

LIMITING CASES OF DTA CURVES OF ONE-STEP REACTIONS AND THEIR APPLICATION
TO THE STUDY OF COMPLEX PROCESSES

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ABSTRACT

Useful relationships are discussed for DTA studies of reactions in solution which are based on two proved concepts:

1. For missing thermal feedback, i. e. linear increase of the reaction temperature, the influence of the kinetic cell constant, c , appears exclusively as a product with the specific time of the reaction, u .
2. Interference of temperature feedback by the reaction heat is considered by the ratio of the maximum temperature difference (DTA peak height) over the specific temperature difference of the reaction. This can be understood from the Semenov Theory of Thermal Ignition of Gases under Adiabatic Conditions.

INTRODUCTION

With view to the application of DTA to kinetic problems, the following questions arise:

- How may kinetic information be obtained independent of the conditions of measurement?
- What are the most adequate conditions for such measurements?

The usual way to reveal the reaction type or even mechanism is to discuss the reaction rate as a function of the reactant concentrations. In mass-action based isothermal reaction kinetics, the reaction order is the sole quantity for the description of the type of kinetics independently of the activation parameters.

In contrast, for conditions when temperature is equated to time via the heating rate, we have stated the existence of even two key quantities of reaction mechanism which are independent of each other, shape index S and reaction type index M , the latter being available from the halfwidth, h , of the rate curve and a fitted one-step reference reaction with activation data E , k_{∞} (= A factor). These "mechanistic coordinates" yield two corresponding reaction orders, which for unit concentration of the reactant are represented by

$$n_M \approx 0.211 \cdot [(\lg k_{\infty} + \lg u)^2 \cdot h \cdot R/E]^{1.92} \quad (\text{cf. eq. (3)}) \quad (1)$$

$$n_S \approx 1.50 \sqrt{5/(1.82 - S)} \quad (2)$$

For absence of a one-step process, both reaction orders must differ.

THE LIMITING CASES OF DTA CURVES

The striking difficulties in the kinetic discussion of DTA curves are that

- 1) the quantity measured, the temperature difference $\Theta(t)$ between reference and sample, causes a deviation of the reaction temperature from the desirable linear correlation to time,
- 2) the DTA curve maximum shows a lag compared to the rate maximum.

One way to eliminate at least the second problem is to calculate the heat flow curve from the DTA curve by using the Newton temperature balance equation and the kinetic cell constant of first order, which is e. g. admissible in an "all-liquid" apparatus with stirring equipment. However, the resulting curve is still including the heat-feedback effect (=FB). Another concept is the use of a heat-compensating device as original DSC instead of DTA. Nevertheless, DTA has the clear advantage to yield kinetic information not influenced by heat-regulating circuits which could falsify the kinetics by their own time constants. Thus, we preferred the way of revealing the nature of the deviations of the experimental halfwidth (\approx signal width) and shape index (\approx signal asymmetry) from their ideal values, available from the true rate curves. These studies have established a semiempirical theory for the interrelation between heat-decay and chemical reaction during linear temperature rise of the heat bath.

The specific time, u , of a first-order reaction referred to the rate maximum is given by the expression

$$u = E/[mR(\ln k_{\infty} + \ln u)^2] = \frac{R}{mE} \cdot T_m^2 \quad (3)$$

The specific temperature difference is the product of u with the heating rate, m . For a DTA curve, the following limiting cases may be considered:

		c	u	Θ_m	h	S
1. Ideal adiabatic curve		0	∞	0	∞	∞
2. Heat impulse curve		0	0	F	∞	∞
3. "Ideal" DTA curve (no FB)		>0	(∞)	0	h_c	S_c
4. Heat decay curve		>0	0	∞	$\ln 2 \cdot m/c$	∞
5. Ideal rate curve (no FB)		∞	(∞)	0	$2.25 \cdot m \cdot u$	0.58
6. Rate impulse curve		∞	0	∞	0	∞/∞

$F = V \cdot |\Delta H| \cdot [A]_0 / C_p$ = calorific factor (K) (4), ΔH = reaction enthalpy,

Θ_m = maximum temperature difference sample/ref., C_p = heat capacity

Basing on these limiting cases (espec. 3-6), we were able to construct practicable transformation equations for h_{exp} and S_{exp} . Earlier attempts to derive such expressions have been described in my monograph, but were partially unsuccessful.

