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Evaluation of the Dynamic Response of a New Heat Flux Calorimeter for Kinetic Purposes

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A new reaction calorimeter has been developed for measuring the kinetics of reactions accompanied by small thermal effects. For kinetic purposes, the calorimeter was calibrated by simulating the heat flow in accord with a certain kinetic equation. This was accomplished by applying a software-controlled voltage to a resistor placed inside the calorimeter. The obtained isothermal data were deconvoluted and treated using two different kinetic methods to explore the effect of deconvolution on the values of the kinetic parameters.

Introduction

Differential scanning calorimetry (DSC) and reaction calorimetry (RC) are widely used to study the kinetics of thermally stimulated reactions in the condensed phase.[1,2] These methods allow one to monitor the heat flow as a function of time. The heat flow from a reaction system is directly proportional to the reaction rate and the heat of reaction, as follows

$$\phi(t) = Q\frac{d\alpha}{dt} \tag{1}$$

where $\phi(t)$ is the heat flow, Q is the reaction heat, and $d\alpha/dt$ is the reaction rate. The latter quantity is customarily represented by

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{2}$$

where $k(T)$ is the rate constant, $f(\alpha)$ is the reaction model, and α is the extent of reaction. The reaction model can take various forms depending on the reaction mechanism.[3] According to eq 1, at each moment of time, the extent of reaction is determined as the partial area of a thermal peak

$$\alpha = \frac{1}{Q}\int_0^t \phi(t)\,dt \tag{3}$$

The temperature dependence of the rate constant is satisfactorily described by the Arrhenius equation

$$k(T) = A\exp\!\left(\frac{-E}{RT}\right) \tag{4}$$

where T is the temperature, R is the gas constant, A is the preexponential factor, and E is the activation energy. The three kinetic characteristics A, E, and $f(\alpha)$ are sometimes called the "kinetic triplet". Evaluation of these kinetic characteristics is an objective of kinetic analysis.

The trustworthiness of kinetic evaluations is based on both the quality of the experimental measurements and the reliability of the kinetic computations. The quality of the measurements is ensured by temperature and heat calibrations, which make use of certain standards.[2] The reliability of the kinetic computations could be secured by using a standard reaction whose Arrhenius parameters and reaction model are known precisely. Given the kinetic complexity of even the simplest processes,[4] as well as the dependence of kinetic parameters on experimental conditions, the very existence of standard reaction kinetics appears to be rather questionable.

In a previous work,[5] we proposed an electronic solution to the problem of the kinetic standard for DSC measurements. The basic idea was to make use of the Joule effect or, in other words, the heating effect of an electric current passing through a resistor. This effect is often used for heat calibration of DSC and RC instruments[2,6] through the installation of a heater (an electric resistor) in the place of the sample. This enables a known amount of heat to be generated by the application of a certain voltage to the heater. We have shown that a similar principle can be used for kinetic calibrations if the heat flow from the electric heater is generated according to a certain kinetic law. That study showed that kinetic calibration is necessary for a large-time-constant DSC ($\tau \approx 60$ s), especially at faster heating rates.

In this paper, we apply a similar approach to different calorimetric data to identify a method of deconvolution that is best suited for kinetic purposes. Deconvolution is applied to signals that were actually measured. The effect of deconvolution on the activation energy and reaction order is evaluated by using multiple linear regression (MLR) and isoconversional methods.

Apparatus

The new apparatus built in our laboratory is called the micro differential fluxmetric calorimeter (μDFC). It consists of two thermopiles surrounding sample compartments (Figure 1). Each thermopile contains 628 thermocouples that make up the fluxmeter. The sensitivity of this apparatus is equal to 40 μW, and the sample capacity is 15 mL.

