

APPLICATION OF NON-EQUILIBRIUM THERMODYNAMICS TO PROBLEMS OF THERMAL ANALYSIS *

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ABSTRACT

On the basis of non-equilibrium thermodynamics, the kinetic equations of thermal analysis are derived for several important chemical consecutive and concurrent reactions. These equations are solved analytically and numerically and the obtained solutions are discussed. Hereby hints are obtained for the further development of thermal methods. It is shown that, in most cases, the kinetics of coupled chemical reactions can only be determined with special selective methods.

INTRODUCTION

The development of analytical techniques has provided the possibility of determining the conversion of a sample under non-isothermal conditions with high quality. In the last ten years, experimental conditions have been improved so that the thermodynamic and kinetic parameters can, in many cases, be determined directly from the experimental results. To take further advantage of this development, it is also necessary to improve both the theoretical basis of the models and the analytical determination of the reaction-specific quantities. In this field, the theory of non-isothermal reactions has also made significant progress. A detailed review was presented by Koch in 1977 [1].

Nevertheless, the interpretation of experimental results is not entirely satisfactory. The various theoretical models and experiments are one reason for the incomparability of results. Furthermore, it is often possible to describe one experiment with the same statistical significance by various theoretical models. In this situation, it is necessary to answer the question what requirements of analytical techniques have to be fulfilled in order to determine the reaction kinetics and the parameters involved in a correct way.

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A reliable criterion for the interpretation of measurements is not available at present. However, such a criterion is necessary for the development of analytical equipment to control the technology of non-isothermal industrial processes and to obtain unambiguous information from the experimental investigation in laboratories. The solution of these problems is important from the point of view of the optimum use of both energy and raw materials. This paper outlines a theoretical concept of a uniform treatment of non-isothermal analysis experiments on the basis of non-equilibrium thermodynamics with the aim of improving further experimental equipment.

THEORETICAL BASIS

The basic equations

Equation of mass balances

In a homogeneous system with K components B_i ($i = 1, 2, \dots, K$), R chemical reactions take place with the stoichiometric equations



On the left-hand side of eqn. (1), there are the reactants B_1 to B_{M_r} and on the right-hand side, the reaction products $B_{M_{r+1}}$ to B_K . ΔH_r is the reaction enthalpy of the r th reaction. In the course of the chemical reaction, the concentrations c_i of reactants B_i ($c_i = \rho_i/\rho$, where ρ_i is the mass density of the reactant B_i , ρ = the total mass density, and $\rho = \sum_{i=1}^K \rho_i$) change with time. The rates of the mass changes can be described with the aid of the mass balance equation

$$\rho \frac{dc_i}{dt} + \text{div } \vec{J}_{B_i} = \sum_{r=1}^R \omega_r \nu_{ir} M_{B_i} \quad (2)$$

where ω_r is the rate of the r th chemical reaction, M_{B_i} the molar mass and \vec{J}_{B_i} the diffusion flux of the component B_i . The diffusion flux \vec{J}_{B_i} and the rate of the chemical reaction ω_r depend on the temperature. Therefore the heat conduction must be taken into consideration in the calculation of the concentrations.

However, under certain conditions, the diffusion and heat conduction produce only small effects compared with the chemical reactions. In this case, the following assumptions can be made.

(a) The sample is homogeneous. (In this case the concentrations c_i are functions of the time only, the diffusion fluxes vanish, and we therefore confine ourselves to homogeneous reactions.)

(b) The heat conduction of the sample is large enough or the sample so

small that the temperature is constant throughout the sample and that a time-dependent change of the temperature in the surroundings also takes place inside the sample without delay.

(c) The surroundings absorb (or give up) the reaction heat so quickly that thermal equilibrium is always maintained. The last two assumptions permit us to neglect heat conduction. Therefore we may consider the temperature as a given function of time [$T = T(t)$]. We often use linear time dependence of the temperature ($T = T_0 + qt$ where $T_0 =$ initial temperature and $q =$ heating rate). With all these assumptions, we obtain from eqn. (2)

$$\rho \frac{dc_k}{dt} = q\rho \frac{dc_k}{dT} = \sum_{r=1}^R \omega_r(T, c) \nu_{kr} M_{B_k} \quad (3)$$

For the integration of this system of ordinary differential equations, we need the initial concentrations and the reaction rates $\omega_r(T, c)$. In the following we will discuss the temperature and concentration dependences of ω_r .

