

THERMOANALYTICAL STUDIES OF THE KINETIC OF REVERSIBLE REACTIONS

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A method is described for determination of the kinetic parameters of reversible reactions under isothermal and non-isothermal conditions in thermal analysis. Reversible reactions of the first and second orders and of mixed types are considered. The kinetic parameters of the forward and reverse reactions are determined on the basis of the initial integral data of the thermoanalytical experiment. The results of processing a computerized experiment demonstrated that the suggested method is satisfactorily applicable.

A reaction is reversible if the reaction products are capable of reacting and reproducing the initial substances. Strictly speaking, any chemical reaction is reversible. However, in the majority of cases the equilibrium of the reaction is largely shifted towards one or the other side, and hence the reaction appears practically to proceed in one direction. If the rates of the forward and reverse reaction are comparable within the investigated temperature and concentration ranges, the reaction is said to be reversible, characterized by a decrease in the observed reaction rate as the reaction products accumulate. Finally, dynamic equilibrium is established, in which the forward and the reverse reaction proceed at equal rates and the overall rate observed experimentally is zero.

To determine the kinetic parameters of reversible reaction experimentally, it is not sufficient to know the type of the reactions; it is also necessary to follow the product concentrations in the course of the reaction. It is therefore an actual problem to determine the effective kinetic constants of the forward and reverse reactions under thermoanalytical conditions, when integral data are obtained (usually a mass or heat change in the course of the reaction). This paper deals with the solution of this problem.

The general form of the reversible reaction is $aA + bB \rightleftharpoons cC + dD$. Depending on the values of the coefficients, reversible reactions may be of the first order (both the forward and reverse reaction being of the first order), of a mixed type (one of the

reactions being of the first order, and the other of the second order), or of the second order (both the forward and the reverse reaction being of the second order). All possible types of reversible reactions are listed in Table 1.

Let us consider the scheme of studying reversible reactions under the conditions of isothermal calorimetric thermal analysis (differential thermal analysis or differential scanning calorimetry). In the experiments, the temperature T , the rate of heat evolution \dot{q} , and the current and final heat evolution absorption q and q_∞ are determined. Without limiting the generality of the following discussion we will assume that the forward reaction is exothermic and the reverse reaction endothermic. In this case, the relationship between the activation energy of the forward reaction E_1 and that of the reverse reaction E_2 is [2, 3] $E_2 - E_1 = Q$, where Q is the thermal effect of the forward reaction (in the reverse case, $E_1 = E_2 + |Q|$) and q and $\dot{q} > 0$.

Reversible reaction of the first order: $A \rightleftharpoons C$

The rate of heat evolution in the forward reaction is

$$\dot{q}_1 = QK_1 \left[A_0 - \frac{q_1}{Q} + \frac{q_2}{Q_*} \right] \quad (1)$$

and that in the reverse reaction is

$$\dot{q}_2 = Q_*K_2 \left[C_0 + \frac{q_1}{Q} - \frac{q_2}{Q_*} \right] \quad (2)$$

where A_0 and C_0 are the initial molar concentrations of the starting substance and the reaction product, respectively; $K_1 = K_{10} \exp(-E_1/RT)$; $K_2 = K_{20} \exp(-E_2/RT)$ are the rates of the forward and the reverse reaction, respectively; Q_* is the thermal effect of the reverse reaction ($Q_* = -Q$); and 1 and 2 are subscripts indicating the forward and the reverse reaction, respectively.

$$\dot{q} = \dot{q}_1 + \dot{q}_2 = Q(A_0K_1 - C_0K_2) - (K_1 + K_2)q \quad (3)$$

taking into account that $\dot{q} = q_1 + q_2$.