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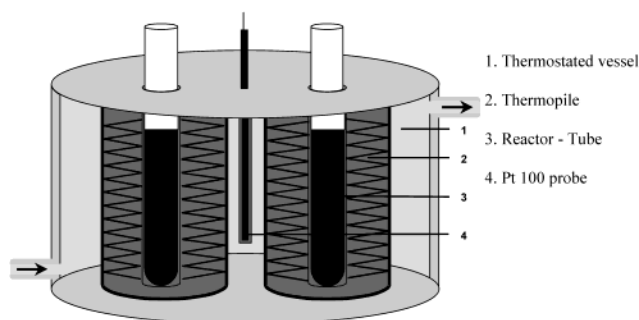† University of Nice–Sophia Antipolis.
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Figure 1. μDFC apparatus.

1. Thermostated vessel
2. Thermopile
3. Reactor - Tube
4. Pt 100 probe

One compartment holds a standard glass tube with the sample solution to be studied. The other compartment holds a tube with the solvent that is used as a reference. The two thermopiles are thermostated at given isothermal temperatures between 5 and 95 °C or heated/cooled at low rate (below 0.5 °C/min). The differential signal from the two thermopiles is measured by a Keithley 2000 multimeter. We developed a TestPoint (Capital Equipment Corp.) program to control the temperature of the thermostated vessel and to create data files of experimental readings of the time, temperature, and differential heat flux.

Simulations

As a heater, we used a 1000-Ω precision resistor manufactured by Vishay-Sfernice, Inc. (France). According to the manufacturer, this resistor has a temperature coefficient of resistance between 0 and -20×10^{-6}/°C. The actual temperature coefficient of resistance was measured to be -18.6×10^{-6}/°C in the temperature range 20–160 °C.

Software was written to generate a desired variation in the voltage. The resulting varying voltage was applied to the resistor using a digital-to-analog converter (Omega, Omegabus D3181) connected to the serial port of a personal computer. An analog-to-digital converter (Metrix DPM 48/40000 MF) was employed to measure the electric current, whose value can alternatively be used to estimate the heat flow as follows

$$\phi(t) = I(t)^2 \rho \qquad (5)$$

where $I(t)$ is the electric current. A comparison of the heat flow estimated by eq 5 with that estimated by eq 6 helps to ensure that the temperature variation of the resistance does not introduce a noticeable error into the value of the heat flow. For all experiments, both estimates for the heat flow were identical. This suggests that the effect of the temperature variation of the resistance is essentially negligible.

If all of the electrical energy is converted into heat energy, then the heat flow from the resistor can be determined as follows

$$\phi(t) = \frac{U^2(t)}{\rho} \qquad (6)$$

where $U(t)$ is the voltage at time t and ρ is the resistance of the resistor. To vary the heat flow according to a specific kinetic law (i.e., eq 2), the voltage should be varied according to

$$U(t) = \sqrt{\rho Q \frac{d\alpha}{dt}} \qquad (7)$$

which is obtained from eqs 1 and 6. According to eq 7, the variation in voltage should be proportional to the square root of the reaction rate. Substitution of eq 4 into eq 2 yields

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \qquad (8)$$

This equation is used to simulate the rate of a single-step reaction. For a given kinetic triplet [A, E, and $f(\alpha)$], integration of eq 8 allows one to obtain the function $\alpha = \alpha(t)$. Integration is performed numerically by using the trapezoidal rule. Substitution of the obtained $\alpha(t)$ function into eq 8 gives the reaction rate as a function of time. Further substitution of the reaction rate into eq 7 yields the necessary variation of voltage.

Experimental Section

All computations were performed using TestPoint software to control and record the data coming from the μDFC. The software also regulates the voltage in accord with a specified kinetic triplet and the heat of reaction.

Although the developed software allows multistep kinetics to be simulated, for illustration purposes, we chose a single-step reaction. The parameters of eqs 7 and 8 were taken to be $Q = 50$ J, $f(\alpha) = 1 - \alpha$, $\ln(A/\text{s}^{-1}) = 36$, and $E = 120$ kJ·mol^{-1}. The process was simulated at four isothermal temperatures $T = 50, 55, 60$, and 65 °C. For the simulations, the electric resistor was immersed into silicon oil in a sample glass tube. A similar resistor was immersed into silicon oil and placed in the reference tube of the apparatus. No voltage was applied to the reference resistor. Measured data were then calibrated by applying a heat pulse at each of the isothermal temperatures.

