Thermochimica Acta, 92 (1985) 253-255
Elsevier Science Publishers B.V., Amsterdam

KINETIC INTERPRETATION OF DTA CURVES - A PROBLEM BETWEEN ADIABATIC CALORIMETRY, RATE-BASED REACTION KINETICS AND IMPULSE KINETICS

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ABSTRACT

DTA curves reveal six important limiting cases, when they are discussed as functions of the kinetic cell constant and of the maximum signal height Θ_m (or, alternatively, of the specific reaction time u_m):

Values of	c	u_m	Θ_m
1. Ideal adiabatic curve	0	∞	0
2. Heat impulse curve	0	0	∞
3. DTA curve without heat feedback	>0	∞	0
4. Heat-decay curve	>0	0	∞
5. Rate curve without heat feedback	∞	∞	0
6. Rate impulse curve	∞	0	∞

Hence, empirical expressions were developped in order to classify and to interpret DTA signals obtained in uniform solution, independent of physical conditions.

INTRODUCTION

For isothermal kinetic measurements, the usual path to classification based on directly available data is the discussion of the rate constant and their dependence on the amount of active species. In simple cases, the kind of behaviour is characterized by a constant number, the reaction order.

In contrast, for kinetic experiments performed at linearly increased temperature, two independent order-related quantities are available, since the temperature is an additional variable and since bell-shaped rate signals include two geometric characteristics, the signal width (or, alternatively, the height Θ_m) and the asymmetry. The first feature is descriptive of the reaction type index, referred to an assumed first- or second-order reference reaction,

$$M = \frac{E}{h(\lg k_\infty + \lg u_m)^2} \tag{1}$$

including the specific time

$$u_m = \frac{E}{mR(\ln k_\infty + \ln u_m)^2} \approx \frac{R}{mE} T_m^2 , \tag{2}$$

(E = activation energy; k_∞ = A factor; m = heating rate; h = halfwidth; R=gas const) the second of the shape index S. Hence, representations of M = f(S) as a function of both starting concentration of reactant and heating rate represent the best description of the kinetics of a reacting system[1-4].

For DTA, the desired linear change of the reaction temperature with time is

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Proceedings of ICTA 85, Bratislava

falsified by the heat originating from the reaction. Nevertheless, experiments in an "all-liquid" apparatus lead to DTA curves which can be evaluated exactly, using an interpretation based on the mechanistic coordinates S and M of the corresponding rate curve (i. e., transformation to infinite cell constant).

"UC"-THEORY

We have tested a concept which requires for all expressions used that a term u·c (=factor of specific time with cell constant at peak maximum) is dominant. For first-order reactions, first-order heat decay and infinite u_m (i.e., zero signal height Θ_m), the three limiting curves with respect to c-variation are easily available [5], when the temperature program is T = mt:

1. Ideal adiabatic curve $\Theta(t) = \frac{V\Delta H}{C_p} [A]_o [1 - \exp(-uk)]$ (3)
2. Ideal DTA curve (no thermal feedback) $\Theta(t) = \underbrace{\frac{V\Delta H}{C_p}[A]_o}_{\text{Calorific factor}} \cdot \exp[-c(t-t_0)] - \exp(-uk) + c\exp[-c(t-t_0)] \cdot \int_{t_0}^{t} \exp[c(\xi-t_0)-uk]d\xi$ (4)
3. Ideal rate curve $v(t) = [A]_o \cdot \int_{t_0}^{t} k(m\xi) \cdot \exp(-uk) \cdot d\xi,$ (5)

where $uk = \int_{t_0}^{t} k(m\xi)\, d\xi$ (6) and $\ln k(mt) = \ln k_\infty - E/Rmt.$ (7)

Assuming infinite heat feedback ($u_m \to 0$) and zero or infinite heat decay ($c \to 0$ and $c \to \infty$), step functions are only obtained,

4. Heat impulse curve: $\Theta_m(t) = 0$ for $t < t_0$; Θ_m for $t \geq t_0$) (8a,b)
5. Reaction impulse curve: $v_m(t) = 0$ for $t <> t_0$; ∞ for $t = t_0$ (9a,b)

Whilst in these cases the significant time interval is zero, for true, positive and constant c values one obtains the

6. First-order heat-decay curve $\Theta(t) = \Theta_m \exp[-c(t - t_0)]$ (10)

Two further cases ensue from the discussion of finite, nonzero u_m values and zero or infinite cell constant. Simple analytical descriptions are missing here. However, by application of numerical integration we could generate series of theoretical DTA curves due to nonlimiting cases [6,7]. From the results we concluded that

- the term u·c is unique in many empirical, approximate expressions, such as for the calculation of the "ideal" halfwidth and shape index
- for an approximate description of the heat feedback effect, an additional term Θ_m/u_m is mostly sufficient.

The first statement had been expected after tedious endeavours to develop approximate expressions for theoretical DTA curves $\Theta(t)$ [5].

HEAT FEEDBACK

The second statement from above has an analogy in the early studies of N.N. Semenov (Adiabatic Self Ignition Theory in the Gas Phase [8]).Based on the Arrhenius equation and some approximations, Semenov defined for a first-order process a dimensionless temperature (=Semenov temperature)

$$\Theta_s = E(T_1 - T_o)/(RT_o^2) = \ln(k_1/k_2) \qquad (11)$$

when a gas showed self heating from temperature T_O to T_1 (= pre-explosion rise). If the term E/RT_o^2 which is characteristic of the reaction exceeds unity, an explosion must occur. This term is inversely related to the specific time u_m (see eqn. 2) which appears in systems exposed to a time-linear temperature rise [3]. Therefore, also the appearance of a term $\Theta_m/u_m \triangleq (T_2-T_1)/u_m$ wherein T_1 and T_2 correspond to both halftimes is not surprising with view to eqn. 2.

CONCLUSIONS

Based on eqns. 2, 5 and 12, empirical relationships were derived by the evaluation of numerous computer-generated model curves in order to correct the halfwidth and shape index of experimental DTA curves in solution; for a detailed representation, see [6,7,9]. These are plausibly based on known physicochemical laws and are appropriate for an unique kinetic discussion because they reveal and eliminate the influence of physical data (heating rate, cell constant, maximum signal height) and kinetic data (activation energy, preexponential factor). The validity of the expressions was independently proved by picking up the data files of more then hundred first- and second-order experiments of various systems, stored in our computer library which contains more then 2000 experimental files [9]. An access to laws governing complex reaction mechanisms is possible by the use of linear superpositions of the first- and second-order expressions, assisted by comparative computer studies[7].

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