Thermochimica Acta, 225 (1993) 153–163
Elsevier Science Publishers B.V., Amsterdam

Determination of chemical kinetics by DSC measurements.
Part 2. Experimental results

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(Received 31 March 1992; accepted 29 January 1993)

Abstract

In part 1 (Thermochim. Acta, 225 (1993) 143) a method to evaluate DSC measurements was developed and tested with simulated data. Part 2 contains experimental results for three different chemical reactions for which the kinetic data are determined. Provided correct baseline and time lag corrections are applied, reliable kinetic data can be obtained using this evaluation method.

In contrast to other methods of evaluating DSC traces to obtain kinetic data, the method described here makes no assumptions about the order of reaction. Thus complex kinetic behaviour such as autocatalysis is readily apparent.

LIST OF SYMBOLS

Da_∞	Damköhler number defined in eqn. (16) of part 1
$E/\mathrm{J\,mol^{-1}}$	activation energy
$F(X)$	function defined in eqn. (10) of part 1
$k_\infty/\mathrm{s^{-1}}$	first-order reaction rate constant extrapolated to infinite temperature
m/g	initial sample weight
$\dot{Q}/\mathrm{W}$	heat flow
$\dot{Q}_\mathrm{B}/\mathrm{W}$	heat flow after baseline correction
$\dot{Q}_\mathrm{m}/\mathrm{W}$	maximal heat flow of a chemical reaction curve
$\dot{Q}_\mathrm{max}/\mathrm{W}$	maximal heat flow of a melting curve
$\dot{Q}_\mathrm{tot}/\mathrm{J}$	total evolved heat of reaction
$R/\mathrm{J\,mol^{-1}\,K^{-1}}$	gas constant
t/s	time
t_c/s	cure time
T/K	temperature

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T_m/K	temperature corresponding to $\dot{Q}_m$
X	conversion

Greek letters

β/K s^{-1}	heating rate
Δh/J g^{-1}	reaction enthalpy per gram reaction mixture
$\Phi(X)$	dimensionless description of the concentration dependence on the reaction rate
τ°/s	time unit (1 s)
θ/s	time lag constant

1. INTRODUCTION

In part 1 of this study [1], the theoretical foundation of the determination of chemical kinetics by DSC measurements was described. Ideal DSC curves, which contain only the chemical reaction, form the basis of this evaluation method. Measured DSC curves, however, contain more thermal effects than the chemical reaction. Therefore, the main problem of the evaluation is to obtain ideal DSC curves by correction of real DSC measurements. Only with accurate correction of the measured data are meaningful results of the reaction kinetics obtained.

2. CORRECTION OF THE MEASURED DATA

2.1. *Baseline correction*

Initial displacements of the baseline from zero result from mismatching of the thermal properties of the sample and reference material. A further reason is the asymmetry in the construction of the sample and reference holders. This often leads to a sloping and curving baseline.

The displacement of the baseline due to the measuring equipment can be corrected very easily. The correction can be performed by subtracting a measurement with empty capsules from the measurement with the sample. In modern DSC equipment, this correction is made automatically.

A displacement of the baseline due to the chemical reaction can be corrected only as far as the heat capacity of the reaction mixture changes. The principle of this correction is described in ref. 2. A linear relationship between the changes in heat capacity and degree of conversion form the assumption of this correction.

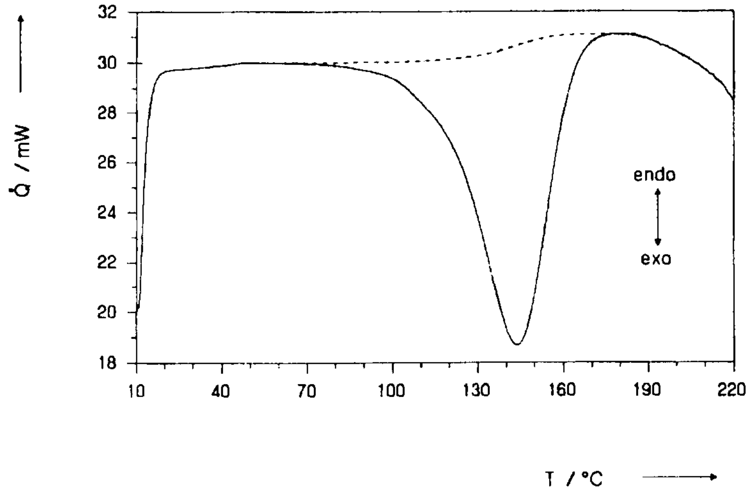

Fig. 1. Measured DSC curve (solid) and its baseline (broken).

