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THERMAL ASPECTS OF CONSTANT RATE TRANSFORMATION

A. I. Borovikova and *V. A. Logvinenko*

INSTITUTE OF INORGANIC CHEMISTRY, NOVOSIBIRSK, 630090, USSR

A mathematical model for the conjugate formulation of the working conditions of the Q-derivatograph is created. There are no simplifying assumptions about the heat transfer processes for reacting active media and for their thermal interaction with the inert surroundings in this model. The energetic significance of the key components of the transfer and the redistribution of the fluxes is calculated by means of special balance relations. The influence of the kinetic and thermal reaction parameters on the nature of the establishment of the constant transformation rate is demonstrated. The accompanying heat phenomena are studied in detail. The essential differences in the behaviour of the TA system during endo and exothermal transformations are discovered. The exothermal reactions introduce significant irregularities, up to sharp oscillations.

In Q-thermogravimetry one is faced not only with the quasi-equilibrium stages of process evolution, but with the transient processes which precede quasi-equilibrium establishment and accompany the exit from it [1]. The special problem is fully non-uniform processes, without any stabilization

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stages, where it is possible to separate the chemical reactions from the non-chemical (say, the thermal) phenomena only at a non-rigorous level (without an applicable mathematical model). The purpose of the separate treatment of the heat transfer is to examine the heat transfer contribution in the constant rate establishment. Assumptions about low heat exchange, as well as the presence or absence of gradients in the reaction space, are accepted in the detailed models. Ultimately, these assumptions are reflected in the resulting relationship between the transformation rate and external control action.

The conjugate mathematical model is formulated and is solved in order to avoid the potential inaccuracy resulting from such assumptions. For the conjugate description in the modelling part of the thermoanalytical system (TA system), the sample, the holder and the inert gas surroundings are involved up to the surface, where the control action is realized. The mathematical formulation of the conjugate problem is recorded via the differential equation system in partial derivatives:

$$\frac{\partial T}{\partial t} = a\left(\frac{\partial^2 T}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial T}{\partial \rho}\right) + \frac{1}{c\gamma} Q \frac{\partial \alpha}{\partial t}$$

$$Q \leqslant \rho \leqslant r$$

$$\frac{\partial \alpha}{\partial t} = k_o \exp \; -E/_{RT} \; f(\alpha)$$

$$\frac{\partial T_1}{\partial t} = a_1\left(\frac{\partial^2 T_1}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial T_1}{\partial \rho}\right)$$

$$r \leqslant \rho \leqslant r_1$$

$$\frac{\partial T_2}{\partial t} = a_2\left(\frac{\partial^2 T_2}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial T_2}{\partial \rho}\right)$$

$$r_1 \leqslant \rho \leqslant r_2$$

Initial conditions:

$$t = 0: T = T_1 = T_2 = T_o, \quad \alpha = \alpha_0$$

Boundary conditons:

$$\rho = 0: \frac{\partial T}{\partial \rho} = 0; \quad \rho = r: -\lambda_1 \frac{\partial T_1}{\partial \rho} = F(T, Q, \alpha, \ldots), \; T = \mathrm{T}_1;$$

$$\rho = r_1: -\lambda_1 \frac{\partial T_1}{\partial \rho} = -\lambda_2 \frac{\partial T_2}{\partial \rho}, \quad T_1 = T_2;$$

$$\rho = r_2: \; T = T_{\mathrm{det}} + k_\beta \, \beta t + k_\alpha \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t_{\mathrm{det}}} - \frac{\mathrm{d}\alpha}{\mathrm{d}t_{\mathrm{mid}}} \right)$$

The form of the unknown function /$F(T,Q,\mathrm{d},...)$/ after approximation by the conservation scheme, which allows a consideration not only of the heat transfer equations, but also of the energy balance for discrete cells, is:

$$-\lambda_1 \frac{\partial T_1}{\partial \rho}\bigg|_r = -\lambda \frac{\partial T}{\partial \rho}\bigg|_r + \beta \left(Q \frac{\partial \alpha}{\partial t} - c\gamma \frac{\partial T}{\partial t} \right)\bigg|_{r-\Delta\rho} + \mathrm{d} \frac{\partial T}{\partial \rho}\bigg|_{r-\Delta\rho} + h \frac{\partial T_1}{\partial \rho}\bigg|_{r+\Delta\rho} + p \frac{\partial T_1}{\partial t}\bigg|_r$$

The solution of this problem yields the space and time components of the temperature fields for the sample and the inert part of the TA system, the degree and rate of the transformation, and density of heat fluxes. Because the problem is solved numerically, it is necessary to have a large outfit of modifying data to run down the dependences of interest. However, it is difficult to evaluate the influence of the heat processes on the transformation rate, with different dimensions for the heat flux, tranformation rate, and change in temperature rate. A more generalized approach to the result of modelling is now required.