Solving Eq. (3), we can establish the relationships $q(t)$ and $\dot{q}(t)$;

$$q = \frac{Q(A_0K_1 - C_0K_2)}{K_1 + K_2} [1 - e^{-(K_1 + K_2)t}] \quad (4)$$

$$\dot{q} = Q(A_0K_1 - C_0K_2) e^{-(K_1 + K_2)t}$$

At $t = \infty$, $\dot{q} = 0$ and the dynamic equilibrium of the forward and reverse reaction is established. The overall heat q_∞ evolved in the experiment is then

Table 1

No.	Type reaction	Parameters of straight	$\frac{q}{m} = \frac{q_\infty - q}{n + m(q_\infty + n)}$		q_∞
			n	m	
1	$A \rightleftharpoons C$	$K_1 + K_2$	—	—	$\frac{Q K_1 A_0}{K_1 + K_2}$
2	$A \rightleftharpoons C + D$	K_1	$\frac{K_2}{Q}$	—	$-\frac{K_1 + \sqrt{K_1^2 + 4K_1 K_2 A_0}}{K_2/Q}$
3	$A \rightleftharpoons C + C$	K_1	$\frac{4K_2}{Q}$	—	$-\frac{K_1 + \sqrt{K_1^2 + 16A_0 K_1 K_2}}{8K_2/Q}$
4	$A + B \rightleftharpoons C + D$	$K_1(A_0 + B_0)$	$-\frac{[K_1 - K_2]}{Q}$	—	$\frac{K_1(A_0 + B_0) - \sqrt{K_1^2(A_0 + B_0)^2 - 4K_1 A_0 B_0(K_1 + K_2)}}{2(K_1 - K_2)/Q}$
5	$A + B \rightleftharpoons C + C$	$K_1(A_0 + B_0)$	$-\frac{[K_1 - 4K_2]}{Q}$	—	$\frac{K_1(A_0 + B_0) - \sqrt{K_1^2(A_0 + B_0)^2 - 4A_0 B_0 K_1(K_1 - 4K_2)}}{2(K_1 - 4K_2)/Q}$
6	$A + A \rightleftharpoons C + D$	$2A_0 K_1$	$-\frac{[4K_1 - K_2]}{Q}$	—	$\frac{2A_0 K_1 - \sqrt{4A_0^2 K_1^2 - A_0^2 K_1(4K_1 - K_2)}}{2(4K_1 - K_2)/Q}$
7	$A + A \rightleftharpoons C + C$	$4A_0 K_1$	$-\frac{4(K_1 - K_2)}{Q}$	—	$\frac{A_0 K_1 - \sqrt{A_0^2 K_1^2 - A_0^2 K_1(K_1 - K_2)}}{2(K_1 - K_2)/Q}$
8	$A + B \rightleftharpoons C$	$K_1(A_0 + B_0) + K_2$	$-\frac{K_1}{Q}$	—	$\frac{(K_1(A_0 + B_0) + K_2) - \sqrt{[K_1(A_0 + B_0) + K_1]^2 - 4A_0 B_0 K_1^2}}{2K_1/Q}$
9	$A + A \rightleftharpoons C$	$4A_0 K_1 + K_2$	$-\frac{4K_1}{Q}$	—	$\frac{[4A_0 K_1 + K_2] - \sqrt{(4A_0 K_1 + K_2)^2 - 16A_0^2 K_1^2}}{8K_1/Q}$

$$q_{\infty} = \frac{Q(A_0K_1 - C_0K_2)}{K_1 + K_2} \quad (5)$$

This value of q_{∞} may also be obtained from Eq. (3) at $\dot{q}=0$.

Hence, the indication that a reversible reaction of the first order proceeds is a linear relationship $\dot{q}(q)$. The absolute value of the slope of this line is $m = (K_1 + K_2)$, and its intercept with the ordinate axis is $n = Q(A_0K_1 - C_0K_2)$. The unknown thermokinetic constants to be determined are K_{10} , K_{20} , E_1 and E_2 . If Q is known, then, by experimentally determining m and n we obtain

$$K_1 = \frac{QC_0m+n}{Q(A_0+C_0)}; \quad K_2 = \frac{QA_0m+n}{Q(A_0+C_0)} \quad (6)$$

If a series of experiments are carried out at different temperatures and the relationships $\ln K_1$ and $\ln K_2$ are plotted vs. $1/T$, all parameters to be determined can be found graphically. They can also be determined algebraically by carrying out two experiments at T_1 and T_2 . It is easily shown from Eq. (6) that

$$E_1 = P \ln \frac{QC_0m_2+n_2}{QC_0m_1+n_1} \quad (7)$$

where $P = (T_2 - T_1)/RT_1T_2$, and $E_2 = E_1 + Q$. Determining E_1 and E_2 from Eq. (6), we can obtain the values of K_{10} and K_{20} ($K_{i0} = K_i \exp(E_i/RT_i)$, $i = 1, 2$).