First, it should be mentioned that the assumptions (a)–(c) are the basis for the equation often used in the literature

$$\frac{d\alpha}{dt} = K(T) f(\alpha) \quad (4)$$

Constitutive equations

The rate of a chemical reaction, ω , depends on thermodynamic and kinetic quantities. The thermodynamic quantities are given by the chemical affinity $A = \sum \nu_i \mu_i$, where μ_i is the molar chemical potential of the component B_i . For real mixtures it has the form

$$\mu_i = g_i(p, T) + RT \ln a_i \quad (5)$$

where $g_i =$ molar Gibbs enthalpy, $a_i =$ activity ($a_i = x_i f_i$), $x_i =$ mole fraction, and $f_i =$ activity coefficient of component B_i . It is useful to separate the affinity into two parts: A^+ for the forward reaction and A^- for the reverse reaction

$$A = A^- - A^+ \\ A^+ = - \sum_{i=1}^M \nu_i \mu_i, \quad A^- = \sum_{i=M+1}^K \nu_i \mu_i \quad (6)$$

The dependence of the reaction rate on the affinity can be described by the non-linear equation [2]

$$\omega = \Lambda (e^{A^+/RT} - e^{A^-/RT}) \quad (7)$$

where Λ is a phenomenological coefficient.

In the case of chemical equilibrium, $\omega = 0$, eqn. (7) [together with eqn. (5)]

in the form

$$\omega = \Lambda \left\{ e^{\Delta g^+ / RT} \prod_{i=1}^M a_i^{-\nu_i} - e^{\Delta g^- / RT} \prod_{i=M+1}^K a_i^{\nu_i} \right\} = 0 \quad (8)$$

where $\Delta g^+ = - \sum_{i=1}^M \nu_i g_i$ and $\Delta g^- = \sum_{i=M+1}^K \nu_i g_i$ yields the law of mass action

$$\prod_{i=1}^K a_i^{\nu_i} = K(p, T) = e^{-\Delta g / RT} \quad (9)$$

Here, $\Delta g = \Delta g^- - \Delta g^+$ and $\Delta g = \Delta h - T\Delta s$ which contains the molar reaction enthalpy Δh and the molar reaction entropy Δs . Both quantities can be separated, like Δg , into parts related to the reactants, Δh^+ and Δs^+ , and the products, Δh^- and Δs^- , with $\Delta h = \Delta h^- - \Delta h^+$ and $\Delta s = \Delta s^- - \Delta s^+$.

The phenomenological coefficient, Λ , in eqn. (7) depends on the state variables T , p , x_i and describes the influence of kinetic quantities on the reaction rate. To obtain the connection with the relations for the velocity constants in the field of reaction kinetics (Arrhenius concept [3]), we state

$$\Lambda = \lambda e^{-(\Delta h^0 / RT)} e^{\Delta s^0 / R} \quad (10)$$

Thereby it follows for the velocity constants of the forward reaction, K^+ , and the reverse reaction, K^-

$$\begin{aligned} K^+ &= \Lambda e^{\frac{\Delta g^+}{RT}} = \lambda e^{-\frac{\Delta s^{*+}}{R}} e^{-\frac{E^+}{RT}} = k_0^+ e^{-\frac{E^+}{RT}} \\ K^- &= \Lambda e^{\frac{\Delta g^-}{RT}} = \lambda e^{-\frac{\Delta s^{*-}}{R}} e^{-\frac{E^-}{RT}} = k_0^- e^{-\frac{E^-}{RT}} \end{aligned} \quad (11)$$

with the activation energies

$$\begin{aligned} E^+ &= \Delta h^0 - \Delta h^+ \\ E^- &= \Delta h^0 - \Delta h^- \end{aligned} \quad (12)$$

and the activation entropies

$$\begin{aligned} \Delta s^{*+} &= \Delta s^+ - \Delta s^0 \\ \Delta s^{*-} &= \Delta s^- - \Delta s^0 \end{aligned} \quad (13)$$

The activation entropies are connected with the "steric" factors. These results can be compared with those obtained in the theory of the transient state in the field of reaction kinetics [3]. It follows that Δh^0 and Δs^0 have to be interpreted as molar standard enthalpy and entropy of activation.

The temperature dependence of λ is given by

$$\lambda = \lambda_0 T^\gamma$$

In most cases, this dependence can be neglected just as the influence of pressure. Therefore the reaction rate, ω , becomes

$$\omega = \lambda_0 e^{-\frac{\Delta h^0}{RT} + \frac{\Delta s^0}{R}} \left\{ e^{\frac{\Delta g^+}{RT}} \prod_{i=1}^M a_i^{-\nu_i} - e^{\frac{\Delta g^-}{RT}} \prod_{i=M+1}^K a_i^{\nu_i} \right\} \quad (14)$$

and with the eqn. (11)

$$\omega = K^+(T) \prod_{i=1}^M a_i^{-\nu_i} - K^-(T) \prod_{i=M+1}^K a_i^{\nu_i} \quad (15)$$

When several chemical reactions take place, the phenomenological equations are given by (neglecting cross effects)

$$\omega_r = \Lambda_r \left(e^{\frac{A_r^+}{RT}} - e^{\frac{A_r^-}{RT}} \right) \quad (16)$$

Furthermore, we confine ourselves to ideal mixtures with $f_i = 1$ and $a_i = x_i$.