Deconvolution of the Signal

The reliability of kinetic data is influenced not only by the precision of the heat flow measurements, but also by thermogenesis. Several methods have been proposed for the deconvolution of thermokinetic data that make use of a first-order differential equation.[7] However, these methods are not suitable for the study of rapidly changing heat effects as measured in a calorimeter with a relatively long time constant. For this reason, a number of other numerical and analogue methods have been proposed.[8] We used a differentiation method based on the convolution of the measured heat flow $W(t)$ by the generated one $\phi(t)$ represented by the following system of linear equations

$$\phi_1(t) = \phi(t) + \tau_1 \frac{d\phi(t)}{dt}$$

$$\phi_2(t) = \phi(t) + \tau_2 \frac{d\phi_1(t)}{dt}$$

$$\phi_n(t) = \phi(t) + \tau_n \frac{d\phi_{n-1}(t)}{dt} \dots \qquad (9)$$

where $W(t) = \lim_{n \to \infty} \phi_n(t)$ and τ_1, τ_2, ..., τ_n are the calorimeter time constants of successive orders. In practical cases, a limited number (usually one to three) of linear equations is used. The parameters of the equations can easily be determined by heat pulse calibration. We have developed a program for determining the time constants and deconvoluting the measured heat flow.

Kinetic Evaluations

There are two major approaches to kinetic analysis.[9] The first approach is based on the force-fitting of kinetic data to an assumed reaction models, $f(\alpha)$. In the case of nonisothermal data, the model-fitting methods are usually applied to a single heating rate experiment that usually results in estimations of very uncertain values of the activation energy.[10] For isothermal data, a series of experiments at different temperatures is necessary. These methods usually yield a single value of the activation energy that is rather insensitive to possible changes in the reaction mechanism.[10]

The most popular isothermal model-fitting method is based on eq 10

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k(T) + n \ln(1 - \alpha) \qquad (10)$$

By plotting the left-hand side of eq 10 against $\ln(1 - \alpha)$, one can find the values of $\ln k(T)$ and n for each temperature. Then, the values of E and $\ln A$ can be estimated by plotting $\ln k(T)$ vs $1/T$. An alternative approach is to use model-free isoconversional methods.[10] Without assuming a particular form of the reaction model, these methods allow for unambiguous evaluations of the activation energy as a function of the extent of reaction. These methods are based on the isoconversional principle, which states that the reaction rate at a constant extent of conversion is a function of only the time. An isothermal process can be described by the following isoconversional equation

$$\ln t_\alpha = \ln g(\alpha) - \ln A_\alpha + \frac{E_\alpha}{RT_{iso}} \qquad (11)$$

(Henceforth, the subscript α will be used to indicate the values related to a given extent of conversion.) The application of isoconversional methods requires a series of experiments to be conducted at different isothermal temperatures or different heating rates.

Results and Discussions

Deconvolution of the measured isothermal data was done by the differentiation method (eq 9). This method allows one to reconstruct the profile of the thermal pulse as shown in Figure 2.

Time constant parameters were determined at each isothermal temperature for first-, second-, and third-order differentiation method (Tables 1−3, respectively).

