
| 8 | 74.9 | 5.2216 | 0.480 | −2998.9 | −99.96 |
| 9 | 76.3 | 5.8300 | 0.482 | −2999.2 | −99.97 |

TABLE 3

Values of the determined kinetic parameters

| Type of kinetic | $E/R$/K | $Da_\infty$ | $\overline{\Delta h}$/J g$^{-1}$ |
|---|---|---|---|
| $\Phi_1(X) = (1 - X)^2$ | 10029 ± 14 | $1.107 \times 10^{10}$ | −100.15 |
| $\Phi_2(X) = (1 + 10X)(1 - X)^2$ | 9981 ± 14 | $0.944 \times 10^{10}$ | −99.84 |

represents a second-order reaction, and $\Phi_2(X)$ an autocatalytic reaction.

The results obtained are shown in Tables 1 and 2. It can be seen that the conversion $X_m$ is practically independent of the heating rate. With these results, the activation energy or $E/R$ values can be obtained from the Arrhenius diagram. Table 3 contains the determined values of the kinetic parameters $E/R$, $Da_\infty$ and $\overline{\Delta h}$.

The obtained values of $Da_\infty$ deviate clearly from the prescribed $Da_\infty$. This results from the extrapolation of $r_{0\infty}$ to infinite temperature, so that a small deviation of $E/R$ causes a wide deviation of $Da_\infty$. If one uses a temperature which is more realistic of the reaction (e.g. 350 K), the determined values of the temperature-dependent Damköhler number

$$Da(T) = Da_\infty \, e^{-E/RT} \tag{17}$$

deviate less than 2% for $\Phi_1(X)$ and less than 0.5% for $\Phi_2(X)$ from the prescribed $Da(T)$. Figures 1 and 2 show the comparison between the expected and the calculated $\Phi(X)$ curves.

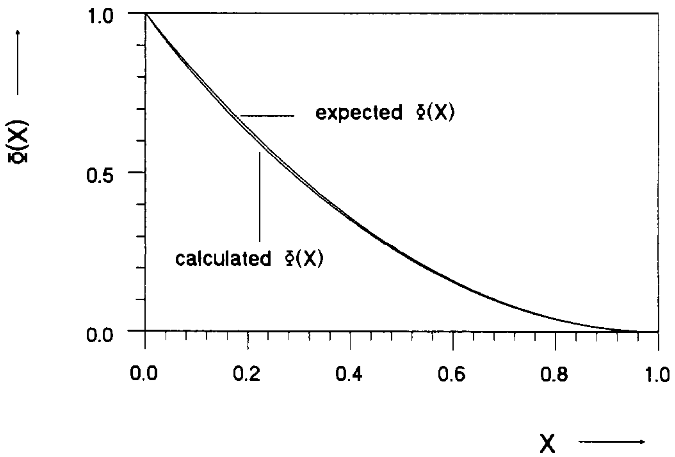

Fig. 1. Comparison between the calculated and expected $\Phi_1(X) = (1 - X)^2$.

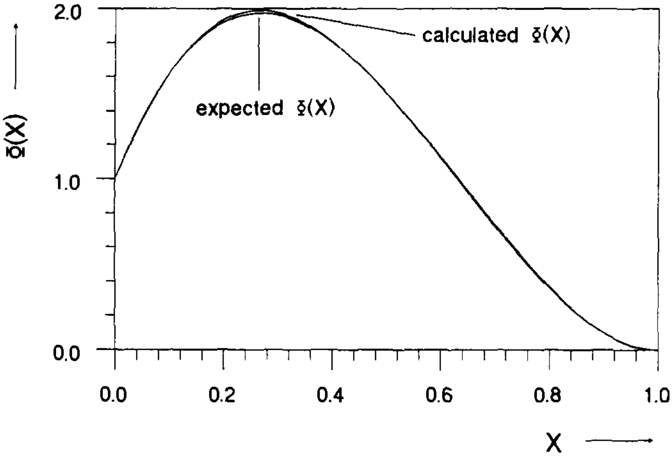

Fig. 2. Comparison between the calculated and expected $\Phi_2(X) = (1 + 10X)(1 - X)^2$.

## 4. CONCLUSIONS

The comparison between the calculated and prescribed kinetic parameters demonstrates that the presented evaluation method can recalculate these prescribed parameters, at least for theoretical DSC curves.

A real measured DSC curve has to be corrected by known methods of correcting a curve containing only the chemical reaction. This correction of real DSC measurements, however, is the main problem in the evaluation from DSC measurements and will be discussed in Part 2 [8].

An important assumption of the presented evaluation method is the separation of the reaction rate *r*. If the measured DSC peak contains more than one reaction, then the reaction rate is not separable. In this case the evaluation method fails.

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## APPENDIX: DERIVATION OF EQN. (14)

By differentiating eqn. (13) one obtains

$$\frac{\mathrm{d}F(X)}{\mathrm{D}X} = 1 + X\left[G(X) - 2(1 + XG(X)) + (1 - X)\frac{\mathrm{d}}{\mathrm{d}X}(XG(X))\right] \tag{A1}$$

If eqn. (A1) is substituted in eqn. (12) with eqn. (13), one obtains

$$\frac{\mathrm{d}\ln\Phi(X)}{\mathrm{d}X} = \frac{\mathrm{d}}{\mathrm{d}X}[\ln(1 + XG(X)) + \ln(1 - X)^2] + \frac{G(X)}{(1 - X)(1 + XG(X))} \tag{A2}$$

From the integration of eqn. (A2) with the initial condition $\Phi(0) = 1$, one gets eqn. (14).