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TEMPERATURE–TIME AND TEMPERATURE–CONCENTRATION CURVES IN REACTION CALORIMETRY

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ABSTRACT

In experimental studies on the dynamic behaviour of continuous reaction systems, there is an urgent need of reliable kinetic data on suitable exothermic model reactions. This has caused a renewed interest in attempts to obtain such data from careful analyses of temperature–time curves observed in adiabatic batch experiments.

The present communication deals with some theoretical and experimental aspects of adiabatic reaction calorimetry and provides numerical solutions of the temperature–concentration relation in non-adiabatic systems.

NOMENCLATURE

A	heat-transfer surface area
c	concentration of key-reactant
c_0	initial concentration of key-reactant
c_p	average volumetric heat capacity
E	energy of activation
h	overall heat-transfer coefficient
n	reaction order
Q	heat of reaction (positive for exothermic reactions)
R	gas constant
t	time
T	absolute temperature of reacting mixture
T_0	initial temperature of reacting mixture
T_a	activation-energy temperature, Eqn. (1)
T_c	ambient temperature
T_i	inflection-point temperature, Eqn. (7)
T_m	maximum adiabatic reaction temperature, Eqn. (4b)
T_{max}	maximum non-adiabatic reaction temperature
U	reaction rate
x	reactant conversion, Eqn. (12a)
y	dimensionless reaction temperature, Eqn. (12a)
Z	frequency factor, Eqn. (1)

Z_n	modified frequency factor, Eqn. (5b)
θ	dimensionless temperature variable, Eqn. (6b)
θ_0	dimensionless temperature parameter, Eqn. (6b)
τ	dimensionless time, Eqn. (6b)
φ	dimensionless heat-transfer parameter, Eqn. (12b)

INTRODUCTION

For the purpose of investigating the thermal stability of continuous stirred reaction systems, we scanned the available literature in search of convenient exothermic model reactions for conducting liquid-phase perturbation experiments. Because of practical limitations inherent in the latter experiments, such model reactions should satisfy rather restrictive requirements with regard to the heat of reaction, the energy and entropy of activation and the solubility of the reactants. Moreover, within the range of conditions applied in the perturbation experiments, the expression for the reaction rate should preferably be of the type

$$U(c, T) = Z\, c^n \exp(-T_a/T) \qquad \text{with} \qquad T_a = E/R \tag{1}$$

Apart from the fact that very few reactions seem to cope with the particular combination of properties required for the perturbation experiments, we were also faced with the problem of evaluating the kinetic constants n (reaction order), T_a (activation-energy temperature) and Z (frequency factor) of promising model reactions at moderate reactant concentrations. The conventional method of determining these parameters is based on concentration–time measurements in isothermal batch systems at various temperature levels. However, with strongly exothermic reactions involving appreciable reactant concentrations, it is virtually impossible to keep the temperature of the reacting mixture sufficiently constant. We therefore considered the feasibility of conducting kinetic measurements in adiabatic batch systems (Gordon[1,2]).

ADIABATIC REACTION CALORIMETRY

In perfectly adiabatic batch systems, the variation of reactant concentration c and reaction temperature T with time t is represented by the equations

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -U \qquad \text{and} \qquad c_p \cdot \frac{\mathrm{d}T}{\mathrm{d}t} = QU \tag{2}$$

Hence,

$$\frac{\mathrm{d}T}{\mathrm{d}c} = -\frac{Q}{c_p} \tag{3}$$

Assuming Q/c_p to be constant (*i.e.* independent of temperature and composition), the integration of Eqn. 3 leads to the simple linear relation

$$T = T_m - \frac{Q}{c_p} \cdot c \qquad \text{or} \qquad c = \frac{c_p}{Q}(T_m - T) \tag{4a}$$

satisfying the initial and final conditions

$$
\begin{aligned}
&t = 0\ , \quad c = c_0\, , \quad T = T_0 \\
&t = \infty\ , \quad c = 0\ , \quad T = T_m = T_0 + \frac{Q}{c_p} \cdot c_0
\end{aligned}
\tag{4b}
$$