Kinetic equations

With regard to the assumptions (uniform system without diffusion $\vec{J}_i = 0$ and convection $\vec{v} = 0$, ideal mixtures), the mass balance reads

$$\frac{dc_k}{dt} = \sum_{r=1}^R \nu_{kr} \left\{ K_r^+ \prod_{i=1}^M c_i^{-\nu_{ir}} - K_r^- \prod_{i=M+1}^K c_i^{\nu_i} \right\} \quad (17)$$

Equation (17) describes the progress of the chemical reaction and enables an accurate calculation of the time dependence on the concentration to be made.

To obtain uniform solutions of eqn. (17), it is necessary to know the initial concentration, c_k^0 , and the time dependence of the temperature. For simple reactions, it is possible to find analytical solutions. It is often useful to introduce a progress variable, ξ_r , for each reaction because in this way a decoupling or a partial decoupling of the differential equations is attained. The progress variables ξ_r are connected with the reaction rate

$$\omega_r = \frac{d\xi_r}{dt} \quad (18)$$

Hence eqn. (3) becomes

$$\frac{dc_k}{dt} = \sum_{r=1}^R \nu_{kr} \omega_r \frac{M_{B_k}}{\rho} = \sum_{r=1}^R \nu_{kr} \frac{d\xi_r}{dt} \quad (19)$$

This integrates to

$$c_k = c_k^0 + \sum_{r=1}^R \nu_{kr} \xi_r \quad (20)$$

with $\xi_r = 0$ at the start of reaction ($t = 0$). ξ is proportional to

$$\alpha = \frac{\xi(t)}{\xi_e}$$

α ranges from zero to one and ξ_e is the progress variable at the end of the reaction.

Equations (17), (19) and (20) yield

$$\frac{d\xi_r}{dt} = K_r^+ \prod_{i=1}^{M_r} \left(c_i^0 + \sum_{s=1}^R \nu_{is} \xi_s \right)^{-\nu_{ir}} - K_r^- \prod_{i=M+1}^K \left(c_i^0 + \sum_{s=1}^R \nu_{is} \xi_s \right)^{\nu_{ir}} \quad (21)$$

The analytical solution of these differential equations is only known in special cases (e.g. for isothermal processes [2]), but in many cases it is possible to neglect the reverse reaction. The rate equation then reduces to

$$\frac{d\xi_r}{dt} = K^+(T) \prod_{i=1}^{M_r} \left(c_i^0 + \sum_{s=1}^R \nu_{is} \xi_s \right)^{-\nu_{ir}} \quad (22)$$

These equations are the “kinetic laws” of chemical kinetics. For the determination of the concentration of a reactant product at various times, these equations must be integrated. In kinetic studies of reactions, it is common to fit the calculated expressions into experimental data using appropriate parameters (e.g. activation energies, frequency factors, reaction orders). Generally, the more information on the reaction that is available, the more exactly the unknown parameters can be determined. Some of the more important expressions following from eqn. (22) will now be derived.

A SINGLE CHEMICAL REACTION

A single reaction without reverse reaction

The rate of reaction of a single chemical reaction without reverse reaction will first be discussed. The rate equation ($r = 1$, $\xi_1 = \xi$, $T = qt + T_0$) is

$$\frac{d\xi}{dT} = \frac{1}{q} K^+(T) \prod_{i=1}^M (c_i^0 + \nu_i \xi)^{-\nu_i} \quad (23)$$

This equation corresponds exactly to the commonly used kinetic equation [4]

$$\frac{d\alpha}{dT} = \frac{1}{q} K(T) f(\alpha)$$

Equation (23) may be integrated by separation of variables

$$\frac{1}{q} \int_{T_0}^T K^+(T) dT = \int_0^\xi \frac{d\xi}{\prod_{i=1}^M (c_i^0 + \nu_i \xi)^{-\nu_i}} = g_n(\xi) \quad (24)$$

The left-hand side, the “exponential integral”

$$\int_0^T K^+(T) dT = \int_0^T K_0 e^{-\frac{E}{RT}} dT = K_0 p(T) \quad (25)$$

can be presented with good approximation in the analytical form [5]

$$p(T) \approx \frac{RT^2/E}{\sqrt{1+4(RT/E)}} e^{-\frac{E}{RT}} \quad (26)$$

The function $g_n(\xi)$ depends on the order $n = \sum \nu_i$ of the reaction.

