4. STUDY OF THE KINETICS UNDER NON-ISOTHERMAL CONDITIONS

4.1 Fundamental problems

4.1.1 Principles of kinetic data evaluation

The description of kinetics presents the problem of finding the dependence of the reaction rate on the parameters which define a given system. As far as heterogeneous processes involving solids are concerned, there are a large number of parameters to be considered[1]; they are temperature, pressure, composition of the system, the size and distribution of particles, etc. In most cases, the effect of the individual factors is studied separately.

When studying heterogeneous processes, there arises a difficulty due to the fact that the process may not be monotonous, i.e., no single process can be taken as the rate controlling process in the entire region of investigation. In most cases, during the initial reaction step, the rate is determined by the nucleation of a new phase; during the later stages, it is determined by the growth. The velocity, however, is controlled either by the phase-boundary reaction or by transport of reacting species. In these cases, the kinetic analysis is directed to arrange the experimental conditions in such a way as to make possible the investigation of kinetics of a single partial process.

If the required experimental conditions are met, satisfactorily, then the rate of the process, r can be described by the two functions

$$r = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = \mathrm{k}(T)\,\mathrm{f}(\alpha) \tag{4.1}$$

where the first function $\mathrm{k}(T)$, is only temperature dependent, while the second one, $\mathrm{f}(\alpha)$, is a function of the instantaneous phase composition of the system in question provided that the composition can be represented by the conversional transformation, α. It is the task of empirical kinetics to find the analytical form of both functions; that is, to determine the so-called kinetic parameters. Provided that all other possible variables are held constant, the thermodynamic process or simply process, is determined by the two quantities, α and T, as a function of time $[\alpha = \bar{\alpha}(t),\ T = \bar{T}(t)]$. Their time profile is investigated experimentally.

The most common experimental method is based on the investigation of the isothermal course of the process, that is, on an experimentally determined dependence of $\alpha = \bar{\alpha}(t)$ at $T =$ const. for a set of temperatures. Upon integration, eqn. (4.1) yields

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \mathrm{g}(\alpha) = \mathrm{k}(T)\,t\,. \tag{4.2}$$

The linear dependence of $\mathrm{g}(\alpha)$ on t makes it possible to find by way of trial and error the function which best corresponds to the experimental data, $\alpha = \bar{\alpha}(t)$. When defining the form of the thermal dependence of $\mathrm{k}(T)$, the Arrhenius relation, $Z \exp(-E/RT)$, is usually the most convenient and the constants, Z and E, are determined by graphical plotting $\log k(T)$ against reciprocal temperature, $(1/T)$.

The realisation of an isothermal measurement is based on the assumption that the initial nonequilibrium state of the system (the required onset of the process investigated) is obtained before the investigated process can advance to a measurable degree of transformation (the actual onset of the process). With heterogeneous systems, this requirement presents a number of experimental difficulties. As a result of fast heating, which is necessary in order to reach the desired working temperature, there arises a variable temperature gradient in the sample (a non-uniform distribution of temperature) so that the process becomes non-isothermal and thermally uncontrolable. This is particularly true for heterogeneous processes which are brought to a temperature which is far from the equilibrium temperature.

These obstacles can be avoided by using non-isothermal methods of investigation where the time dependence of temperature is intentionally programmed, frequently in a linear manner. Naturally, the temperature gradient still exists but it has a uniform character.

Upon the integration of eqn. (4.1), the following relation is obtained

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = g(\alpha) = \int_{T_{eq}}^{T} \frac{k(T)}{\phi}\,\mathrm{d}T. \tag{4.3}$$

This solution can be rewritten in the general form

$$\alpha = \bar{\alpha}(t, \phi). \tag{4.4}$$

After algebraic manipulation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \left(\frac{\partial \bar{\alpha}}{\partial T}\right)_{\phi} + \left(\frac{\partial \bar{\alpha}}{\partial \phi}\right)_{T} \frac{\mathrm{d}\phi}{\mathrm{d}T} \tag{4.5}$$

and because $\mathrm{d}\phi/\mathrm{d}T = 0$ (ϕ = constant), then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \left(\frac{\partial \bar{\alpha}}{\partial T}\right)_{\phi} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} \times \frac{\mathrm{d}t}{\mathrm{d}T} = \frac{\mathrm{d}\alpha}{\mathrm{d}t} \times \frac{1}{\phi}. \tag{4.6}$$

The same approach may be used for any type of heating (quadratic, hyperbolic, etc.).

The same course can be adopted for the class of isothermal processes expressed by eqn. (4.2), the solution of which may also be written in explicit form

$$\alpha = \bar{\alpha}(t, T). \tag{4.7}$$

It is formally valid that

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial \bar{\alpha}}{\partial t}\right)_{T} + \left(\frac{\partial \bar{\alpha}}{\partial T}\right)_{t} \frac{\mathrm{d}T}{\mathrm{d}t} = \left(\frac{\partial \bar{\alpha}}{\partial t}\right)_{T} \tag{4.8}$$

as under an isothermal measurement the temperature is constant, and thus, $\mathrm{d}T/\mathrm{d}t = 0$.