A comparison of the measured and simulated extents of reaction for the same value of time shows a lag that increases significantly with the temperature (Figure 3). The lag is markedly reduced by the first-order deconvolution (Figure 4). The second-order deconvolution essentially eliminates the lag for $T < 65$ °C and $\alpha > 0.05$ (Figure 5). For the isothermal experiment conducted at 65 °C and for $\alpha < 0.15$, a small residual lag
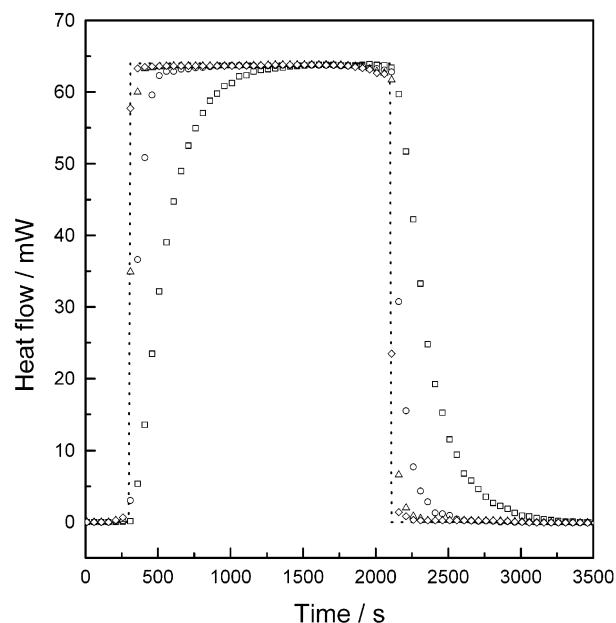

Figure 2. Effect of deconvolution on the measured heat pulse for different differentiation orders compared with simulated heat pulse ($\cdot\cdot\cdot$, simulated heat pulse; □, measured data; ○, first-order deconvoluted data; △, second-order deconvoluted data; ◇, third-order deconvoluted data). Temperature is 50 °C.

Table 1. Time Constant Evaluations of First-Order Deconvolution for the Different Isothermal Temperatures

T_{iso} (°C)	50	55	60	65
τ_1 (s)	265	263	261	260

Table 2. Time Constant Evaluations of Second-Order Deconvolution for the Different Isothermal Temperatures

T_{iso} (°C)	50	55	60	65
τ_1 (s)	311	304	296	289
τ_2 (s^2)	10870	9748	8436	6934

Table 3. Time Constant Evaluations of Third-Order Deconvolution for the Different Isothermal Temperatures

T_{iso} (°C)	50	55	60	65
τ_1 (s)	312	305	297	291
τ_2 (s^2)	10 641	9278	7805	6260
τ_3 (s^3)	41 798	40 767	38 624	34 618

still remains after the second-order deconvolution is applied. Unfortunately, the third-order deconvolution does not improve the situation. Moreover, deconvolution methods of high orders tend to amplify the noise significantly.[8] For these reasons, the third-order deconvolution was not used to carry out the kinetic analyses. To apply deconvolutions of higher orders, one needs to effectively filter out the noise in the raw data, which might require a significant increase in the frequency with which data are recorded.

Because we used a software-controlled simulated heat flow whose kinetic parameters were precisely known (see Simulation section), the measured signals could be used to quantify both the time response of the apparatus and the effect of the deconvolution method on the determination of the kinetic parameters. The two kinetic methods (eqs 10 and 11) were used to evaluate the ability of the apparatus to produce data suitable for the corresponding kinetic analyses.
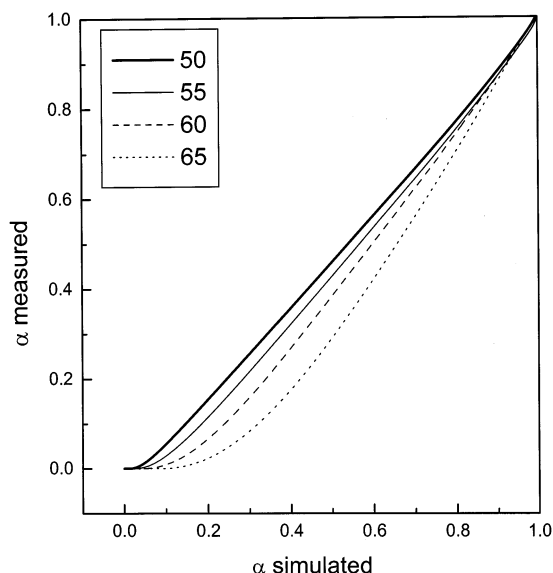
Figure 3. Correlation between simulated and measured extents of reaction. The numbers by the symbols indicate the isothermal temperatures used (in °C).
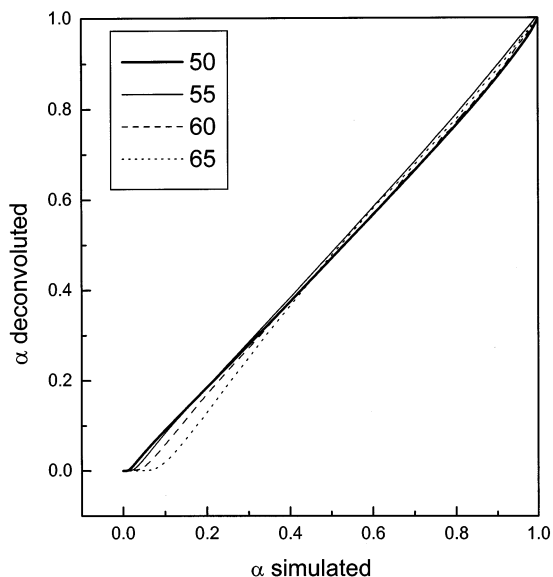