In general, the concentration of reactant or a product can be determined experimentally at various times. For a first-order reaction, the specific conversion is given by

$$\xi = c_1^0(1 - e^{-J(T)}), \quad \nu_1 = -1 \quad (27)$$

for a second-order by

$$\xi = c_1^0 c_2^0 \frac{1 - e^{(c_1^0 - c_2^0)J(T)}}{(c_2^0 - c_1^0) e^{(c_1^0 - c_2^0)J(T)}}, \quad \nu_1 = \nu_2 = -1 \quad (28)$$

or

$$\xi = \frac{(c_1^0)^2 J(T)}{1 + 2c_1^0 J(T)}, \quad \nu_1 = -2$$

$$J(T) = \frac{1}{q} \int_{T_0}^T K^+(T) dT = \frac{K_0^+}{q} [p(T) - p(T_0)] \quad (29)$$

These expressions [eqns. (27)–(29)] describe the progress variable ξ as a function of the heating rate q [$J(T)$ depends on q] and the initial concentrations.

A single reaction with reverse reaction

For the further development of experimental equipment, it is of interest to determine the influence of a reverse reaction on the specific reaction rate. In this case, the rate may be expressed as

$$\frac{d\xi}{dt} = K^+ \prod_{i=1}^M (c_i^0 + \nu_i \xi)^{-\nu_i} - K^- \prod_{i=M+1}^K (c_i^0 + \nu_i \xi)^{\nu_i} \quad (30)$$

An analytical solution of eqn. (30) is only known for isothermal cases

$$\int_0^\xi \frac{d\xi}{K^+ \prod_{i=1}^M (c_i^0 + \nu_i \xi)^{-\nu_i} - K^- \prod_{i=M+1}^K (c_i^0 + \nu_i \xi)^{\nu_i}} = t \quad (31)$$

The integral may be calculated by the method of partial fractions. If ξ is plotted against t , a curve of the form of Fig. 1 is obtained in the case of a first-order reaction. ξ_0 represents the progress variable at the equilibrium

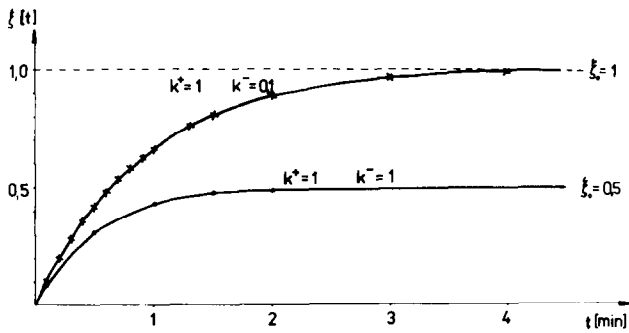


Fig. 1. Slope of the progress variable $\xi(t)$ as a function of time for a first-order reaction at different rate constants K^+ and K^- and under isothermal conditions.

state, which can be determined by the law of mass action

$$\prod_{i=1}^K (c_i^0 + \nu_i \xi_0)^{-\nu_i} = \frac{K^-}{K^+} \quad (32)$$

Equation (31) for a first-order reactions yields

$$\xi(t) = \xi_0 (1 - e^{-(K^+ + K^-)t}) \quad (33)$$

where ξ_0 is given by

$$\xi_0 = \frac{c_1^0 K^+ - c_2^0 K^-}{K^+ + K^-} \quad (34)$$

The initial rate at time $t=0$ is denoted by ω_0 and depends on the initial concentrations c_1^0 and c_2^0 , so that

$$\omega_0 = \left(\frac{d\xi}{dt} \right)_{t=0} = c_1^0 K^+ - c_2^0 K^- \quad (35)$$

K^- can be determined from ω_0 if $c_1^0 = 0$ and K^+ can be determined if $c_2^0 = 0$.

Under non-isothermal conditions, the solution of eqn. (30) is more complex. A solution of this equation for a first-order reaction ($A = B$) gives

$$\xi(T) = \frac{1}{q} e^{-\frac{1}{q} J(T)} \int_{T_0}^T [c_1^0 K^+(T') - c_2^0 K^-(T')] e^{\frac{1}{q} J(T')} dT' \quad (36)$$

with

$$J(T) = \int_{T_0}^T [K^+(T') + K^-(T')] dT' \quad (37)$$

The equilibrium conversion $\xi_0(T)$ is also a function of temperature. If the temperature T is much greater than E^+/R , ξ approaches ξ_0^∞ , which can be expressed as

$$\xi_0^\infty = \frac{c_1^0 K_0^+ - c_2^0 K_0^-}{K_0^+ + K_0^-} \quad (38)$$

In Fig. 2, possible examples are given schematically. The slope of the curve $d\xi/dT$, the rate of reaction, is not always positive. This is an interesting result for the interpretation of experimental data [6].