Figure 1 demonstrates a practical example of this baseline correction for the reaction discussed in more detail in section 4.3.

2.2. *Time lag correction*

A second correction is of great importance when determining kinetic data from DSC measurements. This correction is caused by the time lag between the sample temperature and the measured temperature. The time lag constant θ can be obtained from melting curves of standard samples, for example indium [2]. If the ratio $\dot{Q}/\dot{Q}_{\max}$ is plotted in a logarithmic scale, the time lag constant θ can be determined from the slope of the straight line, corresponding to the equation

$$\frac{\mathrm{d}[\ln(\dot{Q}/\dot{Q}_{\max})]}{\mathrm{d}T} = -\frac{1}{\beta\theta} \tag{1}$$

Figure 2 shows the determination of θ from the indium melting curve. Using the time lag constant θ, an ideal DSC curve can be recalculated from a measured, baseline-corrected DSC curve $\dot{Q}_{\mathrm{B}}$ by

$$\dot{Q} = \dot{Q}_{\mathrm{B}} + \theta\frac{\mathrm{d}\dot{Q}_{\mathrm{B}}}{\mathrm{d}t} \tag{2}$$

The evaluation method described in Part 1 makes use of a series of DSC measurements at different heating rates. In such a case the influence of the time lag constant is of major importance in the determination of the activation energy, as the results of different measurements are combined. Then, the activation energy is used to determine the dimensionless

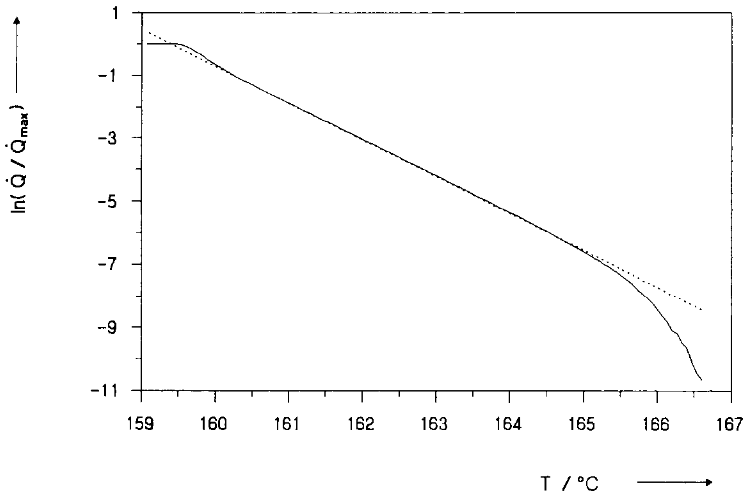

Fig. 2. Decreasing part of an indium melting peak (solid) in logarithm scale with the broken line used for the determination of θ.

parameter describing the concentration dependence of the reaction rate $\Phi(X)$. Therefore the course of $\Phi(X)$ is also dependent on the time lag constant.

This can be demonstrated by a series of simulated DSC curves of a first-order reaction $\Phi(X) = 1 - X$ with the prescribed data of Table 1. These curves were 'corrected' by eqn. (2) with time lag constants of $\theta = +10$ s and $\theta = -10$ s. From the evaluation of these series of DSC curves, the data shown in Table 1 and Fig. 3 were obtained. A comparatively small time lag of $\theta = +10$ s or $\theta = -10$ s changes all calculated data, with the exception of the heat of reaction Δh. Most commercial DSC equipment have a time lag of this magnitude; therefore an evaluation of DSC curves without a time lag correction does not produce accurate kinetic data for the reaction.