The rate of a process being defined by eqn. (4.1) or

$$\frac{d\alpha}{dt} = \left(\frac{\partial\bar{\alpha}}{\partial t}\right)_T = \left(\frac{\partial\bar{\alpha}}{\partial T}\right)_\phi \times \phi = \frac{d\alpha}{dT} \times \phi. \tag{4.9}$$

Recently the work of MacCallum and Tanner[2] has initiated rather extensive discussions[3–10] concerning the correctness of the mathematical treatment of data obtained under non-isothermal measurements. The equation

$$\frac{d\alpha}{dt} = \left(\frac{\partial\hat{\alpha}}{\partial t}\right)_T + \left(\frac{\partial\hat{\alpha}}{\partial T}\right)_t \frac{dT}{dt} \tag{4.10}$$

became the center of discussion; the question was how to interpret the individual total and partial rate terms. It should be noted that this equation resulted from the derivation of a general equation, $\alpha = \hat{\alpha}(T, t)$, and it is necessary to investigate its origin. It can be understood in two different ways:

a) As a function describing the given process in the system that obeys eqn. (4.1), which may be rewritten in the general form $\dot{\alpha} = F(\alpha, T)$. Hence, for a given temperature-on-time dependence, the function, $\hat{\alpha}$, represents the solution of the differential equation (4.1). This solution is dependent on the manner of temperature programming. Thus, for a constant heating rate, ϕ, the solution is $\alpha = \bar{\alpha}(t, \phi)$ (see eqn. 4.4). The expression is easily rearranged as follows: $\alpha = \bar{\alpha}(t, T/t) \equiv \hat{\alpha}(t, T)$. This clearly demonstrates the difference between the functions denoted $\bar{\alpha}$ and $\hat{\alpha}$, as well as between the meaning of their partial derivatives. This is also discussed in detail by Šesták and Kratochvil[10].

b) As a true constitutive equation, where the function dependence $\hat{\alpha}$ is valid invariably for any admissible process given by $[\alpha = \hat{\alpha}(\cdot);\ T = \hat{T}(t)]$, which the considered system undergoes. However, such a description would physically correspond to a material controlled by an internal clock, such as a material undergoing a spontaneous ageing. This, naturally, does not seem to be the case for an ordinary chemical reaction as treated by standard methods of chemical kinetics.

The above is worth mentioning as it indicates the importance of properly defining the limits of different approaches. It shows the difference between the constitutive equation established on one hand by long experience and/or of a suitable theory, and the admissible processes measured experimentally. The best framework for such considerations, however, uses the concept of rational thermodynamics[11].

4.1.2 The integration of the kinetic equation under non-isothermal conditions

Beside a knowledge of the proper form[1,10] of the functions $k(T)$ and $f(\alpha)$, the integration of eqn. (4.1) requires also the analytical expression for temperature programming. For a non-isothermal system[1], the relationship between the temperature, T, and time, t, is given by

$$dT/dt = \phi T^m \tag{4.11}$$

where dT/dt is the heating rate and ϕ and m are constants. Hence,

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_{T_0}^{T} \frac{k(T)}{\phi T^m} dT = P(T) \tag{4.12}$$

where the functions, $g(\alpha)$ and $P(T)$, depend only on the fractional conversion, α, and the temperature T, respectively. The integration limits are chosen in accordance with the beginning of the process. A choice of T_0 based on the view that the start of the heating is identical with the commencement of the kinetic investigation is misleading, since it can even result in the arbitrary choice of T_0 equal to absolute zero. The process of integration of eqn. (4.12) is carried out on two different levels. Establishment of the function, $P(T)$, is mathematically complicated but is based on the known form of the $k(T)$ function given as the Arrhenius exponential-type equation[1]. The problem of the integration of the left hand side of eqn. (4.12) is quite different because the function $f(\alpha)$ is usually not known.

4.1.2.1. $p(x)$ function (integration of the Arrhenius equation at rising temperature). Concerning the integration procedure, the simplest method would be to employ the linear variation of the reciprocal absolute temperature[12–15]

$$\int_{T_0}^{T} k(T)\frac{dT}{\phi T^2} = \int_{1/T_0}^{1/T} \frac{Z}{\phi}\exp\left(-\frac{E}{RT}\right) d\left(\frac{1}{T}\right)$$
$$= \frac{ZE}{R\phi}\left[-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{4.13}$$

where Z and E are the kinetic parameters to be determined (the pre-exponential factor and the activation energy respectively). Such experimental conditions are not currently available, although this idea is worthy of consideration[19] with the advent of sophisticated furnace temperature controllers. Unfortunately, from the viewpoint of the present mathematics, the most common experimental approach used thus far requires a constant heating rate, ϕ. It yields the linear temperature proportionality with time

$$T = T_0 + \phi t \quad \text{and/or} \quad dT/dt = \phi \tag{4.14}$$

As already noted, the temperature, T_0, is the lower integration limit from which the temperature increase holds a real meaning with regard to the investigated process.