If Q is not known in advance, its value can be determined in the following manner:

$$\frac{K_1(T_2)}{K_1(T_1)} = \frac{QC_0m_2+n_2}{QC_0m_1+n_1} = e^{PE_1}$$

$$\frac{K_2(T_2)}{K_2(T_1)} = \frac{QA_0m_2-n_2}{QA_0m_1-n_1} = e^{PE_2}$$

Then

$$\frac{(QA_0m_2-n_2)(QC_0m_1+n_2)}{(QA_0m_1-n_1)(QC_0m_2+n_2)} = e^{PQ} \quad (8)$$

is a transcendental equation for determining the value of the thermal effect Q of the reaction. We can then calculate all other kinetic constants as described above.

It should be noted that the linear relationship $\dot{q}(q)$ is also characteristic for one-stage irreversible reactions of the first order and for two parallel one-stage monomolecular reactions [4]. However, it is easy to demonstrate that, for reversible reactions, the straight lines obtained in the coordinates $\dot{q}(q)$ at temperature change intersect, whereas this is not the case for one-stage monomolecular reactions and

two parallel monomolecular reactions. Additionally, only reversible reactions are characterized by changes in the relationship rate of heat evolution vs. heat evolution, \dot{q} vs. q , when an unchanged amount of the starting substance is diluted by the end-product.

Mixed-type reversible reaction: $A \rightleftharpoons C + D$

For simplicity's sake, let us assume that $C_0 + D_0 = 0$, though the calculation scheme is also valid when the initial concentrations of the products differ from zero. The rate of heat evolution in the forward reaction is

$$\dot{q}_1 = QK_1 \left[A_0 - \frac{q_1}{Q} + \frac{q_2}{Q_*} \right]$$

that in the reverse reaction is

$$\dot{q}_2 = Q_*K_2 \left[\frac{q_1}{Q} - \frac{q_2}{Q_*} \right]$$

and the overall rate of heat evolution observed experimentally is

$$\dot{q} = Q(A_0K_1) - K_1q - \frac{K_2q^2}{Q} \quad (9)$$

The general form of this parabolic relationship is shown in Fig. 1a. In the experiment, for an exothermic forward reaction, a preferential part of the parabola will appear with q changing from zero to q_∞ .

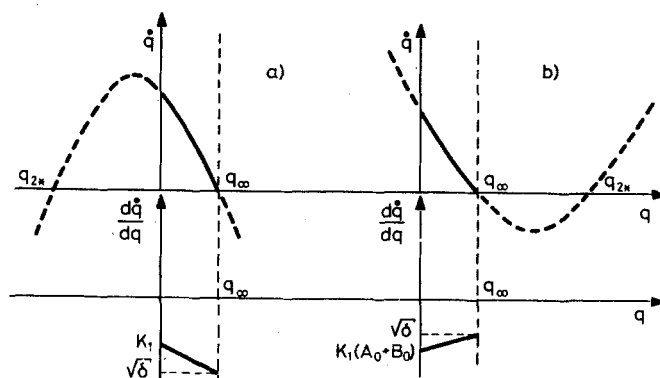


Fig. 1 Qualitative form of the relationships \dot{q} vs. q and $d\dot{q}/dq$ vs. q for reversible reactions, (a) mixed-type reaction, (b) second-order reactions

By solving Eq. (9), we can establish the relationships $q(t)$ and $\dot{q}(t)$;

$$q(t) = \frac{2a(1 - e^{-\sqrt{\delta}t})}{(b + \sqrt{\delta}) \left(1 - \frac{b - \sqrt{\delta}}{b + \sqrt{\delta}} e^{-\sqrt{\delta}t} \right)} \quad (10)$$

$$\dot{q}(t) = \frac{4a\delta e^{-\sqrt{\delta}t}}{(b + \sqrt{\delta})^2 \left(1 - \frac{b - \sqrt{\delta}}{b + \sqrt{\delta}} e^{-\sqrt{\delta}t} \right)^2}$$

where $a = QA_0K_1$, $b = K_1$ and $\delta = K_1^2 + 4A_0K_1K_2$.