TABLE 1

Prescribed and determined kinetic data of different time lag constants

	Prescribed	Determined		
		$\theta = 0$ s	$\theta = +10$ s	$\theta = -10$ s
Δh/J g^{-1}	−100	−100.07	−100.06	−100.06
E/R/K	10000	10003	10496	9561
Da_∞	10^{10}	0.995×10^{10}	54.3×10^{10}	0.217×10^{10}

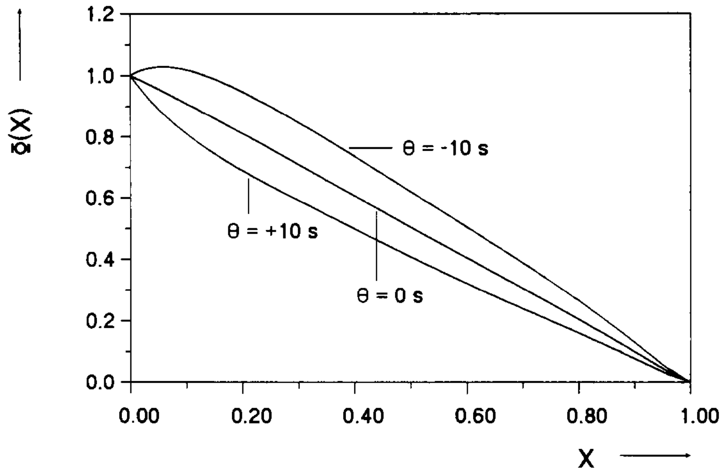

Fig. 3. The determined $\Phi(X)$ of different time lag constants θ.

3. EXPERIMENTAL

A power-compensating DSC (Perkin-Elmer model DSC-7) was used for all measurements. The reactions investigated here as examples were the decomposition of dimethyl 2,2′-azobisisobutyrate, the curing reaction of the two-component adhesive UHU-Endfest 300, and the esterification of methyl maleic anhydride and 2-phenyl ethanol.

The reactions were measured at five or seven heating rates (2–13 K min^{-1}) in the range 0–200°C. As far as possible, only one reaction mixture was used for the measurements at different heating rates. Closed high-grade steel capsules were used for sample and reference. An empty capsule was used as reference. The DSC equipment was temperature and enthalpy calibrated by the melting peaks of indium and tin.

The measurements were evaluated using the computer program TherKin 2.0. The melting curves of indium, biphenyl and benzoic acid were evaluated to determine the time lag constant θ. The values of θ obtained are shown in Table 2. As can be seen, the time lag for the organic

TABLE 2

Determined values of θ of different substances

Heating rate/K min^{-1}	θ/s		
	Indium	Biphenyl	Benzoic acid
5	5.1	6.2	5.8
10	5.1	6.3	5.8

compounds is somewhat larger than that for indium. Because organic reactions were being investigated, a time lag constant of $\theta = 6$ s was used. The determination of the peak boundaries is a subjective decision but the baseline should be continuous. If a change in heat capacity is known to occur or was indicated by the DSC curve, the baseline correction described above was used. For the decomposition of dimethyl 2,2′-azobisisobutyrate, a linear baseline correction was sufficient. For the other reactions a baseline correction of the type shown in Fig. 1 was used.

4. RESULTS

4.1. *Decomposition of dimethyl 2,2′-azobisisobutyrate*

The dimethyl 2,2′-azobisisobutyrate was dissolved in dibenzyl ether to a concentration of 0.91 mol l^{-1} and stored below −10°C. The results obtained are shown in Table 3, Figs. 4 and 5, and Table 4.

The conversion X_m at maximum heat flow is practically constant, as discussed in part 1. The determination of the activation energy and $\Phi(X)$ from the data above are given in Figs. 4 and 5.

The Arrhenius diagram (Fig. 4) shows the expected linear relation between the measured points. The linear relationship between $\Phi(X)$ and X shown in Fig. 5 demonstrates that the decomposition is a first-order reaction within the experimental limits of error.