Figure 4. Correlation between simulated and measured extents of reaction after first-order deconvolution. The numbers by the symbols indicate the isothermal temperatures used (in °C).
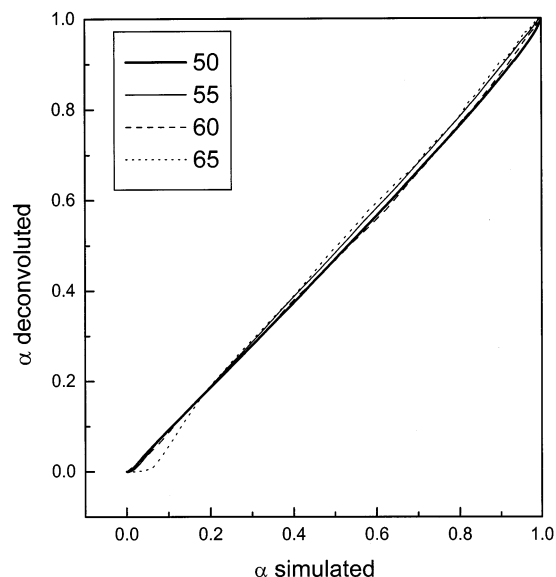

Figure 5. Correlation between simulated and measured extents of reaction after second-order deconvolution. The numbers by the symbols indicate the isothermal temperatures used (in °C).

Table 4. Reaction Order Computed According to Eq 10 for Measured (n_m), First-Order Deconvoluted (n_d), and Second-Order Deconvoluted (n_{d^2}) Signal[a]

T_{iso} (°C)	$n_m{}^b$	$n_d{}^b$	$n_{d^2}{}^b$
50	1.008	0.977	1.017
55	1.005	1.049	0.989
60	0.952	1.006	1.015
65	0.840	1.054	0.931

[a] Values determined over the region $\alpha = 0.1-09$. [b] Theoretical value $n = 1$.

Table 5. Activation Energy Computed According to Eq 10 for Measured (E_m), First-Order Deconvoluted (E_d), and Second-Order Deconvoluted (E_{d^2}) Signal[a]

T_{iso} (°C)	$E_m{}^b$ (kJ mol^{-1})	$E_d{}^b$ (kJ mol^{-1})	$E_{d^2}{}^b$ (kJ mol^{-1})
50, 55, 60	114.09	120.76	119.46
55, 60, 65	114.14	138.35	128.32
50, 55, 60, 65	113.55	128.40	121.33

[a] Values determined over the region $\alpha = 0.1-09$. [b] Theoretical value $E = 120$ kJ mol^{-1}.

Table 4 provides the values of n computed with the multiple linear regression method represented by eq 10. The deconvolution algorithm significantly improved the accuracy of the results only for $T = 60$ and 65 °C, and in these cases, the first-order algorithm is sufficient. Surprisingly, deconvolution did not improve the accuracy of the reaction order for $T = 50$ and 55 °C, perhaps because the precision attained without deconvolution is already sufficient. In this case, the mathematical treatment would only introduce an error through the noise amplification caused by the numerical method. The use of the second-order deconvolution algorithm improved the accuracy of the determination of n when the heat production rate was high with respect to the apparatus time constant (i.e., at higher values of the isothermal temperature).