Under conditions of dynamic equilibrium, it follows from Eqs (9) and (10) that the overall heat evolved in the experiment is

$$q_\infty = \frac{2QA_0K_1}{K_1 + \sqrt{K_1^2 + 4A_0K_1K_2}} = \frac{Q}{RK_2} [\sqrt{K_1^2 + 4A_0K_1K_2} - K_1] \quad (11)$$

It is characteristic of such a mixed-type reversible reaction that the value of \dot{q} decreases sharply with increasing q , owing to the reverse endothermic reaction being of a higher order than the forward reaction. Therefore, with increasing q , the absolute value of $\frac{d\dot{q}}{dq}$ increases from K_1 to $\sqrt{\delta}$ (Fig. 1a).

To identify this type of reaction and to determine the kinetic parameters, the quadratic equation (9) can be written in the following form:

$$\dot{q} = \frac{K_2}{Q} (q_{1*} - q)(q - q_{2*}) \quad (12)$$

where q_{1*} and q_{2*} are the roots of the equation at which \dot{q} becomes zero. Since $\dot{q} = 0$ when the process passes into dynamic equilibrium, one of these roots is $q_{1*} = q_\infty$. It then follows from Eq. (12) that the following relationship is valid:

$$\frac{\dot{q}}{q_\infty - q} = \frac{K_2}{Q} (q - q_{2*})$$

where the second root is $q_{2*} = \frac{K_1 - \sqrt{\delta}}{2K_2/Q}$. Expressing $\sqrt{\delta}$ by q_∞ from Eq. (11), we finally obtain

$$\frac{\dot{q}}{q_\infty - q} = K_1 + \frac{K_2}{Q} (q + q_\infty) \quad (13)$$

Thus, for mixed-type reversible reactions, linearization in the coordinates $\dot{q}/(q_\infty - q)$ vs. $(q_\infty + Q)$ is characteristic. For this straight line, $m = K_2/Q$ and

$n = K_1$. By carrying out a series of experiments at different temperatures and plotting the relationship $\ln n$ vs. $1/T$, we can simultaneously determine K_{10} and E_1 . We can determine the values of K_2 and Q (if they are unknown) in the following manner. Since $n/m = QK_1/K_2$ and $E_2 = E_1 + Q$, we obtain $n/m = QK_{10} \exp(Q/RT)/K_{20}$. By plotting the relationship $\ln \frac{n}{m}$ vs. $1/T$, from the slope of this line, we can determine the value of Q and subsequently E_2 and $K_{20} = mQ \exp(E_2/RT_0)$. All these kinetic parameters can also readily be obtained algebraically from the data of two experiments carried out at temperatures T_1 and T_2 . It is easy to demonstrate that the following relationship are valid:

$$E_1 = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{n_2}{n_1}; \quad Q = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{n_1 m_2}{n_2 m_1} \quad (14)$$

The value of Q can also be calculated on the basis of q_∞ . Since $K_2 = Qm$, it follows from Eq. (11) that

$$Q = \frac{q_\infty(n + q_\infty m)}{A_0 n} \quad (15)$$

Reversible reactions of the second order: $A + B \rightleftharpoons C + D$

Under the conditions $C_0 = D_0 = 0$. We have the following equations:

$$\dot{q}_1 = QK_1 \left[A_0 - \frac{q_1}{Q} + \frac{q_2}{Q_*} \right] \left[B_0 - \frac{q_1}{Q} + \frac{q_2}{Q_*} \right] \quad (16)$$

$$\dot{q}_2 = Q_* K_2 \left[\frac{q_1}{Q} - \frac{q_2}{Q_*} \right]$$

and, since $Q_* = -Q$, we obtain

$$\dot{q} = K_1 A_0 B_0 Q - K_1 (A_0 - B_0) q + \frac{K_1 - K_2}{Q} q^2 \quad (17)$$

