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Kinetics and thermodynamics of heat conduction microcalorimetry

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ABSTRACT: Heat conduction microcalorimetry offers an important technique in the context of physical organic chemistry for the study of chemical reactions in solution. The thermodynamic basis of the technique is discussed. Model reaction schemes are used in an examination of the dependence on time of the rate of heat production. The impact of rate constants and enthalpies of reaction on the recorded dependence is reviewed for first- and second-order reactions. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: heat conduction microcalorimetry; kinetics; thermodynamics

INTRODUCTION

In the last decade, microcalorimetry[1,2] has made enormous progress, contributing new techniques to the task of studying rates and mechanisms of chemical reactions in solution.[3–5] One such technique is heat conduction microcalorimetry. A small closed reaction vessel is in contact with a heat sink such that the vessel is held at constant temperature. The flow of heat between reaction vessel and heat sink is monitored. The recorded quantity is the thermal power, the rate of heat production dq/dt in the reaction vessel as a result of chemical reaction. Progress of chemical reaction in monitored by recording dq/dt as a function of time where limit($t \rightarrow \infty$)(dq/dt) is zero.

Here, we explore key features of the thermodynamic analysis underlying this technique. We comment on the dependence on time of dq/dt for first- and second-order chemical reactions. We describe the impact of enthalpies of reaction and rate constants on the dependence of dq/dt on time. The sign of dq/dt depends on whether a given chemical reaction is either exo- or endothermic. We consider both possibilities. The integrated heat for a first-order reaction is calculated as a function of time.

THERMODYNAMICS

At temperature T and pressure p, the enthalpy of a closed system having composition ξ can be defined[6] using the equation

$$H = H[T, p, \xi] \tag{1}$$

The general differential of Eqn. (1) is

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_{T,\xi} \mathrm{d}p + \left(\frac{\partial H}{\partial \xi}\right)_{T,p} \mathrm{d}\xi \tag{2}$$

For isobaric changes, dp is zero and dH equals the differential heat dq passing between the system and surroundings, being positive for endothermic and negative for exothermic processes. In heat conduction microcalorimetry, the closed system is held at constant temperature. Then,

$$\mathrm{d}q = \left(\frac{\partial H}{\partial \xi}\right)_{T,p} \mathrm{d}\xi \tag{3}$$

There is therefore an interesting link with the thermodynamic treatment underlying titration microcalorimetry.[7] In Eqn. (3), dξ is the extent of chemical reaction in the time period dt. Then,

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \left(\frac{\partial H}{\partial \xi}\right)_{T,p} \frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{4}$$

Equation (4) is the basic equation for heat conduction calorimetry. If the chemical reaction in the sample cell involves a single chemical reaction, then $(\partial H/\partial \xi)_{T,p}$ is the

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enthalpy of reaction, $\Delta_r H$. Hence

$$(\mathrm{d}q/\mathrm{d}t) = \Delta_r H(\mathrm{d}\xi/\mathrm{d}t) \tag{5}$$

Here $\Delta_r H$ describes a change in a state variable and is therefore independent of the rate of chemical reaction and the chemical pathway between reactants and products. Equation (5) also identifies the key problem in that the observed $\mathrm{d}q/\mathrm{d}t$ is given by the product of two terms, $\Delta_r H$ and $\mathrm{d}\xi/\mathrm{d}t$, which are not known *a priori*. Both $\Delta_r H$ and $\mathrm{d}\xi/\mathrm{d}t$ depend on the chemical composition of the solution in the sample cell. If the solution is dilute in both reactants and products, $\Delta_r H$ can be replaced by the standard enthalpy of reaction, $\Delta_r H^\circ$. Hence $\mathrm{d}q/\mathrm{d}t$ is proportional to the rate of reaction $\mathrm{d}\xi/\mathrm{d}t$. The latter is calculated using the law of mass action. Analysis of experimental results therefore relies on information concerning the order and molecularity of the chemical reaction in the sample cell. Granted this information, one can compare observed and calculated dependences of $\mathrm{d}q/\mathrm{d}t$ on time and hence test proposed mechanisms of reaction.