Table 5 provides the values of E computed with the isothermal multiple linear regression method. For the lower values of the temperature ($T = 50, 55, 60$ °C; line 1 in Table 5), the use of first- and second-order deconvolution algorithms led to better accuracy in the parameter E. This was not true for higher temperatures (line 2) and was true only when the second-order deconvolution algorithm was used and all of the temperatures were considered (line 3, Table 5). The use of a second-order deconvolution algorithm significantly improved the accuracy in the determination of this parameter, except at the higher temperatures (line 2). In this case, the use of the first- and second-order deconvolution algorithms led to relative errors in E of 15.29 and 6.94%, respectively. In the same way, the relative errors of ln A (not shown in this table) were 18.35% (ln $A = 42.6$) and 8.11% (ln $A = 38.9$), respectively. As we have previously shown,[10,11] the values of E and ln A obtained by using model-fitting methods are strongly correlated and can therefore deviate significantly from the true values without noticeably affecting the goodness of data fit. This statement is illustrated in Figure 6, which shows that E and ln A are indeed very strongly correlated ($r = 0.999\,97$). The discovery of such a correlation should be considered as a warning
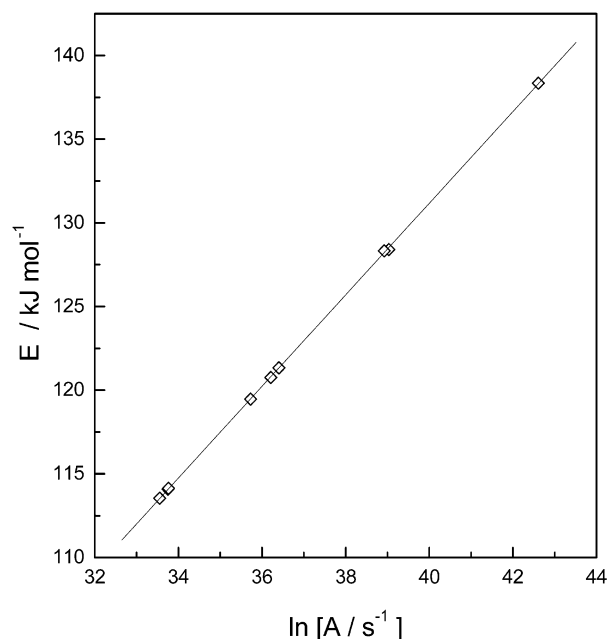
Figure 6. Correlation between E and $\ln A$ values obtained with the multiple linear regression method of eq 10 for the three cases presented in Table 5.

Table 6. Isothermal Activation Energies for Measured (E_m), First-order Deconvoluted (E_d), and Second-Order Deconvoluted (E_{d^2}) Signal According to Eq 11 for $\alpha = 0.5$

T_{iso} (°C)	E_m (kJ mol^{-1})	E_d (kJ mol^{-1})	E_{d^2} (kJ mol^{-1})
50, 55, 60	106.13	121.82	117.95
55, 60, 65	97.16	122.36	124.02
50, 55, 60, 65	101.20	121.65	122.03

Table 7. Isothermal Activation Energies Computed for Measured (E_m), First-Order Deconvoluted (E_d), and Second-Order Deconvoluted (E_{d^2}) Signal According to Eq 11

T_{iso} (°C)	$E_m{}^{a,b}$ (kJ mol^{-1})	$E_d{}^{a,b}$ (kJ mol^{-1})	$E_{d^2}{}^{a,b}$ (kJ mol^{-1})
50, 55, 60	102.77	119.48	119.19
55, 60, 65	94.80	115.78	117.50
50, 55, 60, 65	98.42	117.24	118.07

[a] Theoretical value $E = 120$ kJ mol^{-1}. [b] Value averaged over the region $\alpha = 0.1-0.9$.

sign that the estimated parameters might take on erroneous values, despite the fact that they still can be used to reproduce the measured kinetic curve.