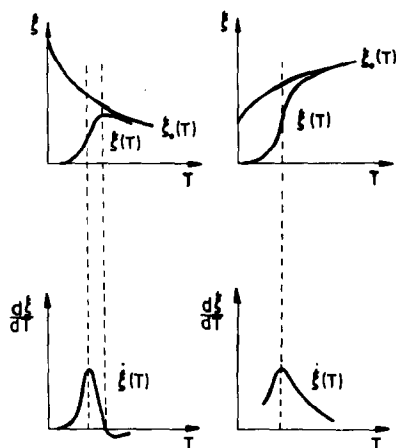


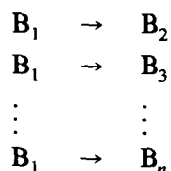
Fig. 2. Variation of the equilibrium conversion $\xi_0(T)$ under non-isothermal conditions and the slope of the resulting progress variable $\xi(T)$ and conversion rate $d\xi/dT$, respectively.

Qualitatively similar results are obtained for more complicated reactions. However, the integration of the corresponding differential equations is difficult or impossible in most cases, e.g. second-order reactions yield Riccati-differential equations which can only be integrated in special cases [7]. A third-order reaction yields a differential equation of Abels type [7].

COUPLED CHEMICAL REACTIONS

Analytical solutions of the kinetical equations

An analytical solution of the differential equations of coupled chemical reactions cannot be given in most cases. Only in the case of the simplest competitive and consecutive reactions is the solution known. In the case of competitive first-order reactions, represented as



the rate equations at linear heating rate can be expressed as

$$\begin{aligned}\frac{d\xi_1}{dT} &= \frac{1}{q} K_1^+ (c_1^0 - \xi_1 - \xi_2 - \dots - \xi_n) \\ \frac{d\xi_2}{dT} &= \frac{1}{q} K_2^+ (c_1^0 - \xi_1 - \xi_2 - \dots - \xi_n) \\ &\vdots \\ \frac{d\xi_n}{dT} &= \frac{1}{q} K_n^+ (c_i^0 - \xi_1 - \xi_2 - \dots - \xi_n)\end{aligned}\quad (39)$$

From these equations follow

$$\xi_i(T) = \frac{c_1^0}{q} \int_{T_0}^T K_i^+(T') e^{-J(T')} dT' \quad (40)$$

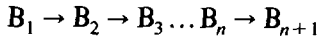
and

$$\xi_1 + \xi_2 + \dots + \xi_n = c_1^0 (1 - e^{-J(T)}) \quad (41)$$

with

$$J(T) = \frac{1}{q} \int_{T_0}^T [K_1^+(T') + K_2^+(T') + \dots + K_n^+(T')] dT' \quad (42)$$

The rate-equations for consecutive first-order reactions which can be represented as



may be expressed as

$$\begin{aligned}\frac{d\xi_1}{dT} &= \frac{1}{q} K_1^+ (c_1^0 - \xi_1) \\ \frac{d\xi_2}{dT} &= \frac{1}{q} K_2^+ (c_2^0 + \xi_1 - \xi_2) \\ &\vdots \\ \frac{d\xi_n}{dT} &= \frac{1}{q} K_n^+ (c_n^0 + \xi_{n-1} - \xi_n)\end{aligned}\quad (43)$$

From these equations follow

$$\xi_1 = c_1^0 (1 - e^{-J(T)}) \quad (44)$$

$$\xi_2 = \frac{1}{q} e^{-J_2(T)} \int_{T_0}^T K_2^+(T') [c_2^0 + \xi_1(T')] e^{J_2(T')} dT' \quad (45)$$

\vdots

$$\xi_n = \frac{1}{q} e^{-J_n(T)} \int_{T_0}^T K_n^+(T') [c_n^0 + \xi_{n-1}(T')] e^{J_n(T')} dT' \quad (46)$$

with

$$J_n(T) = \frac{1}{q} \int_{T_0}^T K_n^+(T') dT'$$

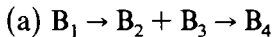
These equations express the influence of all concentrations upon the rate of a single reaction [8]. The dependence of the concentration c_k upon the temperature may be expressed by means of the progress variables as

$$c_n(T) = c_n^0 + \sum_{r=1}^R \nu_{nr} \xi_r(T) \quad (47)$$

In this way, Koch [1] found the equations for two competitive and two consecutive first-order reactions.