The kinetic data are shown in Table 4 and are compared with the manufacturer's data which were determined with toluene as solvent [3]. The rate constants of Table 4 were recalculated from the Damköhler number Da_∞ for a first-order reaction ($Da_\infty = k_\infty \tau^0$). In order to check the results obtained, the corrected DSC measurements were compared to simulated DSC curves using the data above (Table 3). Figures 6 and 7 show the best and the worst agreement of the measurement and the simulation.

TABLE 3

Results of the single measurements of the decomposition of dimethyl 2,2′-azobisisobutyrate

Filename	β/ K min^{-1}	Sample weight/ mg	Q_{tot}/mJ	$\dot{Q}_m/Q_{tot}$/ 10^{-3} s^{-1}	T_m/°C	X_m	Δh/J g^{-1}
2Azo03.kor	3	33.360	−6056	1.9671	111.4	0.603	−181.5
2Azo05.kor	5	31.660	−5695	3.2413	116.4	0.601	−179.5
2Azo07.kor	7	29.730	−5158	4.5799	119.6	0.593	−173.5
2Azo09.kor	9	24.030	−4268	5.7109	122.0	0.595	−177.6
2Azo10.kor	10	30.760	−5442	6.5022	123.0	0.594	−176.9
2Azo11.kor	11	34.870	−6181	7.1469	124.0	0.583	−177.3
2Azo13.kor	13	26.150	−4641	8.3630	125.7	0.595	−177.5

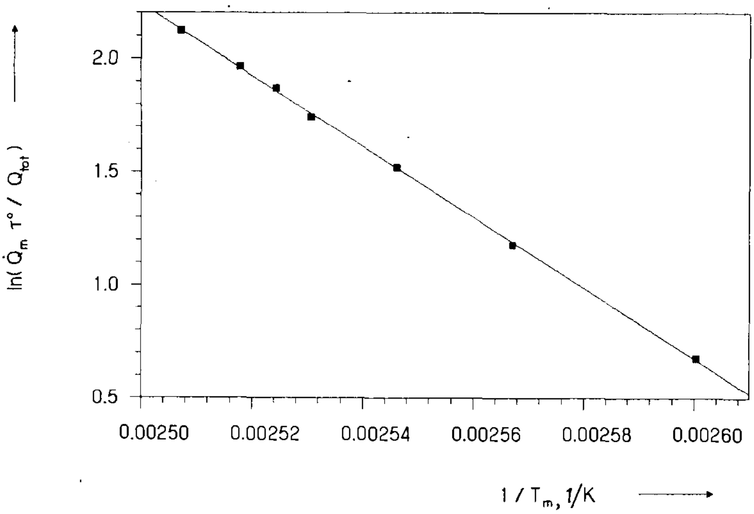

Fig. 4. Arrenius diagram of the decomposition of dimethyl 2,2′-azobisisobutyrate.

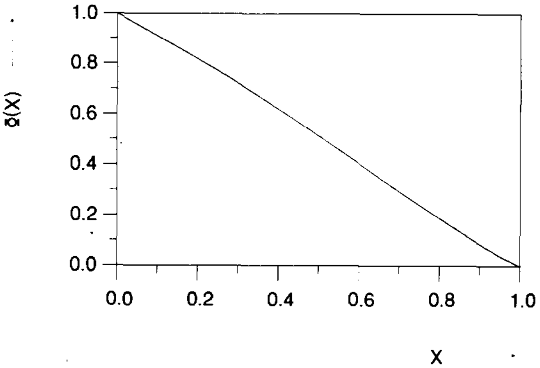

Fig. 5. Determined curve of Φ(*X*) of the decomposition of dimethyl 2,2′-azobisisobutyrate.