The E values obtained by using the isoconversional method for $\alpha = 0.5$ are shown in Table 6. It can be seen that using the measured data without deconvolution did not yield as accurate value of the activation energy. The first- and second-order deconvolutions decreased the relative errors in E from 10−20 to 1.5−3.4%. In the case of $\alpha = 0.5$, the value of E obviously could not be affected by the larger signal lags that occur at the small and large values of α. Therefore, the first-order deconvolution was sufficient.

The effect of the second-order deconvolution is clearly shown in Table 7. The first-order deconvolution for the three lowest temperatures (i.e., the smallest lags) gives rise to a greater value of the activation energy. For these temperatures, the average value of E in the region $\alpha = 0.1-0.9$ (Table 7) is consistent with the activation energy used for the simulations (i.e., 120 kJ mol^{-1}). The use of high-temperature data causes the activation
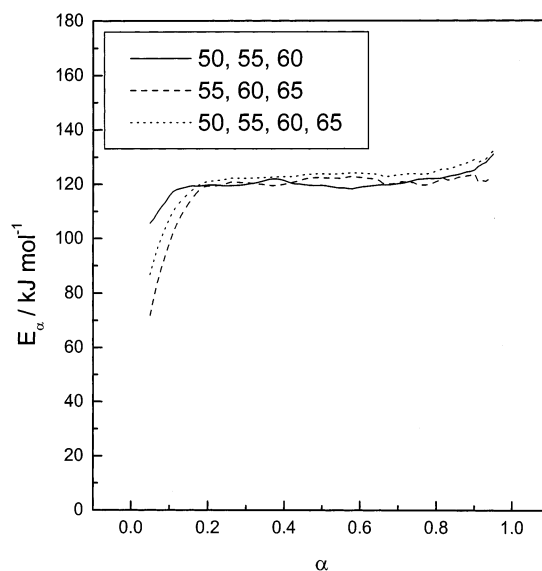

Figure 7. E_α dependencies estimated from second-order deconvoluted data when using different sets of isothermal temperatures. The numbers by the symbols indicate the isothermal temperatures used (in °C).

energy to decrease. The average value of the activation energy also decreases. The accuracy in the determination of E by the isoconversional method is noticeably increased through use of the second-order deconvolution. Because the observed deviation in the activation energy increases with the temperature, it is reasonable to assume that the deviation is caused by the residual lag in the measured signal.

It also should be noticed that the estimated activation energy is essentially constant in the region $\alpha = 0.1-0.9$ (Figure 7), which suggests that the process can be described by a single-step rate equation. This provides a justification for the use of eq 10 in the method of multiple linear regression. Note that the discovery of a dependence of E on α suggests the occurrence of multistep kinetics, which would invalidate the use of eq 10.[10] Therefore, using the isoconversional method (eq 11) and obtaining a constant activation energy appear to be necessary conditions that must be met to justify the use of eq 10.

Conclusions

The described device allows for the simulation of heat flows in accord with desired kinetic parameters. The heat flows were measured by our new apparatus called μDFC. The suitability of the measurements for kinetic evaluations was tested by comparing the evaluated kinetic parameters against the parameters used in the simulations. The measured nondeconvoluted data were found to give rise to a systematic deviation in the activation energy that increased with temperature. This undesired effect was eliminated by the use of the second-order deconvolution.

By using the multiple linear regression and isoconversional methods, we found that high-time-constant calorimeters, such as that described in this paper, can be used to produce reliable estimates of the kinetic parameters provided that the data are properly deconvoluted. First-order deconvolution seems to be sufficient for accurate estimation of the reaction order, n. However, the second-order algorithm is needed to attain good precision in estimating the activation energy, E. We also

suggest that, in the case of an unknown reaction mechanism, one should apply the model-free isoconversional method because it allows for ready detection of the reaction complexity in the form of a variation in the effective activation energy.

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