Simultaneous consecutive first- and second-order reactions

The simultaneous first- and second-order reactions can be represented as



In this case the rate may be expressed as

$$\frac{d\xi_1}{dT} = \frac{1}{q} K_1^+(c_1^0 - \xi_1) \quad (48)$$

$$\frac{d\xi_2}{dT} = \frac{1}{q} K_2^+(c_2^0 + \xi_1 - \xi_2)(c_3^0 - \xi_2)$$

Integration yields

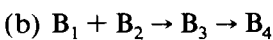
$$\xi_1(T) = c_1^0(1 - e^{-J_1(T)}) \quad (49)$$

$$\xi_2(T) = c_3^0 - \frac{c_3^0 e^{-G(T)}}{\left(1 + \frac{c_3^0}{q} \int_{T_0}^T K_2^+(T') e^{-G(T')} dT'\right)} \quad (50)$$

$J_1(T)$ and $G(T)$ are given as

$$J_1(T) = \frac{1}{q} \int_{T_0}^T K_1^+(T') dT' \quad (51)$$

$$G(T) = \frac{1}{q} \int_{T_0}^T K_2^+(T') [c_2^0 - c_3^0 + \xi_1(T')] dT'$$



$$\frac{d\xi_1}{dT} = \frac{1}{q} K_1^+(c_1^0 - \xi_1)(c_2^0 - \xi_2) \quad (52)$$

$$\frac{d\xi_2}{dT} = \frac{1}{q} K_2^+(c_3^0 + \xi_1 - \xi_2)$$

$$\xi_1(T) = \frac{c_1^0 c_2^0 [1 - e^{(c_1^0 - c_2^0)J_1(T)}]}{c_2^0 - c_1^0 e^{(c_1^0 - c_2^0)J_1(T)}} \quad (53)$$

$$\xi_2(T) = \frac{1}{q} e^{-J_2(T)} \int_{T_0}^T K_2^+(T') [c_3^0 + \xi_1(T')] e^{J_2(T')} dT' \quad (54)$$

with

$$J_{1,2}(T) = \frac{1}{q} \int_{T_0}^T K_{1,2}^+(T') dT' \quad (55)$$

(c) $B_1 + B_2 \rightarrow B_3$, $B_3 + B_4 \rightarrow B_5$

$$\frac{d\xi_1}{dT} = \frac{1}{q} K_1^+(c_1^0 - \xi_1)(c_2^0 - \xi_2)$$

$$\frac{d\xi_2}{dT} = \frac{1}{q} K_2^+(c_3^0 + \xi_1 - \xi_2)(c_4^0 - \xi_2) \quad (56)$$

$$\xi_1(T) = \frac{c_1^0 c_2^0 [1 - e^{(c_1^0 - c_2^0)J_1(T)}]}{c_2^0 - c_1^0 e^{(c_1^0 - c_2^0)J_1(T)}} \quad (57)$$

$$\xi_2(T) = c_4^0 - \frac{c_4^0 e^{-G(T)}}{\left(1 + \frac{c_4^0}{q} \int_{T_0}^T K_2^+(T') e^{-G(T')} dT'\right)} \quad (58)$$

with

$$J_1(T) = \frac{1}{q} \int_{T_0}^T K_1^+(T') dT' \quad (59)$$

$$G(T) = \frac{1}{q} \int_{T_0}^T K_2^+(T') [c_3^0 - c_4^0 + \xi_1(T')] dT' \quad (60)$$

The analytical solutions are of particular interest because it is easier to estimate the dependence of the reaction rate on the parameters which can be readily influenced by the heating rate or the initial concentrations.

Mathematically, analytical solutions can be calculated more easily by means of the non-linear heating rate. Solutions are given for first- and second-order reactions by Koch [1]. However, these methods were dropped in favour of the experimentally more suitable linear heating technique because the complete values for the exponential integrals are available.

For the examination of the kinetic parameters calculated with the help of linear heating rates, the non-linear heating investigation will obtain more importance in the future because the non-linear heating programmes can be adapted to the parameters obtained by the linear heating rate. Only if the

results of different heating programmes are consistent with each other will the correct interpretation be most probable.

Numerical solutions of the kinetic equations

Numerical calculations for several chemical reactions help to obtain more information about the differences of the reaction processes of different models (different reaction order, coupled reaction and so on). For comparison of data, the same kinetic parameters (frequency factor K_0^+ and the activation energy E), the same heating rate and the same initial concentrations are used in different models. The initial concentrations are equal to the stoichiometric coefficients, whereas the concentrations of the final product are zero at the start of reaction. Furthermore, the following values are used.