Eliminating the reactant concentration, we obtain the following expression for the rate of temperature change in adiabatic batch systems:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = Z_n (T_m - T)^n \exp(-T_a/T) \tag{5a}$$

with

$$Z_n = Z \left[\frac{c_p}{Q}\right]^{n-1} = Z \left[\frac{c_0}{T_m - T_0}\right]^{n-1} \tag{5b}$$

The differential Eqn. (5a) can be integrated in terms of tabulated exponential integrals (Abramowitz and Stegun[5]). For example, in the case of a second-order reaction ($n = 2$), one finds

$$\tau = \left[\mathrm{Ei}(\theta_0) - \mathrm{Ei}(\theta)\right] - \left[\frac{\exp(\theta_0)}{\theta_0} - \frac{\exp(\theta)}{\theta}\right] \tag{6a}$$

where

$$\tau = \frac{Z_2\, T_m\, t}{\dfrac{T_a}{T_m} \exp\left(\dfrac{T_a}{T_m}\right)}, \quad \theta = \frac{T_a}{T} - \frac{T_a}{T_m}, \quad \theta_0 = \frac{T_a}{T_0} - \frac{T_a}{T_m} \tag{6b}$$

A typical temperature–time plot calculated from Eqn. (6a) is shown in Fig. 1, corresponding to the parameter values $T_a = 10\,500\ ^\circ\mathrm{K}$, $T_0 = 300\ ^\circ\mathrm{K}$ and $T_m = 350\ ^\circ\mathrm{K}$; with rising reaction temperature, the dimensionless temperature variable θ then drops from $\theta_0 = 5$ to zero. Sigmoid temperature–time curves of this type are frequently observed in adiabatic reaction calorimetry.

The location of the inflection-point temperature T_i in Fig. 1 follows from the relation

$$\frac{T_a (T_m - T_i)}{T_i^2} = n \quad \text{for} \quad n > 0 \tag{7}$$

derived by differentiating Eqn. 5a with respect to t or T. Since the reaction temperature is restricted to the temperature range $T_0 \leqslant T \leqslant T_m$, no inflection point is observed if T_i would be lower than T_0. The condition for obtaining a truly sigmoid temperature–time curve therefore is

$$\frac{T_a(T_m - T_0)}{T_0^2} = \frac{E}{RT_0} \cdot \frac{Qc_0}{c_p\, T_0} > n \tag{8}$$

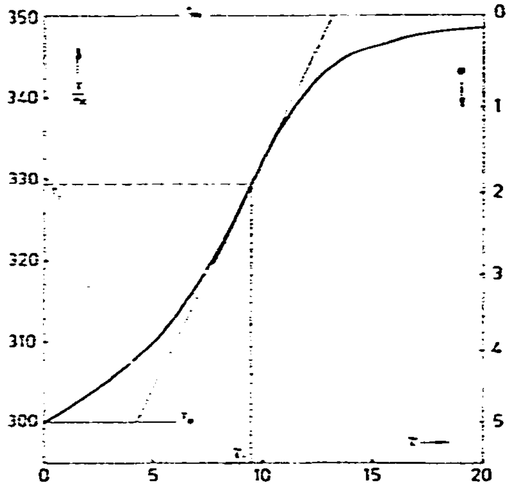

Fig. 1. Typical temperature–time curve in adiabatic reaction calorimetry, calculated from Eqn. 6a with $\theta_0 = 5$ (corresponding temperatures: $T_a = 10\,500$ K, $T_0 = 300$ K and $T_m = 350$ K).

If the condition in Eqn. (8) is satisfied, Eqn. (7) may be used to calculate T_a/n directly from observed values of T_m and T_i. The inflection-point temperature can be determined fairly accurately from the maximum of a plot of $\mathrm{d}T/\mathrm{d}t$ *versus* T; an example of this type of graph is shown in Fig. 2 (based on the parameter values used in Fig. 1). Such graphs are most readily obtained through continuous differentiation of the experimental temperature signal by means of appropriate electronic devices and subsequent recording of the derivative as a function of the corresponding reaction temperature.