This equation is of the same type as that for the mixed-type reversible reaction, Eq. (9). The common form of this parabolic relationship is shown in Fig. 1b. For reversible reactions of this type, a slight decrease in the value of \dot{q} with increasing q is characteristic, as a result of the forward and reverse reactions being of the same order. Therefore, in contrast to the mixed-type reaction, $d\dot{q}/dq$ will decrease in absolute value with time (with increasing q) from

$$K_1(A_0 + B_0) \quad \text{to} \quad \sqrt{K_1^2(A_0 + B_0)^2 - 4K_1 A_0 B_0 (K_1 - K_2)}:$$

The overall amount of heat evolved in this type of reversible reaction is

$$q_{\infty} = \frac{K_1(A_0 + B_0) - \sqrt{K_1^2(A_0 + B_0)^2 - 4K_1A_0B_0(K_1 - K_2)}}{2(K_1 - K_2)Q} =$$

$$= \frac{2K_1A_0B_0Q}{K_1(A_0 + B_0) + \sqrt{K_1^2(A_0 + B_0)^2 - 4K_1A_0B_0(K_1 - K_2)}} \quad (18)$$

For $q(t)$ and $\dot{q}(t)$, relationships of the type in Eq. (10) are valid, where $a = QK_1A_0B_0$, $b = K_1(A_0 + B_0)$ and $\delta = K_1^2(A_0 + B_0)^2 - 4K_1A_0B_0(K_1 - K_2)$. Processing Eq. (17) analogously to Eq. (12), we obtain

$$\frac{\dot{q}}{q_{\infty} - q} = K_1(A_0 + B_0) - \frac{K_1 - K_2}{Q}(q_{\infty} + q) \quad (19)$$

i.e. a relationship of the same form as in the case of mixed-type reversible reactions. Hence, the scheme for determining kinetic parameters in this case is fully analogous to the former one.

It should be noted that the linear relationship $\dot{q}/(q_{\infty} - q)$ vs. $(q_{\infty} + q)$ is characteristic for all types of reversible reactions, i.e. in the kinetic context all possible cases are analogous to one another. In Table 1, the values of parameters m and n for these straight lines are listed for all possible types of reversible reactions. If $m=0$ and $n>0$, the reaction is of type 1. If m and $n>0$, and the relationship $\ln m$ vs. $1/T$ is linear, the reaction is of the type 4, 5, 6, 7. Full identification of the type of reversible reactions is possible only if the one-component or two-component starting material and the reaction products are known.

For reversible reactions, the most essential kinetic information is that relating to the state of dynamic equilibrium reached in the system, namely the concentrations of the reactants in the equilibrium state and the equilibrium constant $K = K_1/K_2$. For the reversible reactions considered above, if the type of the reaction and its thermal effect have been established, these data can be obtained, merely from the experimentally determined overall heat evolution in the course of the reaction, q_{∞} .

The accuracy of determination of the kinetic parameters in the described manner depends on the accuracy of the temperature, q and \dot{q} measurements. If the accuracy of temperature measurement is 1 deg, and the accuracy of q and \dot{q} measurements is 2% (these values being fully realistic for modern thermoanalytical instruments), evaluation of the error in the activation energy determined via Eqs (7) and (14) yields a value of the order of 5%.

To check the proposed schemes for determining kinetic parameters, a computerized experiment was carried out; the initial parameters were: $K_{10} = 10^5 \text{ s}^{-1} (10^{-6} \text{ m}^3/\text{mol})^2$; $K_{20} = 2.3 \cdot 10^7 \text{ s}^{-1} (10^{-6} \text{ m}^3/\text{mol})^2$;