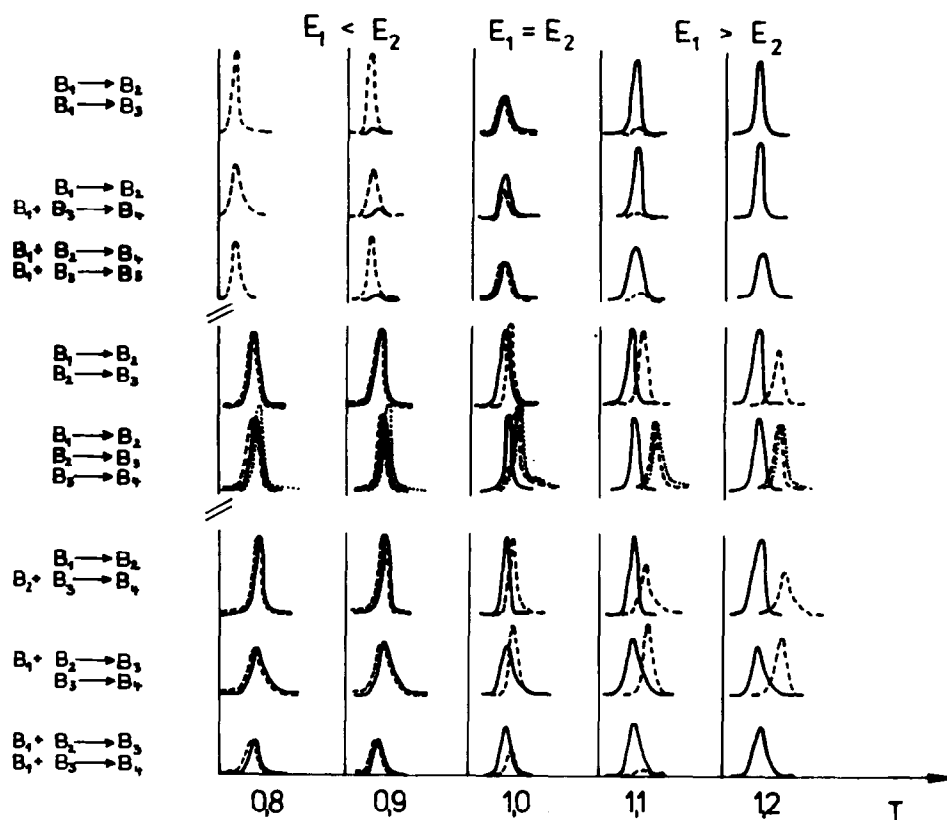


Fig. 3. Schematic representation of the conversion rate curves as a function of the temperature at different kinetic equations with $E_1 = 84 \text{ kJ mole}^{-1}$, $E_2/E_1 = 0.8, 0.9, 1, 1.1, 1.2$, $E_3/E_1 = 1, 1.2$, and $q = 6 \text{ K min}^{-1}$.

$$K_0^+ = 10^{18} \text{ sec}^{-1}$$

$$E_1 = 84 \text{ kJ mole}^{-1} \quad E_2/E_1 = 0.8; 0.9; 1; 1.1; 1.2$$

$$E_3/E_1 = 1; 1.2$$

$$q = 6 \text{ K min}^{-1}$$

The reactions and the rate equations are given in eqns. (39), (43), (48), (52) and (56). A summary of the rate curves is given in Fig. 3.

DISCUSSION

Two factors determine the interpretation of the experimental results, the physical reality of the model chosen and the difference of numerical values for different models in connection with the model chosen.

For discussion, we must examine in which cases the model of homogeneous reactions can be applied to solid state reactions. Many experimental results show that this model cannot be accepted for the interpretation of solid state reactions. Examples for "quasi-homogeneous" reactions in the solid state are order-disorder phase transformations, but the decomposition of solids can also be discussed in this way if the rate of formation of nuclei and the diffusion rate are large in comparison with the rate of chemical reaction, i.e. the concentrations of the reactants are dominant in the reaction rate.

If the concept of homogeneous reaction is valid, the calculations show that, in the case of concurrent reactions [e.g. eqn. (39)], only one maximum of the reaction rate can be observed (Fig. 4). This result is important for the experimental investigations and the further development of analytical equipment. Furthermore, the results of the calculations for different kinetic

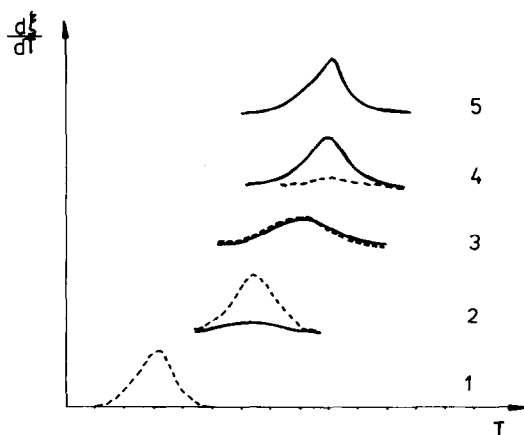


Fig. 4. The conversion rate curves of the competitive reactions $B_1 \rightarrow B_2$, $B_1 \rightarrow B_3$ as functions of the temperature at different values of the activation energy (Fig. 3).