In practice, the integrated temperature–time relation Eqn. (6) is of little use for deriving kinetic constants T_a and Z_n from experimental T, t or $\mathrm{d}T/\mathrm{d}t$, T curves. For the latter purpose, the differential Eqn. (5a) is transformed into

$$\ln\left[\frac{1}{(T_m - T)^n} \cdot \frac{\mathrm{d}T}{\mathrm{d}t}\right] = \ln Z_n - \frac{T_a}{T} \tag{9a}$$

or, for sufficiently small time intervals,

$$\ln\left[\frac{1}{(T_m - \bar{T})^n} \cdot \frac{\Delta T}{\Delta t}\right] = \ln Z_n - \frac{T_a}{\bar{T}} \tag{9b}$$

with

$$\Delta t = t_{k+1} - t_k, \quad \Delta T = T_{k+1} - T_k, \quad \bar{T} = \tfrac{1}{2}(T_{k+1} + T_k) \tag{9c}$$

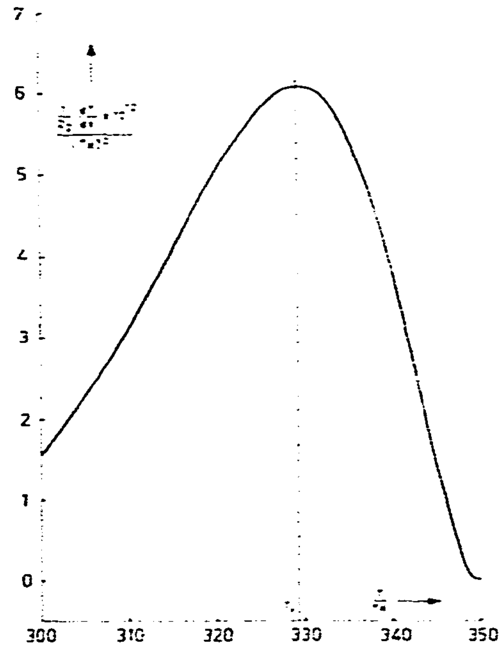

Fig. 2. The rate of temperature change as a function of temperature in adiabatic reaction calorimetry, calculated from Eqn. (5a) with $n=2$, $T_a=10\,500$ °K and $T_m=350$ °K.

According to these expressions, a plot of the left-hand side of Eqn. (9a) or (9b) *versus* the reciprocal (average) reaction temperature should yield a straight line, from which T_a and Z_n can be derived by suitable regression methods. This procedure largely depends on the availability of reliable values for the reaction order n (which should be constant throughout the temperature and concentration range involved) and for the maximum adiabatic reaction temperature T_m (which can usually be estimated quite accurately from the experimental T, t curve).

Starting from the T, t curve, the quantities defined in Eqn. (9c) are calculated from a series of successive temperature readings at a number of narrowly spaced times t_1, t_2, t_3, ... Substitution of these values into Eqn. (9b) then gives the linear relation from which T_a and Z_n can be derived. If a dT/dt, T plot is available, this curve can be used directly in combination with Eqn. (9a) for calculating T_a and Z_n. The uncertainty inherent in evaluating the slope of the T, t curve from finite ΔT and Δt values then does not arise.

An example of the results obtained with the former method (*viz.* analysis of the T, t curve) is shown in Fig. 3, which is based on measurements conducted in a simple Dewar calorimeter of the type used by Pritchard and Skinner[4] (see also Skinner, Sturtevant and Sunner[5]). The reaction under consideration is one of the model reactions selected for our perturbation experiments, *viz.* the homogeneous first-order decomposition of hydrogen peroxide in acid solution catalyzed by ferric ions (Baxendale[6]). Both this method and the development of a sufficiently stable differentiating circuit for obtaining smooth dT/dt. T curves are subject to further investigation at our laboratory