UC-THEORY

Primarily, we had stated by computer simulations (ref. 1,2)-which were partially restricted to our standard heating rate of 1.5K/min, ref.1 - that for a first-order reaction and small FB ($\Theta_m \ll m \cdot u$), halfwidth and shape index may be represented as follows,

$$h_c = 2.25 m u \frac{uc + a_1/(a_2 + u)}{uc} \quad (5), \quad S_c = 0.58 \frac{(uc)^{1.25} + b_1}{(uc)^{1.25}} \quad (6).$$

(u and c considered as constant; a_1, b_1 empirical constants)

Obviously, the dimensionless product uc is dominating in these expressions; as also in the case of a second-order process (ref. 2).

The effect of temperature feedback is generally taken into consideration by insertion of a term proportional to the ratio $\Theta_m/(mu)$, which again is a dimensionless quantity, a relative temperature change. If, for adiabatic conditions, a reactive gas is heated up from a starting temperature T_0 to temperature T , an explosion must occur if the difference $T - T_0$ is greater than $(R/E) \cdot T_0^2$ (ref.3). The latter term is strictly analogous to the specific temperature difference μ , defined by us via eq. (3) (ref. 1), but instead of T_0 the temperature at the peak maximum, T_m , is used.

The transformation formulae for S and h were tested using experimental DTA curves of more than 100 one-step processes (correlation coefficients of the Arrhenius straight lines > 0.99) with the result that they are generally applicable to the kinetic evaluation of DTA experiments, at least in a stirring equipment (ref. 4). We have used them without any severe difficulties for all experiments since 1969; very slow A-factors ($< 10^8 \text{ min}^{-1}$) reveal deviations from theory which may be corrected by the additional use of a factor $1 + a_2/\lg k_\infty$ for h. The influence of the condition parameters is evident from eqs. (3), (5), (6) and from the table. Either small u or c values restrict the temperature- or time range applicable for the kinetic evaluation, so that it becomes rather difficult to separate the influences of activation energy and A-factor (cf. kinetic compensation effect). Reactions with small activation energy, a high A-factor or the use of small cell constants or fast heating rates (approach to the impulse cases) provide for rather adiabatic conditions, which are less adequate for kinetic studies.

Surprisingly, the height of a DTA peak of a first-order reaction is for the ranges $0.5 < uc < 5$, $|\Delta H| < 100 \text{ kcal/Mol}$ and small FB ($\Theta_m < 0.7$) given by the very simple approximation

$$\Theta_m \approx F \cdot \frac{a_3}{(uc)^n}, \quad \text{using } a_3 \approx 0.5, n \approx 0.7 \quad (7).$$

n is not strictly constant; it may easily be derived that $n = 0$ for disappearing cell constant (adiabatic conditions), but $n = 1$ for infinite c ("rate" conditions, cf. Kissinger 1956). The critical reactant concentration for the explosion limit for DTA in solution can be estimated by relationships based on the FB-term $\Theta_m/(m \cdot u)$, e. g.

c is large:

$$[A]_{\text{crit}} = e \cdot u \cdot c \cdot m \cdot u \cdot F_A \quad (\text{Semenov Theory and Kissinger's assumptions, 1956; (8a)})$$

c is medium: Koch's theory of non-isothermal rate kinetics, 1977)

$$[A]_{\text{crit}} = [8.7 + 0.53 \cdot \ln(uc)] m \cdot u \cdot F_A \quad (\text{computer simulations, ref. 1}) \quad (8b)$$

c is small:

$$[A]_{\text{crit}} = (T_{\text{b.p.}} - T_0) \cdot F_A \quad (\text{boiling point limit; fast kinetics}) \quad (8c)$$

using the abbreviations $e = 2.71828\dots$; $F_A = C_p / (V \cdot |\Delta H|)$; V = reaction volume

CONCLUSION

The "uc-Theory" offers a clue to solve a fundamental kinetic problem by DTA studies, namely calculation of unique kinetic coordinates of a reacting system which represent a pre-stage of the reaction mechanism. Whenever isothermal methods seem not sufficient, for a solution kineticist the DTA method is the most efficient tool for the studies of complex processes showing "slow" initial steps. Therefore, the late but, nevertheless, satisfactory association of the uc-Theory with a physicochemical meaning opens - after our very tedious studies over twenty years - a general experimental access to a novel section of reaction kinetics from the elevated, non-isothermal level, aimed at the classification of kinetic phenomena, and characterized by growing relations to cybernetics, informative theory, graph theory, and molecular dynamics.

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