The conservation law was applied with this aim in terms of "heat displacement", according to the variational method [2].

Conservation law:

$$c\gamma \left(T(x,y,z,t) - T_0 \right) = -\mathrm{d}_{\mathrm{IV}} \, H + \int_o^t W \mathrm{d}t$$

H = heat displacement vector,
W = heat source power.

For the sample with the source (in radial coordinates)

$$c\gamma \left(T(\rho,t) - T_0 \right) = -\frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho H) + Q \int_o^t \frac{\partial \alpha(\rho,t)}{\partial t} \mathrm{d}t$$

by definition:

$$\frac{\partial H(\rho,t)}{\partial t} = q\,(\rho,t) = \text{heat flux density}$$

The heat balance in the differencial form is:

$$c\gamma \int_o^r \frac{\partial T(\rho,t)}{\partial t}\,\rho d\rho = -rq\Big|_r(t) + Q\int_o^r \frac{\partial \alpha(\rho,t)}{\partial t}\,\rho d\rho$$

The heat balance in the integral form is:

$$c\gamma \int_o^r (T(\rho,t) - T_0)\,\rho d\rho = -r\int_o^t q\Big|_r(t)\mathrm{d}t + Q\int_o^t\int_o^r \frac{\partial \alpha(\rho,t)}{\partial t}\,\rho d\rho\,\mathrm{d}t$$

Thus, all part of the balance are presented in a form which allows observation of both the features of the components and their energy significance. The linear heating is a particular case of the described equation system [3]. Figures 1 and 2 demonstrate the heat balances for endo-and exo-thermal transformations.

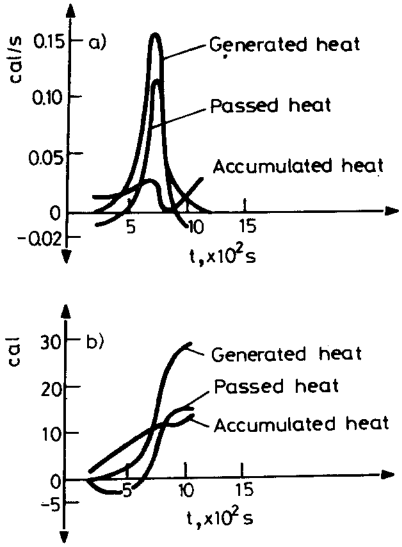

Fig. 1 Sample differential (a) and integral (b) heat balances for exothermal reaction (linear heating, $\beta = 5$ deg/min). Initial data: $E = 22$ kcal/mol, $K_o = 1.6 \cdot 10^{11}$ $s^{-1}, n = 1, Q = 100$ cal/cm^3, $\lambda = 0.0024$ cal/cm s deg, $c\gamma = 0.528$ cal/cm^3 deg, $\lambda_1 = 0.0002$ cal/cm s deg, $c_1\gamma_1 = 0.6$ cal/cm^3 deg, $r = 0.25$ cm, $r_1 = 0.31$ cm.

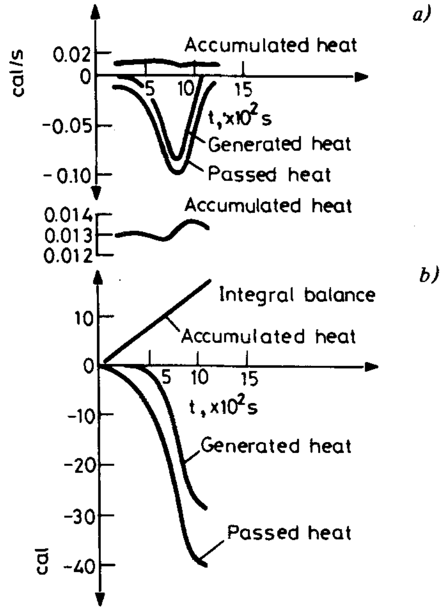

Fig. 2 Sample differential (*a)*) and integral (*b)*) heat balances for endothermal reaction (linear heating $\beta = 5$ deg/min). Initial data: $Q = -100$ cal/cm^3, $\lambda_1 = 0.2$ cal/cm s deg, $c_1 \gamma_1 = 0.6$ cal/cm^3 deg Other data as in Fig. 1.