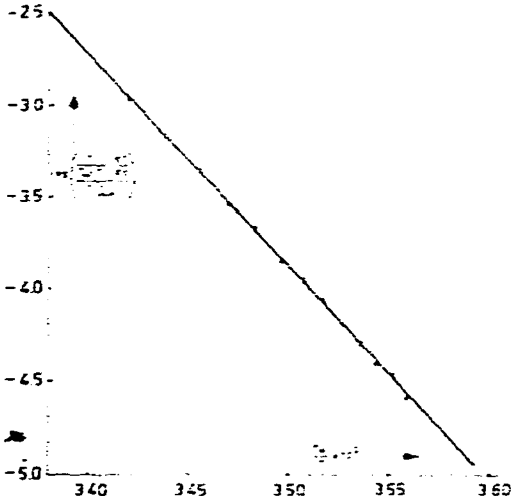

Fig. 3. Modified Arrhenius plot derived from an adiabatic temperature–time curve for the first-order decomposition of hydrogen peroxide (the kinetic constants calculated from the linear relationschip are $T_a = 11\,640$ K and $Z_t = Z = 1.69 \times 10^{14}$ sec^{-1}).

NON-ADIABATIC REACTION CALORIMETRY

The methods outlined in the preceding section are based on the assumption, that the reaction system closely approaches adiabatic behaviour. In order to establish the effect of deviations from adiabaticity due to heat exchange with the surroundings, we did some numerical calculations on reaction systems satisfying the equations

$$\frac{dc}{dt} = -U \qquad \text{and} \qquad c_p \cdot \frac{dT}{dt} = QU - hA(T - T_c) \tag{10}$$

with reaction rate U given by Eqn. (1). Eqns. (10) correspond to systems in which the reaction vessel is completely immersed in a medium of constant temperature T_c; quantity h represents the overall heat-transfer coefficient between the reacting mixture and the surrounding medium and A is the specific heat-exchanging surface area.

From Eqns. (10) and (1), the relation between the reaction temperature and the reactant concentration is found to be

$$\frac{dT}{dc} = -\frac{Q}{c_p} + \frac{hA(T - T_c)}{c_p U} = -\frac{Q}{c_p} + \frac{hA(T - T_c)}{Z c_p c^n} \exp\left(\frac{T_a}{T}\right) \tag{11}$$

Introducing the dimensionless variables

$$x = 1 - \frac{c}{c_0} \qquad \text{and} \qquad y = \frac{c_p T}{Q c_0} \tag{12a}$$

and the dimensionless parameters

$$y_a = \frac{c_p T_a}{Qc_0}, \qquad y_c = \frac{c_p T_c}{Qc_0}, \qquad \varphi = \frac{hA}{Z\, c_p\, c_0^{n-1}} \tag{12b}$$

Eqn. (11) changes into

$$\frac{dy}{dx} = 1 - \varphi \frac{y-y_c}{(1-x)^n} \exp\left(\frac{y_a}{y}\right) \tag{13}$$

For adiabatic systems ($\varphi = 0$) this equation reduces to

$$\frac{dy}{dx} = 1 \qquad \text{and, hence,} \qquad y = y_0 + x = y_m - (1-x) \tag{14a}$$

where

$$y_0 = \frac{c_p T_0}{Qc_0} \qquad \text{and} \qquad y_m = \frac{c_p T_m}{Qc_0} = y_0 + 1 \tag{14b}$$

At constant y_0, the y, x curves of all adiabatic reaction systems, in accordance with Eqns. (3) and (4), thus are represented by a single straight line with slope unity, which starts at ($x = 0$, $y = y_0$) and ends in ($x = 1$, $y = y_m = y_0 + 1$).

Considering reaction systems, which are neither adiabatic nor isothermal ($0 < \varphi < \infty$), the y, x curves again start at ($x = 0$, $y = y_0$), but must eventually end in ($x = 1$, $y = y_c$). For a given value of y_a, the shape of these curves depends on the magnitude of φ (*i.e.* on the degree of non-adiabaticity) and on the value of y_c (dimensionless ambient temperature) relative to y_0 (dimensionless initial temperature).