Table 2

Type of reaction	K	Equilibrium concentration of components			
		A _p	B _p	C _p	D _p
A⇌B	$\frac{q_\infty}{Q A_0 - q_\infty}$	$A_0 - \frac{q_\infty}{Q}$	—	$C_0 + \frac{q_\infty}{Q}$	—
A⇌C+D	$\frac{q_\infty^2}{[Q A_0 - q_\infty] Q}$	$A_0 - \frac{q_\infty}{Q}$	—	$\frac{q_\infty}{Q}$	$\frac{q_\infty}{Q}$
A⇌C+C	$\frac{4q_\infty^2}{Q [Q A_0 - q_\infty]}$	$A_0 - \frac{q_\infty}{Q}$	—	$\frac{2q_\infty}{Q}$	—
A + B⇌C+D	$\frac{q_\infty^2}{A_0 B_0 Q^2 - Q q_\infty [A_0 + B_0] + q_\infty^2}$	$A_0 - \frac{q_\infty}{Q}$	$B_0 - \frac{q_\infty}{Q}$	$\frac{q_\infty}{Q}$	$\frac{q_\infty}{Q}$
A + B⇌C+C	$\frac{4q_\infty^2}{A_0 B_0 Q^2 - (A_0 + B_0) Q q_\infty + q_\infty^2}$	$A_0 - \frac{q_\infty}{Q}$	$B_0 - \frac{q_\infty}{Q}$	$\frac{2q_\infty}{Q}$	—
A + A⇌C+D	$\frac{q_\infty^2}{A_0^2 Q^2 - 4A_0 Q q_\infty + 4q_\infty^2}$	$A_0 - \frac{2q_\infty}{Q}$	—	$\frac{q_\infty}{Q}$	$\frac{q_\infty}{Q}$
A + A⇌C+C	$\frac{4q_\infty^2}{[A_0 Q - 2q_\infty]^2}$	$A_0 - \frac{2q_\infty}{Q}$	—	$\frac{2q_\infty}{Q}$	—
A + B⇌C	$\frac{Q q_\infty}{A_0 B_0 Q^2 - q_\infty Q (A_0 + B_0) + q_\infty^2}$	$A_0 - \frac{q_\infty}{Q}$	$B_0 - \frac{q_\infty}{Q}$	$\frac{q_\infty}{Q}$	—
A + A⇌C	$\frac{Q q_\infty}{[A_0 Q - 2q_\infty]^2}$	$A_0 - \frac{2q_\infty}{Q}$	—	$\frac{q_\infty}{Q}$	—

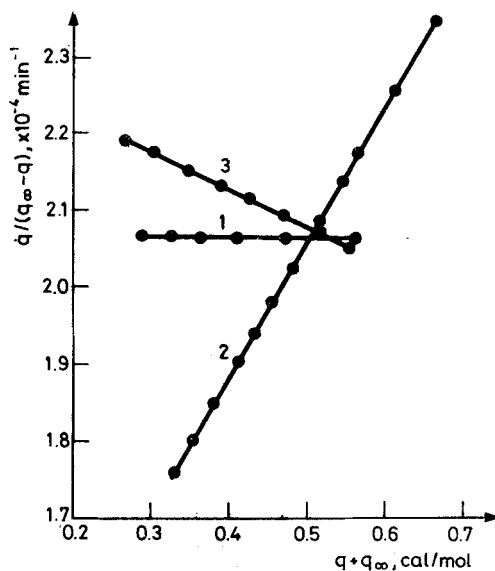


Fig. 2 Relationship $\dot{q}/q_\infty - q$ vs. $q_\infty + q$ for reversible reactions, (1) first-order reactions, (2) mixed-type reactions, (3) second-order reactions

$E_1 = 41.8$ kJ/mol; $E_2 = 62.7$ kJ/mol; $Q = 20.9$ kJ/mol; $A_0 = B_0 = 1$; and $C_0 = D_0 = 0$. Here $s = 0$ and 1 , respectively, for monomolecular and bimolecular reactions. Reversible reactions of the first order ($A \rightleftharpoons C$), of the second order ($A + B \rightleftharpoons C + D$) and of the mixed type ($A \rightleftharpoons C + D$) were considered. The relationship $(\dot{q}/q_\infty - q)$ vs. $(q_\infty + q)$ for these reaction types is shown in Fig. 2, demonstrating that in these coordinates linearization is in fact observed, and that the slope of the straight line is positive for the mixed-type reaction and negative for the second-order reaction. In Table 3, the characteristic parameters m and n are listed, together with q and the calculated values of the thermokinetic parameters. The agreement between the initial and calculated parameters of the forward and reverse reactions demonstrates that the proposed method is well suited for the thermoanalytical study of reversible reactions.