We will present the results of modelling for the Q-working conditions, varying the parameters of the reaction itself. The characteristics of the inert part of the system remain constant. Special calculations for the zero thermal effect of the reaction demonstrate the important role of this parameter in the stabilization process (Fig. 3). The initial superheating is reversed by the temperature drop. This reveals the possibilities of combinations of the reaction and the system features which cause substantial non-uniformity. However, we get accustomed only to chemical explanations of such non-uniformity, say the nuclear growth during the induction period.

Figure 4 shows temperature curves for them same case. For the zero thermal effect, the temperature course at the sample centre exhibits oscillation behaviour. Figure 5 demonstrates the time plot of the heat flux density on the holder surface. For the zero thermal effect, the flux diverts the direction. This means that the task of maintenance of a constant transformation rate, not backed up by heat absorption, calls for heat removal sometimes.

The conditional character of the preselected transformation rate is absolutely evident during work with our model. We are inclined to regard the

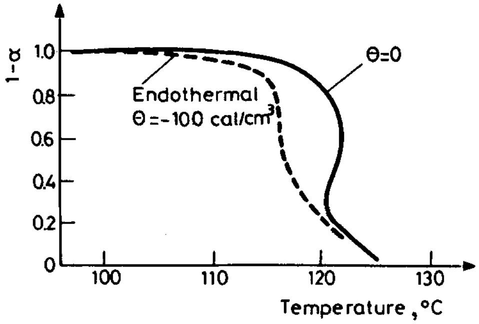

Fig. 3 Influence of thermal effect values on course of transformation. Initial data: * $E = 47.51$ kcal/mol, $K_o = 1.0\cdot10^{23}\ \mathrm{s}^{-1}$, $n = 2/3$, $\frac{d\alpha}{dt_{\mathrm{det}}} = 5\cdot10^{-4}\ \mathrm{s}^{-1}$.

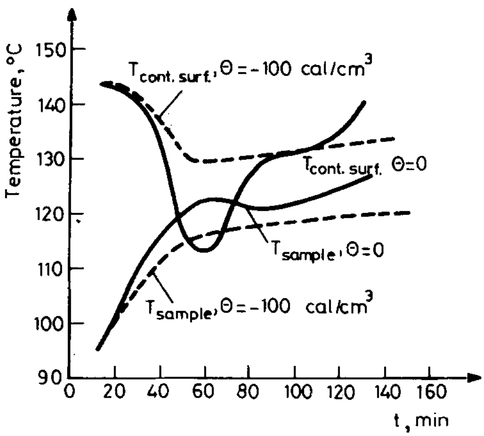

Fig. 4 Temperature at sample centre and control action surface (initial data as in Fig. 3).

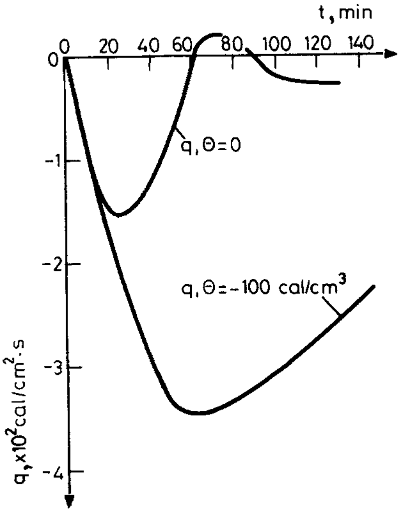

Fig. 5 Time course of heat flux density on sample surface ($\rho = r$, initial data as in Fig. 3).

accurate attainment of a preselected transformation rate as a rather exceptional case. In general, the existence of a heat feed-back through the transformation rate only favours the tendency of the TA system to a certain likely thermal steady-state. Figure 6 illustrates this idea.

We have paid attention to the features of the heat balances in the sample while discussing the dynamic regime. Figure 7 shows the differential balance, conforming to the first curve of Figure 6 (without the steady-state).

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* The parameters of the inert part of the TA system and the thermal properties and geometry of the sample are the same for Figs 3–10.