In the following we explore the dependence of $\mathrm{d}q/\mathrm{d}t$ on time for model first- and second-order reactions. It is informative to consider the integral of $\mathrm{d}q/\mathrm{d}t$, namely q, as a function of time. In practice the recorded $\mathrm{d}q/\mathrm{d}t$ is also a function of parameters characterizing a given calorimeter. Therefore, it is often necessary to calibrate the calorimeter. We do not consider these operational considerations in the analysis presented below.

FIRST-ORDER REACTIONS

We consider the case where a chemical substance X in aqueous solution undergoes spontaneous chemical reaction to form chemical substance Y in a reaction having rate constant k at temperature T. If the amount of X at $t = 0$ equals n_X^0 mol, then at time t the amounts of X(aq) and Y(aq) are $(n_X^0 - \xi)$ and ξ mol, respectively. Hence the law of mass action for chemical reaction in a sample cell having volume V yields

$$(1/V)(\mathrm{d}\xi/\mathrm{d}t) = (1/V)\ k\ (n_X^0 - \xi) \tag{6}$$

From Eqn. (6) at time t,

$$(\mathrm{d}\xi/\mathrm{d}t) = kV[c_X^0 - (\xi/V)] \tag{7}$$

Here c_X^0 is the concentration of chemical substance X at $t = 0$. Hence with increase in extent of reaction $\mathrm{d}\xi$, the rate of reaction $\mathrm{d}\xi/\mathrm{d}t$ decreases. As required $\mathrm{limit}(t \to \infty)\ (\xi/V) = c_X^0$ and $\mathrm{d}\xi/\mathrm{d}t = 0$. From Eqns (6) and (7),

$$\mathrm{d}\xi/\mathrm{d}t = kVc_X^0 \exp(-kt) \tag{8}$$

Then, from Eqn. (5),

$$\mathrm{d}q/\mathrm{d}t = \Delta_r H^\circ kVc_X^0 \exp(-kt) \tag{9}$$

In terms of numerical analysis there are advantages, confirmed where more complicated reactions are involved, in describing the kinetics of chemical reaction using general equations of the form shown above. According to Eqn. (9), $\mathrm{d}q/\mathrm{d}t$ is positive for an endothermic reaction, reflecting the fact that, using the acquisitive convention, heat flows from the surroundings into the sample cell in order to hold the temperature of the sample cell constant. Similarly, according to Eqn. (9), at $t = 0$ $\mathrm{d}q/\mathrm{d}t$ for an exothermic reaction, equals $\Delta_r H^\circ kVc_X^0$ indicating that heat flows out of the sample cell in order that the temperature of the sample cell remains constant. With increase in rate constant k, the heat flows more rapidly, reflecting rapid chemical reaction in the sample cell (Fig. 1). Plots of $\mathrm{d}q/\mathrm{d}t$ against time approach zero as time t approaches infinity for both exothermic and endothermic reactions (Fig. 2)

The integral of Eqn. (9) yields the amount of heat passing between system and heat sink over the time interval $t = 0$ to t. From Eqn. (5),

$$\int_{t=0}^{t} \mathrm{d}q = \Delta_r H^\circ Vc_X^0[1 - \exp(-kt)] \tag{10}$$

For an exothermic reaction, in the $\mathrm{limit}(t \to \infty)$, the total amount of heat passing between the system and surroundings equals $\Delta_r H^\circ Vc_X^0$, which, again using the acquisitive convention, is negative for an exothermic reaction. Thus, for the system modelled in Fig. 3, as $(t \to \infty)$ q equals -5 J. The integral of $\mathrm{d}\xi$ from $t = 0$ to $t \to \infty$ equals c_X^0/V.