If $y_c < y_0$ (and, hence, $T_c < T_0$: cooled reaction vessel), the y, x curve is completely confined to the region below the adiabatic line $y = y_0 + x$. On the other hand, with $y_c > y_m$ (and hence, $T_c > T_m$: heated reaction vessel), the y, x curve is entirely restricted to the region above the adiabatic line. In the intermediate case $y_0 < y_c < y_0 + 1$ (and, hence, $T_0 < T_c < T_m$) the initial slope

$$\left(\frac{dy}{dx}\right)_{t=0} = 1 - \varphi(y_0 - y_c) \exp\left(\frac{y_a}{y_0}\right) \tag{15}$$

is greater than unity and the y, x curve thus starts steeper than the adiabatic line. However, since $y_c < y_m$, the y, x curve must end below the adiabatic line and, therefore, will intersect with the latter line. The location of this intersection point and the maximum of the y, x curve of course depend on the magnitude of y_c and φ.

For non-adiabatic and non-isothermal systems, no analytical solution of the differential Eqn. (13) can be given. In this case, the precise shape of the y, x curve has to be established by numerical integration. Some of the results obtained with an ALGOL integration programme using a modified Runge–Kutta procedure (Zonneveld[7]) are presented in Figs. 4 and 5. These graphs are based on the parameter values $y_a = 300$ and $y_0 = 10$ (and, consequently, $y_m = y_0 + 1 = 11$), which are supposed to be re-

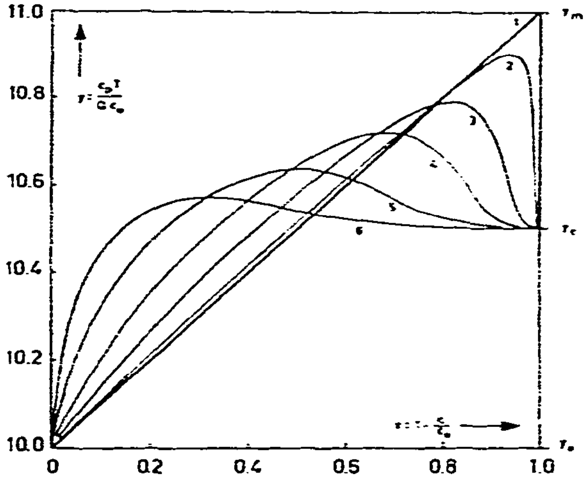

Fig. 4. Non-adiabatic temperature–concentration curves from computer solutions of Eqn. (13) for $\pi=2$, $y_a=300$, $y_0=10.0$, $y_c=10.5$ and the following values of heat-transfer parameter φ: 0(1), 10^{-14} (2), 10^{-13} (3), 3×10^{-13} (4), 10^{-12} (5), 3×10^{-12} (6).

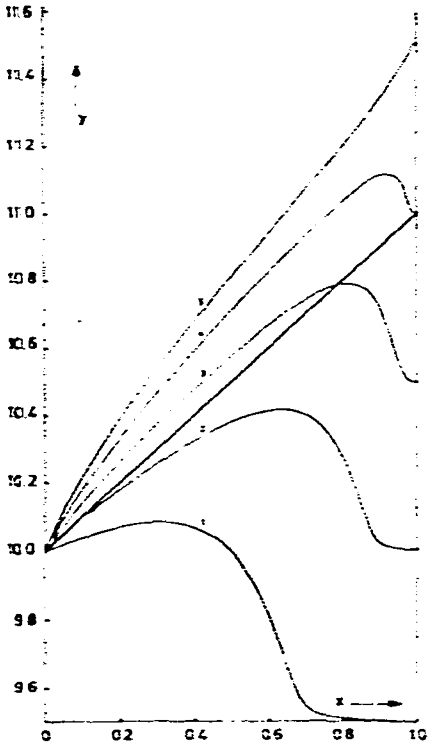

Fig. 5. Non-adiabatic temperature–concentration curves from computer solutions of Eqn. (13) for $n=2$, $y_a=300$, $y_0=10.0$, $\varphi=10^{-13}$ and the following values of the dimensionless ambient temperature, y_c: 9.5 (1), 10.0 (2), 10.5 (3), 11.0 (4), 11.5 (5).

presentative for another model reaction in our perturbation experiments, *viz.* the oxidation of thiosulphate by hydrogen peroxide (Abel[8]).