TABLE 4

Comparison of the measured data and the manufacturer's data for the decomposition of dimethyl 2,2′-azobisisobutyrate

	Measured data	Manufacturer's data
$\Delta h/\mathrm{J\,g^{-1}}$	−177.7	–
$E/\mathrm{kJ\,mol^{-1}}$	130.5	131.4
Da_∞	2.48×10^{15}	3.2×10^{15}
$k_{60^\circ C}/\mathrm{s^{-1}}$	8.66×10^{-6}	8.11×10^{-6}
$k_{70^\circ C}/\mathrm{s^{-1}}$	3.42×10^{-5}	3.17×10^{-5}
$k_{80^\circ C}/\mathrm{s^{-1}}$	1.25×10^{-4}	1.19×10^{-4}

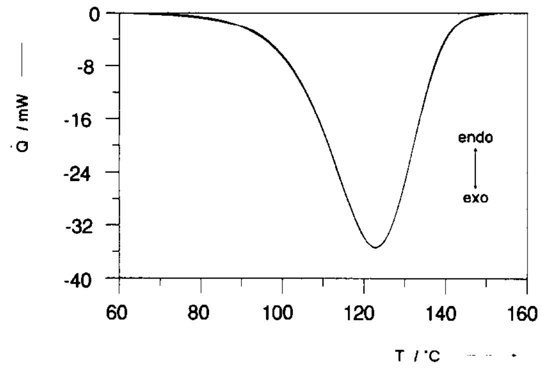

Fig. 6. Best argeement of measured and simulated DSC curves of the decomposition of dimethyl 2,2′-azobisisobutyrate.

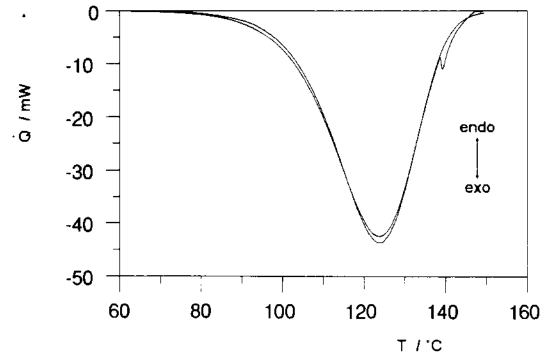

Fig. 7. Worst agreement of measured and simulated DSC curves of the decomposition of dimethyl 2,2′-azobisisobutyrate.

4.2. *Curing reaction of a two-component adhesive*

The curing reaction of a two-component adhesive is a practical example. Two different mass ratios of adhensive agent (B) and hardener (H) were measured at different heating rates. The mass ratios used were B:H = 1:1 and B:H = 2:1. In spite of the long cure time, it was not possible to use one reaction mixture for a series of measurements. Thus for each measurement a new reaction mixture was made up (the deviation of the mixtures was less than 1%). The evaluated results of the curing reaction are shown in Table 5 and Fig. 8.

From additional measurements with different ratios of B:H, it was found that the maximum heat production is obtained at a ratio of B:H = 2:1.

In contrast to Fig. 5, the curve of $\Phi(X)$, Fig. 8, first increases with increasing conversion X. This indicates that this reaction is of an autocatalytic type.

TABLE 5

Measured data for the curing reaction with B:H = 1:1 and B:H = 2:1

B:H	ΔH/J g^{-1}	E/R/K	Da_∞	$F(0.9)$	$\Phi(0.9)$
1:1	−257	6600	6.1×10^4	0.231	0.349
2:1	−305	6640	5.5×10^4	0.161	0.188

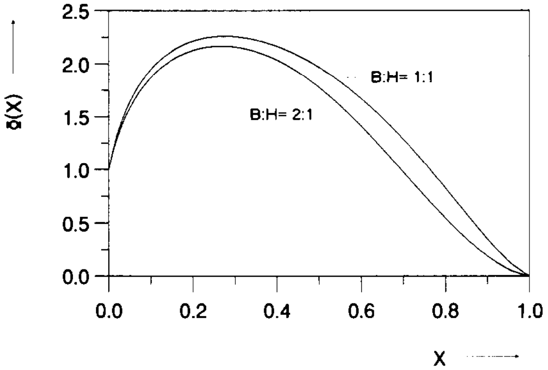

Fig. 8. Determined $\Phi(X)$ with different ratios of adhesive agent (B) and hardener (H).