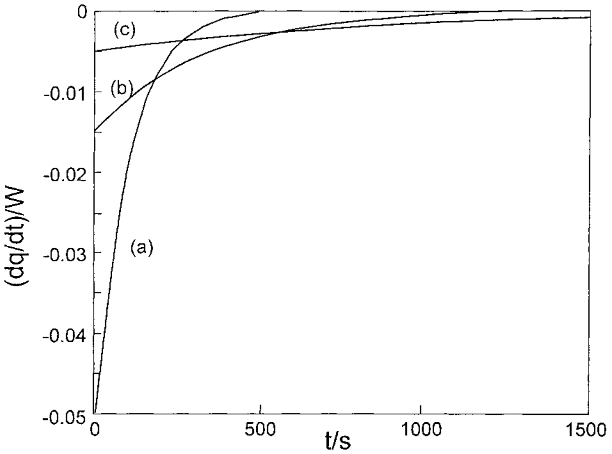

Figure 1. Dependence of $\mathrm{d}q/\mathrm{d}t$ on time for a first-order reaction in a sample cell, volume $5\ \mathrm{cm}^3$, and $\Delta_r H^\circ = -10\ \mathrm{kJ\ mol}^{-1}$; rate constant $k =$ (a) 10^{-2}, (b) 3×10^{-3} and (c) $1 \times 10^{-3}\ \mathrm{s}^{-1}$

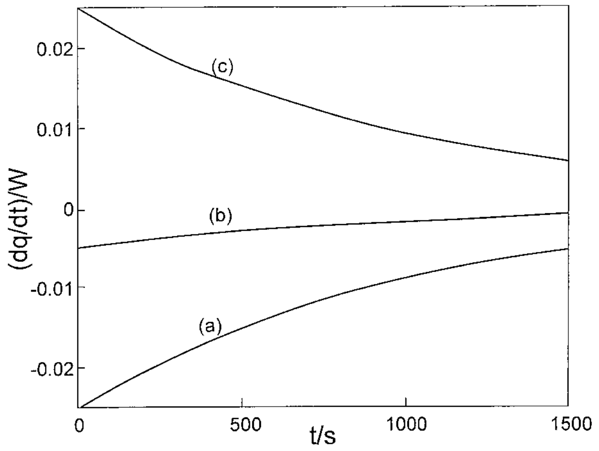

Figure 2. Dependence of d*q*/d*t* on time for a first-order reaction in a sample cell, volume 5 cm^3, where the concentration of reactant X = 0.1 mol dm^{-3} and rate constant $k = 10^{-3}$ s^{-1} and where $\Delta_r H^\circ$ = (a) −50, (b) −10 and (c) + 50 kJ mol^{-1}

SECOND-ORDER REACTIONS

In a given bimolecular reaction in aqueous solution chemical substances X and Y react to form product Z. Then at time *t* (i.e. at extent of reaction ξ), the rate of reaction ($d\xi/dt$) is given by

$$d\xi/dt = k_2 V^{-1}(n_X^0 - \xi)(n_Y^0 - \xi) \tag{11}$$

where V is the volume of the sample cell, or, in terms of concentrations of reactants X and Y, c_X^0 and c_Y^0,

$$d\xi/dt = k_2 V[c_X^0 - (\xi/V)][c_Y^0 - (\xi/V)] \tag{12}$$

As *t* approaches zero for these systems, the limiting d*q*/d*t* is determined by the chemical substance present in the smallest amount. Nevertheless, the general pattern which emerges resembles that calculated for first-order reactions (Fig. 4). The ratio d*q*/d*t* is calculated as a function of time using Eqn. (12) in conjunction with Eqn. (5) with $\Delta_r H^\circ$ for the enthalpy of reaction. In other words, we assume that the thermodynamic properties of the solution are ideal. The ratio d*q*/d*t* shows an initial dramatic increase (for an exothermic reaction) approaching zero in the limit($t \rightarrow \infty$). The integrated heat shows a gradual change to a limiting value determined by $\Delta_r H^\circ$ and the initial concentrations of reactants.