The schemes discussed above are intended for calorimetric thermal analysis; however, they can also be applied for thermogravimetry. This will be shown on the example of a reversible reaction of the first order, $A \rightleftharpoons C$, where A is a solid and C is a gas, since only in this case will substance A undergo a mass change Δm in the course of the reaction. It is assumed of course, that the process takes place in a closed space and that the gas cannot escape. If this is not the case, mass transfer out of the reaction cell must be taken into account. We have

Table 3

Type of reaction	T, K	n	m	q, kJ/mol	Q, kJ/mol	K ₀₁	E ₁ , kJ/mol	K ₀₂	E ₂ , kJ/mol
A⇌C	400	0.539	0	14.50	20.9	0.99 · 10 ⁵ s ⁻¹	41.9	2.1 · 10 ⁷ s ⁻¹	125.03
	420	1.1	0	13.12					
	440	2.07	0	11.73					
	460	3.83	0	10.48					
	500	11.58	0	8.22					
A⇌C+D	400	0.37	0.79 · 10 ⁻⁵	15.72	20.1	0.99 · 10 ⁵ s ⁻¹	41.9	1.36 · 10 ⁷ m ³ /s · mol	122.5
	420	0.67	1.9 · 10 ⁻⁵	14.75					
	440	1.15	4.29 · 10 ⁻⁵	13.85					
	460	1.9	9.07 · 10 ⁻⁵	12.95					
	500	4.5	2.59 · 10 ⁻⁴	11.40					
A+B⇌C+D	400	0.74	0.99 · 10 ⁻⁵	12.57	20.9	0.99 · 10 ⁵ m ³ /s · mol	41.9	2.1 · 10 ⁷ m ³ /s · mol	125.03
	420	1.26	1.34 · 10 ⁻⁵	11.83					
	440	2.3	1.25 · 10 ⁻⁵	11.12					
	460	3.8	0.57 · 10 ⁻⁶	10.47					
	500	9	-1.18 · 10 ⁻⁴	9.35					

$$\frac{dA}{dt} = -K_1 \left(\frac{m_0 A - \Delta m}{\mu_A} \right) + K_2 \left(\frac{m_{0c} - \Delta m}{\mu_c} \right) \quad (20)$$

where m_{0A} , m_{0C} , μ_A and μ_C are the initial densities and molecular masses of A and C , respectively. Since no change in the number of moles occurs in the course of the reaction, it follows from the law of conservation of matter that $\mu_A = \mu_C = \mu$. Then, since $A = (m_0 - \Delta m)/\mu$, from Eq. (20) we obtain

$$\frac{d\Delta m}{dt} = (K_1 m_{0A} - K_2 m_{0C}) - (K_1 + K_2) \Delta m \quad (21)$$

Equation (21) is the analogue of Eq. (3), obtained for the calorimetric experiment. Hence, the scheme for obtaining kinetic parameters is identical with that described above in (6).

Finally, it should be noted that the kinetic parameters of reversible reactions can also be determined in non-isothermal thermal analysis, where programmed heating takes place at a rate of w . The qualitative characteristics of reversible reactions proceeding under non-isothermal conditions are as follows:

(i) A change in sign of the relationship for the heat evolution rate \dot{q} in the course of heating.

- (ii) The existence of two extreme in the curve $\dot{q}(t)$.
- (iii) An extremal relationship $q(t)$.
- (iv) A change in the relationship for the rate of the heat evolution \dot{q} and the amount of heat evolved q relative to unit mass of the starting material when the sample is diluted with the end-product of the reaction.

The scheme for determining the kinetic parameters of reversible reactions under non-isothermal conditions will be demonstrated on the example of a mixed-type reaction, $A \rightleftharpoons C + D$. At the initial thermokinetic parameters given above, the curves $\dot{q}(t)$ and $q(t)$ obtained at heating rates of 5 and 10 deg/min have the shapes shown in Fig. 3. The curve $\dot{q}(t)$ exhibits two extrema, and passes through the equilibrium point $\dot{q} = 0$ at the moment $t = t_*$. The values q and T corresponding to this moment t_* will be denoted q_* and T_* . For the mixed-type reversible reaction, Eq. (9) will be valid. Since $E_2 - E_1 = Q$, we obtain

$$B = \frac{K_{01}}{K_{02}} = \frac{q_*^2}{Q(QA_{0*}^{-q})} e^{-Q/RT_*} \quad (22)$$