4.2.1. *Application of the determined kinetic data*

The kinetic data can be applied to calculate the cure time of the adhesive at a constant temperature. The demanded conversion X_d of the curing reaction is related to the cure time t_c. For isothermal conditions the cure time can be calculated from

$$t_c = \frac{\tau^0}{Da_\infty} e^{E/RT} \int_0^{X_d} \frac{dX}{\Phi(X)} \tag{3}$$

if the time unit $\tau^0 = 1$ s is used. The integral in this equation can be calculated from $F(X)$, corresponding to eqn. (10) of part 1, and $\Phi(X)$. Because $F(X)$ and $\Phi(X)$ are calculated automatically by the program TherKin 2.0

$$t_c = \frac{\tau^0}{Da_\infty} e^{E/RT} \frac{F(X_d)}{\Phi(X_d)} \tag{4}$$

As an example, the cure time of a conversion $X_d = 0.9$ at $T = 25°C$ is required: for B:H = 1:1, a cure time $t_c = 12.7$ h is shown to be needed; and for B:H = 2:1, a cure time $t_c \approx 20.3$ h is required.

4.3. *Esterification of methyl maleic anhydride and 2-phenyl ethanol*

The esterification of methyl maleic anhydride (MMA) and 2-phenyl ethanol (PE) is an example of a more complex reaction.

TABLE 6

Measured data for the esterification of methyl maleic anhydride (MMA) and 2-phenyl ethanol (PE) mixtures of different mole ratios

MMA:PE	$\Delta h/\mathrm{J\,g^{-1}}$	$E/R/\mathrm{K}$	Da_∞
2:1	−59.35	5721	3.31×10^2
1:1	−77.56	6456	61.8×10^2
1:2	−72.00	6517	46.3×10^2

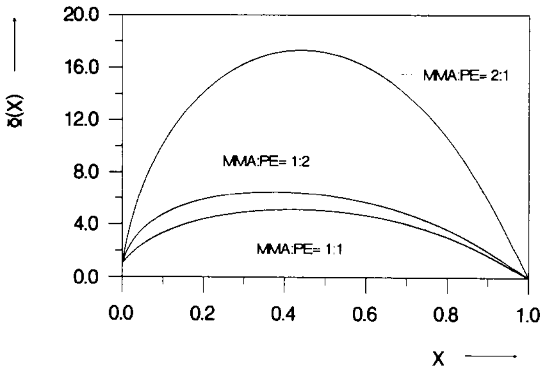

Fig. 9. Determined Φ(*X*) of the esterification of methyl maleic anhydride (MMA) and 2-phenyl ethanol (PE) mixtures with different mole ratios.

Three different mole ratios of MMA and PE were measured at different heating rates. The mole ratios used were MMA:PE = 1:1, MMA:PE = 1:2 and MMA:PE = 2:1. The reaction compounds were mixed without solvent and stored, for a series of measurements, below −10°C.

The evaluation results obtained are shown in Table 6 and Fig. 9. As seen in Fig. 9, the esterification is of an autocalytic type. From additional analytical measurements of the reacted mixture, it was found that the esterification is a reversible reaction. Thus an important condition of the evaluation method, described in Part 1 [1], was not satisfied. Nevertheless the data obtained can be used as a first estimation of the kinetics of the esterification.

In the case of such a complex reaction, an evaluation of the DSC curves is not sufficient on its own. Further sources of information for the reaction have to be used to fully evaluate the kinetics.

5. CONCLUSIONS

The three experimental examples, presented here, indicate that DSC measurements can be used to determine the kinetic data of a chemical reaction. However, meaningful data are only obtained if some essential points are considered. One point is that a series of measurements at different heating rates is necessary. In addition, the correction of the measured curves, especially of the time lag, is of major importance.

The first example was a simple decomposition reaction which is, as expected, a first-order reaction. The other reactions, however, show a dimensionless kinetic parameter $\Phi(X)$ of an autocatalytic type. In such a case, an evaluation of the kinetics using a simple nth order reaction scheme will produce erroneous results. The use of the evaluation method developed in part 1 [1] allows the kinetics to be determined without any assumptions about the order of reaction. As such, it readily identifies those reactions, such as autocatalytic and/or reversible reactions, which do not follow a simple nth order scheme.

ACKNOWLEDGEMENT

These investigations were supported by Schering AG.

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