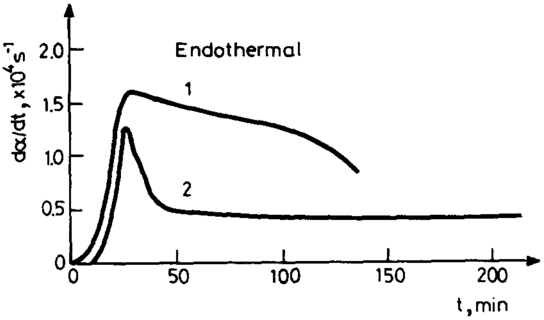

Fig. 6 Influence of kinetic parameters on course of transformation. Curve 1: $E = 47.51$ kcal/mol, $K_o = 1.0 \cdot 10^{23}$ s^{-1}, $n = 2/3$, $Q = -207$ cal/cm^3; curve 2: $E = 31.0$ kcal/mol, $K_o = 1.0 \cdot 10^{16}$ s^{-1}, $n = 2/3$, $Q = -170$ cal/cm^3.

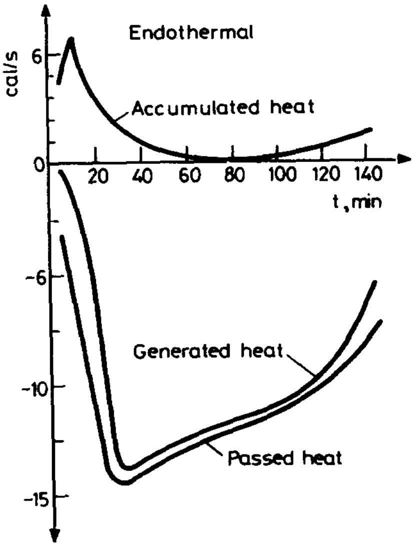

Fig. 7 Differencial heat balance for sample (initial data as in Fig. 6, curve 1). Rate constancy is not reached.

Thermal equilibrium is not established here. As concerns dynamic heating, the differential balance has the peculiarity that the rates of heat generation and heat transfer are rather close to each other and constant in sign. They are energetically more important than the heat accumulation in the sample. The heat transfer is a guide to the rate. The control action process of the transformation rate for the exothermal reaction displays absolutely different behaviour (Fig. 8). Unlike the above-discussed endothermal cases, the indication is the presence of a sharply pronounced oscillation for the transformation rate. The sample temperature exhibits oscillation, as well as the heat flux. Moreover, the heat flux density becomes sign-reversible. It is known, that the reverse reaction is exothermal; it is the exothermicity which produces the key irregularity in the process.

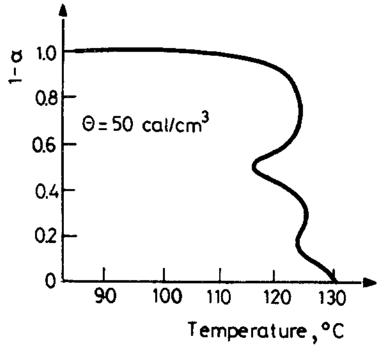

Fig. 8 Character of transformation for exothermal reaction. Initial data: $E = 47.51$ kcal/mol, $K_o = 1.0 \cdot 10^{23}$ s^{-1}, $n = 2/3$, $Q = -50$ cal/cm^3.

The TA system is susceptible to the form of the kinetic function in the reaction rate equation. Let us discuss one more case: the non-dependence of the heat feed-back on the current conversion amount (with the reaction order equal to zero). Figure 9 demonstrates the transformation rate and the heat flux density. The ideal thermal steady-state begins after a conversion of 25% and continues till the end of conversion. Thus, at a steady transformation rate the intensity of heat generation and transfer can be unspecified, but their equality is obligatory. For this case we observe not the dying-down of the heat transfer processes, but their selective redistribution (Fig. 10).

The mathematical tools we use for the heat transfer description are valid for the mass transfer description also. This applies to the equations involving the partial derivatives of the diffusion type, as well as to the concept of the "displacement" (of heat and mass). We plan to use these tools for study of the remaining types of transfer and their inter-influence in the future.