equations allow the conclusion that, generally, the analysis of complex reactions requires selective measuring methods, as is shown, for example, in detail in Fig. 5. If integral measuring methods are used as TG and DTA, in

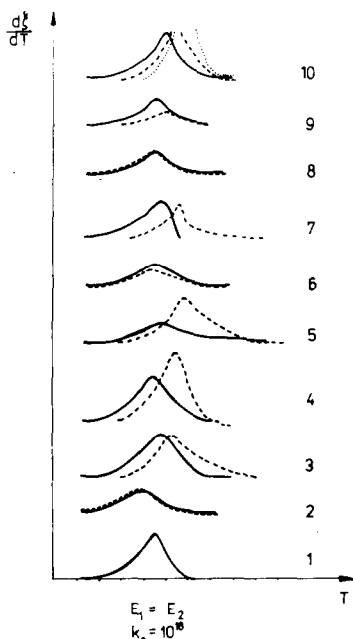


Fig. 5. The conversion rate curves of different complex kinetic equations as functions of the temperature in the case of $E_1 = E_2$ and $K_1 = K_2$. 1, reaction of first-order $B_1 \rightarrow B_2$; 2, competitive reaction of first order $B_1 \rightarrow B_2$, $B_1 \rightarrow B_3$; 3, consecutive reaction of first and second order $B_1 \rightarrow B_2$, $B_2 + B_3 \rightarrow B_4$; 4, consecutive reaction of first order $B_1 \rightarrow B_2$, $B_2 \rightarrow B_3$; 5, consecutive reaction of second and first order $B_1 + B_2 \rightarrow B_3$, $B_3 \rightarrow B_4$; 6, competitive reaction of first and second order $B_1 \rightarrow B_2$, $B_1 + B_3 \rightarrow B_4$; 7, competitive and consecutive reaction of first and second order $B_1 \rightarrow B_2$, $B_1 + B_2 \rightarrow B_3$; 8, competitive reaction of second order $B_1 + B_2 \rightarrow B_4$, $B_1 + B_3 \rightarrow B_5$; 9, competitive and consecutive reaction of second order $B_1 + B_2 \rightarrow B_3$, $B_1 + B_3 \rightarrow B_4$; 10, consecutive reaction of first order $B_1 \rightarrow B_2$, $B_2 \rightarrow B_3$, $B_3 \rightarrow B_4$.

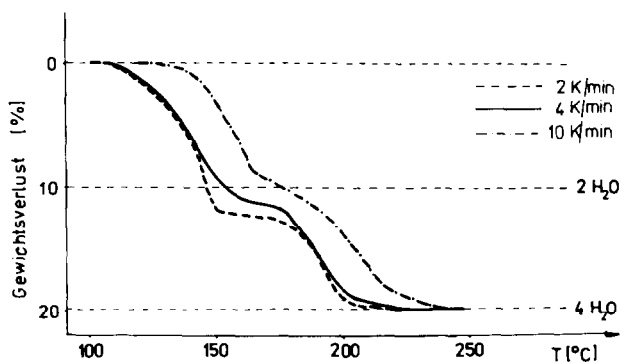


Fig. 6. Thermal decomposition of $K_2Mg(SO_4)_2 \cdot 4 H_2O$ at different heating rates.

principle, by external factors (heating rate, sample size, etc.) the separation of the single reaction steps cannot be attained.

Further, an interesting result was obtained in the case of consecutive reactions, e.g. the decomposition of crystal hydrates. For such reactions, as a rule, the stoichiometric coefficients were determined experimentally from the slope of TG curves [9]. According to our experiments [10,11] and ref. 12, the step in the TG curves does not always correspond to the stoichiometric relations.

A reexamination of the decomposition of leonite $K_2Mg(SO_4)_2 \cdot 4 H_2O$ by means of a high sensitivity thermobalance (Thermoanalyzer TA1, Mettler Instruments A.G., Switzerland) under different experimental conditions yielded the following results. (a) The total weight loss does correspond exactly with the theoretical loss of 4 H_2O molecules (Fig. 6); (b) the minimum of the reaction rate does not correspond to the loss of two molecules of water; and (c) the difference between the two reaction steps is higher the slower the heating rate.

As the theoretical rate curves show, separation of single reaction steps is possible only by fixed kinetic parameters. In general, it can be expected that in the case of consecutive reactions, the steps in the TG curves do not exactly represent stoichiometric relations. Apparently "non-stoichiometric" intermediates result in many cases because the rate curves overlap one another.

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