By carrying out two experiments at different heating rates, w_1 and w_2 , we obtain two relationships $q(t)$ and two sets of values q_{1*} , q_{2*} and T_{1*} , T_{2*} . If these are

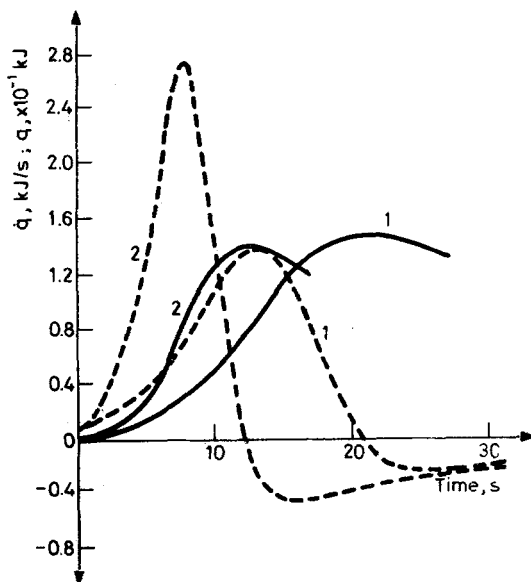


Fig. 3 Form of the curves $\dot{q}(t)$ and $q(t)$ for mixed-type reversible reactions under programmed linear heating conditions. (1) = 5 deg/min, (2) = 10 deg/min; --- $\dot{q}(t)$, ——— $q(t)$

substituted into Eq. (22), a transcendent equation for the determination Q is obtained:

$$\frac{q_{1*}^2(QA_0 - q_{2*})}{q_{2*}^2(QA_0 - q_{1*})} \exp\left(-\frac{Q(T_{2*} - T_{1*})}{RT_{1*}T_{2*}}\right) = 0 \quad (23)$$

On calculating value of Q we can obtain the ratio $K_{01}/K_{02} = B$. By expressing K_1 through K_2 , $K_1 = BK_{02}e^{-E_2/RT} = BK_2e^{Q/RT}$ and substituting this value into Eq. (9), we obtain an equation for the determination of $K_2(T)$:

$$K_2(T) = \frac{\dot{q}Q}{BQ e^{Q/RT}(QA_0 - q) - q^2} \quad (24)$$

In the knowledge of $K_2(T)$, the relationship $\ln K_2(T)$ vs. $1/T$ may then be plotted, and E_2 and K_{20} , and subsequently $E_1 = E_2 - Q$ and $K_{10} = BK_{20}$ can be determined.

This calculation was illustrated by a computerized experiment. The value of Q obtained from Eq. (23) was 21.3 kJ/mol. The values found for E_1 , E_2 , K_{01} and K_{02} were 41.1 kJ/mol, 125.4 kJ/mol, $0.8 \cdot 10^6 \text{ s}^{-1}$ and 22.3 m³/s mol, respectively.

These data are in full agreement with the initial kinetic parameters. Accordingly, the proposed scheme for processing non-isothermal experimental kinetic data is applicable for all types of reversible reactions considered in this work.

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Zusammenfassung — Es wurde eine Methode zur Bestimmung kinetischer Parameter von reversiblen Reaktionen unter isothermen bzw. nicht-isothermen Umständen in der Thermoanalyse beschrieben. Umkehrbare Reaktionen erster Ordnung, zweiter Ordnung sowie Reaktionen vom Mischtyp wurden betrachtet. Die kinetischen Parameter der Hin- bzw. Rückreaktionen wurden auf der Grundlage der Anfangsintegrale der thermoanalytischen Experimente bestimmt. Die Ergebnisse eines computermodellierten Experimentes zeigen, dass die vorgeschlagene Methode befriedigend angewendet werden kann.

Резюме — Дана методология определения кинетических параметров обратимых реакций в условиях изотермического и неизотермического термоаналитического эксперимента. Рассмотрены обратимые реакции первого и второго порядка, а также смешанного типа. Кинетические параметры прямой и обратной реакций определяются на основании исходных интегральных данных термоаналитического эксперимента. Результаты обработки машинного кинетического эксперимента показали хорошую применимость предложенного метода.