Symbols used: T = temperature, K; α = conversion amount; t = time, s; ρ = current radius, cm; r = fixed radius, cm; $a = \lambda/c\gamma$, where λ = heat conductivity, cal/cm s deg; c = heat capacity, cal/g deg γ = density, g/cm^3; β = external heating rate, deg/s; Q = reaction thermal effect, cal/cm^3; E = activation energy, kcal/mol; K_0 = preexponential factor, s^{-1}; n = reaction

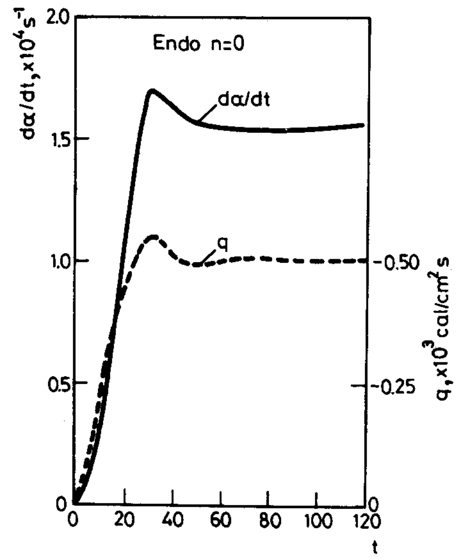

Fig. 9 Influence of kinetic function on process course: the upper curve relates to the transformation rate, and the lower one to the heat flux ($\rho = r$). Initial data: $E = 47.51$ kcal/mol, $K_o = 1.0\cdot 10^{23}$ s^{-1}, $n = 0$, $Q = -207$ cal/cm^3.

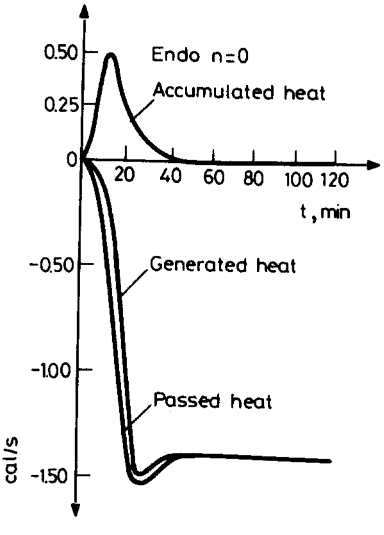

Fig. 10 Differential heat balance for sample. Temperature stabilization is reached (initial data as in Fig. 9.).

order; $\Delta\rho$ = size of calculated discrete cell, cm, $0.05r$; K_β and K_α = coefficients for the imitation of Q-working conditions; β, d, h and p = coefficients, dependent on the thermal properties and geometry of the sample and of the holder.

Indices: 0 = for initial time values; 1 = for the holder; 2 = for the gas surroundings; det = for the preselected values; mid = for the calculated values, after integration and averaging.

References

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2 M. Biot, Variational principles in the heat exhange theory, Moscow, 1975 (Russian translation).

3 A. I. Borovikova and F. Ja. Gimelshein, Proceed. Eighth All-Union Conf. on Thermal Analysis, Kujbishev (1983) 8.

Zusammenfassung – Für die Arbeitsbedingungen des Q-Derivatographen wird ein mathematisches Modell aufgestellt. Dabei werden keine vereinfachenden Annahmen über die Wärmetransportprozesse für die reagierenden Stoffe und über ihre thermische Wechselwirkung mit der inerten Umgebung gemacht. Die Energien der entscheidenden Beiträge des Transports und der Verteilung der Ströme werden mit speziellen Bilanzbeziehungen berechnet. Der Einfluss der kinetischen und thermischen Reaktionsparameter auf die Einstellung einer konstanten Umwandlungsgeschwindigkeit wird gezeigt, die entsprechenden thermischen Vorgänge werden im einzelnen untersucht. Die wesentlichen Unterschiede im Verhalten des Systems bei endo- und exothermen Vorgängen werden aufgezeigt, exotherme Reaktionen bewirken erhebliche Schwankungen bis zu deutlichen Oszillationen.

РЕЗЮМЕ — Создана математическая модель с учетом условий работы Q-дериватографа. В представленной модели нет упрощающих предположений о процессах теплопереноса реакционной среды и их термического взаимодействия с окружающей инертной средой. Энергия этих ключевых компонент переноса и перераспределения потоков была вычислена с помощью специальных уравнений баланса. Показано влияние кинетических параметров и параметров термической реакции на установление постоянной скорости превращения. Детально обсуждено сопровождающее при этом тепловое явление. Установлены существенные различия в поведении ТА системы при эндо- и экзотермических превращениях. Экзотермические реакции вводят значительные нерегулярности вплоть до резких колебаний.