Journal of Thermal Analysis, Vol. 36 (1990) 1595-1597

Note

AN INTEGRAL SCHEME FOR THE THERMOANALYTICAL STUDY OF TWO-STEP REACTIONS

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(Received August 14, 1989)

Consider the simplest two-step reactions proceeding in monomolecular steps: parallel monomolecular reactions A → B; A →C; simultaneous independent monomolecular reactions A → B, C → D; two-step consecutive reactions; reactions involving monomolecular steps A →B → C . In earlier studies [1, 2], technique has been suggested for recognizing the reaction steps, identification of reaction types and determining the kinetic parameters of separate steps from the basic thermoanalytical data for thermogravimetric and scanning calorimetric analyses. However, the approach in [1] for reactions of this type has some disadvantage when applied to independent and consecutive reactions: it requires the second-order derivatives for the amount of heat released or a change in the mass $\ddot{q}$, $\dot{m}$, which can affect the accuracy of results obtained by this method. The present study deals with a calorimetric isothermal thermoanalytical experiment which was used to develop an integral scheme not subject to such limitations in the determining of the kinetic parameters for separate steps. In this scheme, $\int q\,dt$ is used instead of $\ddot{q}$.

The rates of heat release at separate monomolecular steps are described by the following relations

$$\dot{q}_1 = a + bq_1 + cq_2 = c + cq + (b - c)q_1$$

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$$\dot{q}_2 = d + fq_1 + lq_2 = d + lq + (f - l)q_1 \qquad (1)$$

$$\dot{q} = \dot{q}_1 + \dot{q}_2 = (a + d) + (c + 1)q + (b + f - c - 1)q_1$$

where $\dot{q}$ and q are the experimentally determined rates of heat release and the total heat released (absorbed). Expressing q_1 of the last equations from (1) as $\dot{q}$ and q and substituting it into the first equation (1) we integrate it over the time and obtain the final relationship

$$\dot{q} + (la - fa + bd - cd)t - (l + b)q + (bl - cf)\int q dt - (a + d) = 0 \qquad (2)$$

For the case of two concurrent monomolecular reactions $a = A_o B_1 Q_1$; $b = -B_1$; $c = -(Q_1 / Q_2)B_1$; $d = A_o B_2 Q_2$; $f = -(Q_2 / Q_1)B_2$; $l = -B_2$, where Q_i are the thermal effects from the steps; A_o is the number of moles of the starting material, $B_i = K_i \exp(-E_i/RT)$ are the reaction rates at separate steps (K_i are the preexponential factor, E_i are the activation energies at separate steps). In this case eq. (2) takes up the form:

$$\dot{q} = A_o (Q_1 B_1 + Q_2 B_2) - (B_1 + B_2)q \qquad (3)$$

A scheme for determining K_i, E_i from this relation is given in [1].

In case of independent reactions $a = A_o B_1 Q_1$; $b = -B_1$; $c = f = 0$; $d = D_o B_2 Q_2$; $l = -B_2$; and for the consecutive reactions $a = A_o B_1 Q_1$; $b = -B_1$, $c = d = 0$; ; $f = -(Q_2 / Q_1)B_2$; $l = -B_2$ and for reactions of these two types (2) can be expressed as

$$\frac{\dot{q}_o - \dot{q}}{q} = (B_1 + B_2) - B_1 B_2 = \frac{q_\infty t - \int q dt}{q} \qquad (4)$$

Here q_∞ is the experimentally determined total amount of the released (absorbed) heat. For the independent reactions $q_\infty = A_o Q_1 + D_o Q_2$; for the consecutive reactions, $q_\infty = A_o (Q_1 + Q_2)$. The term $\dot{q}_o$ is the rate of heat evolution at the initial moment of time (the moment at which the experimental temperature is attained). Further steps to be taken to identify these types of reactions and to determine the constants for separate steps from eq. (4) are given in [1]. It should be noted that with $\dot{q}_o$ and q_∞, the kinetic parameters can be determined with the values of Q_i, A_o, D_o not known. The present scheme can also be used in a gravimetric thermoanalytical experiment as well as for non-isothermal conditions, particularly if the experiment involves successive stepwise heating of the sample, with the entire temperature range covered during one run. Heating of this type is believed to be most preferable for thermal analysis, insofar as the nonisothermal experiment proceeds mainly under the "quasiisothermal" conditions, most convenient for the kinetic treatment.

References

1 N. I. Vaganova, V. I. Rosenband and V. V. Barzykin, J. Thermal Anal. 34 (1988) 73.
2 N. I. Vaganova, V. I. Rosenband and V. V. Barzykin, J. Thermal Anal. 34 (1988).