PSEUDO-FIRST-ORDER REACTIONS

In the limit that the concentration of one reactant (e.g. c_Y^0) is significantly higher than c_X^0, the kinetics of reaction in the sample cell can be described using the following equation [cf. Eqn. (12)]:

$$d\xi/dt = k_2 V c_Y^0 [c_X^0 - (\xi/V)] \tag{13}$$

At extent of reaction ξ, the contribution of the solutes to the enthalpy of the solution is given by

$$H(\xi) = (n_X^0 - \xi)H_X^\infty + (n_Y^0 - \xi)H_Y^\infty + \xi H_Z^\infty \tag{14}$$

where we again assume that the thermodynamic properties of the solution are ideal. However, in the limit $c_Y^0 >> c_X^0$,

$$dH/d\xi \cong H_Z^\infty - H_X^\infty \tag{15}$$

The pattern shown by the dependence of d*q*/d*t* on time

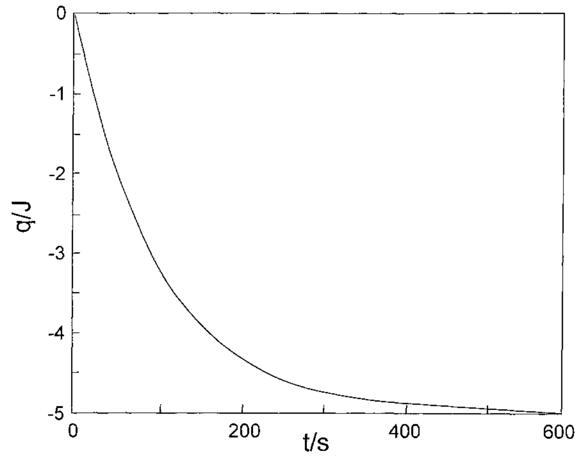

Figure 3. Dependence of *q* on time calculated for a first-order reaction in a reaction vessel, volume 5 cm^3, containing reactant X at a concentration of 0.1 mol dm^{-3}. Rate constant $k = 10^{-2}$ s^{-1} and $\Delta_r H^\circ = -10$ kJ mol^{-1}; limiting *q* at $t = \infty$ equals $[-10^4 \times (5 \times 10^{-6}) \times 100] = 5$ J

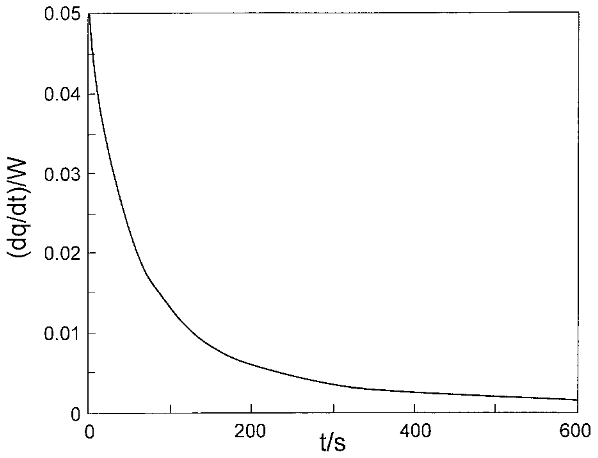

Figure 4. Dependence of d*q*/d*t* on time for a second-order reaction, X + Y → products, where volume of reaction vessel = 5 cm^3, the initial concentrations of both X and Y being 0.1 mol dm^{-3}; rate constant $k = 0.1$ dm^3 mol^{-1} s^{-1} and $\Delta_r H^\circ = 10$ kJ mol^{-1}

through a series of reactions with common substrate X directly reflects the difference in rate constants.

DISCUSSION

The analysis presented here is readily generalized to other types of reaction schemes. In each case an equation is required relating rates of reaction ($d\xi/dt$) to the composition at time t of the system. Then, in conjunction with the rate equation, the form of the predicted dependence of dq/dt is obtained using Eqn. (5).

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