Journal of Thermal Analysis, Vol. 2 (1970) 141–144

HOMOGENEOUS KINETICS WITH PROGRAMMED TEMPERATURE VARIATIONS, I

BASIC PRINCIPLES AND BASIC RELATIONS

J. ZSAKÓ

Department of Chemistry, "Babeş-Bolyai" University, Cluj, Rumania

(Received December 22, 1969)

A new method is proposed for the derivation of kinetic parameters of reactions in homogeneous systems, by carrying out kinetic measurements under conditions of programmed temperature variations, instead of performing them under isothermal conditions at different temperatures. The basic relations are given for simple, paralle and complex reactions, without specifying the analytical shape of the temperature programme function.

In current kinetic measurements the concentration variations are followed under isothermal conditions in order to derive rate constants. From the influence of temperature upon the rate constants, other kinetic parameters are derived, such as activation energy, the pre-exponential factor in Arrhenius' equation.

In the study of the thermal decomposition of solids a special method has been developed: thermogravimetric analysis, in which the temperature is varied linearly. Many attempts have been made to obtain kinetic parameters from thermogravimetric curves and a considerable number of techniques have been worked out for this purpose [1]. In all these methods, to a first approximation, the formalism of homogeneous kinetics is used. Since these heterogeneous reactions are much more complex than homogeneous ones, the validity of the proposed relations and the accuracy of the corresponding methods are rather obscure. It is very difficult to give a clear physical sense to the obtained parameters.

On the other hand, by using the formalism of homogeneous kinetics, the derived relations and methods, after an appropriate adaptation, can find a successful application just in homogeneous kinetics. Our first attempts, both theoretical and experimental ones, have proved the validity of this statement. By using techniques based on programmed temperature variations, the time necessary for investigations is considerably shortened without reducing the accuracy of the results obtained.

By considering the reaction

$$a_1A_1 + a_2A_2 + \ldots + a_nA_n = b_1B_1 + b_2B_2 + \ldots + b_mB_m \qquad (1)$$

the rate of reaction can be defined as

$$v = -\frac{dc}{dt} = -\frac{d[A_i]}{dt} \tag{2}$$

If the reaction is a simple one, under isothermal conditions the following relation is valid:

$$-\frac{dc}{dt} = kf(c) \tag{3}$$

where k stands for the rate constant and $f(c)$ is a function of c (its analytical shape depending upon the nature of the reaction) and contains the initial concentration of each reagent.

In the case of parallel reactions we have

$$-\frac{dc}{dt} = k_1 f_1(c) + k_2 f_2(c) + \ldots + k_n f_n(c) \tag{4}$$

and generally, for complex reactions

$$-\frac{dc}{dt} = F(k_1, k_2, \ldots, k_n, f_1, f_2, \ldots, f_n) \tag{5}$$

The rate constants depend upon temperature. This dependence can be given by the function

$$k = Z T^m e^{-E/RT} \tag{6}$$

where E stands for the activation energy and Z and m are characteristic constants of the reaction. For $m = 0$ this relation gives the Arrhenius equation

$$k = Ze^{-E/RT} \tag{7}$$

If the temperature range is not too large, Eq. (7) can be considered a very good approximation.

From Eqs (3), (4), (5) and (7) we obtain the following relations:
for simple reactions

$$-\frac{dc}{dt} = Ze^{-E/RT} f(c) \tag{8}$$

for parallel reactions

$$-\frac{dc}{dt} = Z_1 e^{-E_1/RT} f_1(c) + Z_2 e^{-E_2/RT} f_2(c) + \ldots \tag{9}$$

and generally, for complex reactions

$$-\frac{dc}{dt} = F(Z_1, Z_2, \ldots Z_n, E_1, E_2, \ldots, E_n, f_1, f_2, \ldots, f_n) \tag{10}$$

These differential equations can be used for deriving kinetic parameters Z and E by means of differential methods, although they do not contain the temperature variation programme. This programme can be expressed by the function

$$T = \phi(t) \tag{11}$$

By considering the inverse function

$$t = \psi(T) \tag{12}$$

the differential of time can be given as

$$dt = \psi'(T)\, dt \tag{13}$$

where $\psi'(T)$ stands for the derivative of the programme function with regard to temperature.

By means of Eqs (8), (9), (10) and (13) we obtain for simple reactions

$$-\, dc = Ze^{-E/RT} f(c)\, \psi'(T)\, dT \tag{14}$$

for parallel reactions

$$-\, dc = [Z_1 e^{-E_1/RT} f_1(c) + Z_2 e^{-E_2/RT} f_2(c) + \ldots]\, \psi'(T)\, dT \tag{15}$$

and generally, for complex reactions

$$-\, dc = F(Z_1, Z_2, \ldots, Z_n, E_1, E_2, \ldots, E_n, f_1, f_2, \ldots, f_n;\ T)\, \psi'(T)\, dT \tag{16}$$

These basic relations can be used for deriving both differential and integral methods.

In the most simple case of simple reactions, we have a differential equation with separable variables. Eq. (14) can be written in the following form:

$$-\frac{dc}{f(c)} = Ze^{-E/RT}\, \psi'(T)\, dT \tag{17}$$

With the obvious limiting condition $c = c_0$ for $T = 0$, we can write:

$$g(c) = -\int_{c_0}^{c} \frac{dc}{f(c)} = Z \int_{0}^{T} e^{-E/RT}\, \psi'(T)\, dT \tag{18}$$

In the particular case of linear temperature variations we have $\psi'(T) = 1/q$, where q stands for the constant heating rate, and relation (18) becomes perfectly analogous to the equation of thermogravimetric curves, proposed by Doyle [2].

By using such a linear temperature programme, the right-hand side of Eq. (18) cannot be integrated in finite form. In spite of this difficulty kinetic parameters can be derived by using appropriate calculation techniques [3]. If a suitable temperature programme is chosen, Eq. (18) becomes integrable. This is the situation if a linear variation of the reciprocal absolute temperature is performed.

Application of programmed temperature variations offers the possibility to work out techniques which ensure the derivation of kinetic parameters Z, E and even reaction orders by using a single kinetic curve, at least in the case of simple reactions.

References

1. J. Sestak, Silikaty, 11, (1967) 153.
2. C. D. Doyle, J. Appl. Polymer. Sci. 5 (1961) 285.
3. J. Zsakó, J. Phys. Chem., 72 (1968) 2406.

Résumé — On propose une nouvelle méthode de calcul des paramètres cinétiques des réactions en milieu homogène. Les mesures cinétiques sont effectuées en programmant les variations de température au lieu d'opérer en thermostat à différentes températures. On donne les relations fondamentales pour les réactions simples, parallèles et complexes, sans prendre en considération la forme analytique de la fonction du programme de la température.

Zusammenfassung — Es wurde eine neue Methode zur Ableitung kinetischer Parameter von in homogenen Systemen verlaufenden Reaktionen vorgeschlagen. Die kinetische Messung wurde unter programmierten Temperaturänderungen ausgeführt, anstatt unter isothermischen Bedingungen bei verschiedenen Temperaturen. Die grundlegenden Beziehungen wurden für einfache, parallele oder komplexerweise verlaufende Reaktionen beschrieben, ohne auf die Form der Funktion des Temperaturprogrammes Rücksicht zu nehmen.

Резюме — Описан новый метод установления кинетических параметров реакций, протекающих в гомогенных системах, путем проведения кинетических измерений в условиях программированно изменяющейся температуры, вместо изотермических измерений при разных температурах. Даны основные выражения для простых, параллельных и комплексных реакций без спецификации аналитической формы функции программы по температуре.