TABLE I

COMPARISON OF CALCULATED AND ASSUMED x_{mid} VALUES

$y_0 = y_c$	y_m	y_{max}	x_{max}	y_{mid}	x_{mid}	
					Calc.	*Ass.*
9.6	10.6	10.2569	0.8180	9.9284	0.3467	0.4090
9.8	10.8	10.5455	0.8701	10.1727	0.3850	0.4350
10.0	11.0	10.8089	0.9043	10.4044	0.4123	0.4522
10.2	11.2	11.0543	0.9277	10.6272	0.4322	0.4638
10.4	11.4	11.2874	0.9444	10.8437	0.4468	0.4722

Recently, this reaction has been employed by several investigators (Cohen *et al.*[9], Keairns and Manning[10], Root and Schmitz[11]) in connection with experimental studies on the properties of various types of continuous reaction systems. Cohen and Spencer[9] also reported values for the activation energy and frequency factor derived from non-adiabatic measurements (see also Griegel[12]). In analyzing their temperature–time curves obtained with reaction mixtures of constant initial reactant concentration and varying initial reaction temperature, the authors assumed that all reaction mixtures considered would have the same reactant concentration c_{mid} at temperature T_{mid} half-way between the initial and maximum reaction temperature (T_0 and T_{max}, respectively).

Clearly, the latter assumption is based on the applicability of Eqn. (4a) or (14a), which only holds for perfectly adiabatic systems. In order to test its utility for non-adiabatic conditions, we calculated values of x_{mid} corresponding to dimensionless temperatures

$$y_{mid} = \tfrac{1}{2}(y_0 + y_{max}) \tag{16}$$

for a number of cases with $y_a = 300$, $\varphi = 10^{-14}$ and various values of $y_0 = y_c$. The results are shown in Table I, which also contains x_{mid} values from Cohen and Spencer's assumption, *viz.*

$$(x_{mid})_{ass.} = \tfrac{1}{2}\, x_{max} \tag{17}$$

where conversion x_{max} corresponds to dimensionless temperature y_{max} (see also Fig. 6). For perfectly adiabatic systems ($\varphi = 0$) both x_{mid} values should of course be equal to 0.5 for all values of y_0. In non-adiabatic systems, however, the quantities y_{mid} and x_{mid} have no particular significance; moreover, the x_{mid} values obtained with Cohen and Spencer's assumption deviate quite considerably from the correct values derived from computer solutions of Eqn. (13). One might therefore be inclined to question the reliability of kinetic constants calculated on the basis of this assumption.

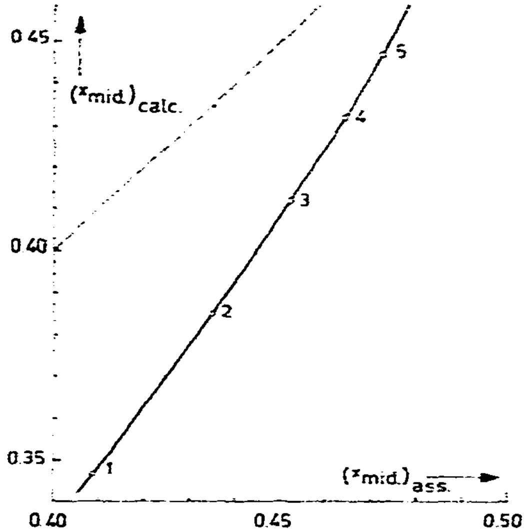

Fig. 6. Comparison of x_{mid} values calculated from computer solutions of Eqn. 13 with x_{mid} values based on Cohen and Spencer's assumption (see also Table I).

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