Values of the exponential-integral, $E_i(-x)$, or of a related integral called the $p(x)$ function[18], are essential to the analyses of these thermal processes. In order to find a suitable analytical formulation, it is convenient to introduce a new variable, $u = E/RT$. Hence, combining eqns. (4.12) and (4.14)

$$\frac{1}{\phi}\int_{x_0}^{x} \frac{\exp(-u)}{u^2} du = \left[\frac{\exp(-u)}{u} - \int_{x}^{\infty} \frac{\exp(-u)}{u} du\right]_{x_0}^{x} \tag{4.15}$$

Because $E_i(-x)$ is defined as $-{}_x\int^{\infty} \exp(-u)\,du/u$. we may write

$$\int_x^{\infty} \frac{\exp(-u)}{u^2}\,du = \frac{\exp(-x)}{x} - E_i(-x) = p(x) \tag{4.16}$$

where the new function, $p(x)$, has been introduced on the basis of work by Akahira[16], Doyle[20], Šatava[21] and Vallet[22]. Although eqn. (4.16) cannot be expressed in a closed form, there exist several series for its approximation*. They are:

(1) For $x > 16$, through integration by parts

$$p(x) = \frac{\exp(-x)}{x^2}\left[1 - \frac{2!}{x} + \frac{3!}{x^2} \ldots + \frac{(-1)^n(n+1)!}{x^n}\right] \tag{4.17}$$

(2) For $x > 15$, according to Schlömilch[23]

$$p(x) = \frac{\exp(-x)}{x(x+1)}\left[1 - \frac{1}{x+2} + \frac{1}{(x+2)(x+3)} \ldots + \frac{(-1)^n An}{(x+2)\ldots(x+n)}\right] \tag{4.18}$$

where An is a specific constant[17].

(3) For $x > 10$, according to Taylor's formula:

$$p(x) = \frac{\exp(-x)}{x}\left[0.577 + \ln x^4 - x + \frac{x^2}{2\times 2!} \ldots + \frac{(-1)^n x^n}{n\times n!}\right] \tag{4.19}$$

(4) For $9 < x < 174$

$$p(x) = \frac{\exp(-x)}{x}\left(\frac{674.567 + 57.412x - 6.055x^2 - x^3}{1699.066 + 841.655x + 49.313x^2 - 8.02x^3 - x^4}\right) \tag{4.20}$$

(5) For $20 < x < 60$, according to Doyle[24]

$$\log p(x) = -2.315 + 0.4567x. \tag{4.21}$$

Although asymptotic series are divergent, a limited number of terms of the series can be used to calculate a value for the $p(x)$ function to an accuracy which depends on x and the number of terms chosen. This was first discussed by Akahira[16], Doyle[25], and later, in more detail, by Biegen and Czandera[26] and Gyulai and Greenhow[26b].

---

*If the pre-exponential factor, Z, is assumed to be linearly dependent on temperature, $Z = Z'T$, then[22]

$$g(\alpha) = -\frac{Z'E^2 p'(x)}{2\phi R^2}$$

where $p'(x) = \frac{\exp(x)}{x}\left(-3.5\times 10^{-6} - \frac{0.001\,029}{x} + \frac{1.948\,765}{x^2} \ldots\right)$.

A table of $\log p'(x)$ functions was composed to investigate the effect of temperature dependence by Vallet[22] who also derived expressions for $Z = Z'T^{1/2}$ and corresponding formula for $p'(x)$ function calculations.

The tabulations of the $E_i(-x)$ function are given by the following investigators:

Akahira[16]	$[x = 20(0.01)50]$
Harris[27]	$[x = 1(1)4(0.4)8(1)50]$
Miller and Hurst[28]	$[x = 0.2(0.05)5(0.1)10(0.2)20(0.5)50(1)80]$
Glaischer and Caylay[29]	$[x = 0.01(0.01)5(0.1)15]$
Jahnke and Embde[30]	$[x = 0.01(0.01)1(0.1)15]$
Abramowitz and Stegun[31]	$[x = 0.5(0.01)2(0.1)7]$ and
USSR tables[32]	$[x = 0.0001(0.0001)1.3(0.001)3(0.005)10(0.1)15]$

and many other tables[32–35].

The function $p(x)$ was calculated by:

Doyle[20]	$[x = 10(1)50]$
Oberländer[36]	$[E = 0.2(0.2)0.2\ T = 25(25)1000;\ 150(10)390]$
Zsako[37]	$[E = 10(2)66,\ T = 273(10)600]$
Biegen and Czandera[26]	$[x = 15(0.1)50]$

and others such as Vallet[22], Smith and Aranoff[38], Redhead[39], Šatava and Škvára[40], and Flynn and Wall[19]; computer programs are also available[26,40,40a].

Because there is insufficient range and detail in the value of x to permit analysis of thermal processes in a wide region of x's, the tables of $p(x)$ function in the region, $E = 7(2)145$, $T = 273(10)1773$ are given in Appendix I. A Tesla computer and Fortran language[40a] were used to sum the series in eqn. (4.20) with a reported error of less than 10^{-7}.

Integrating eqn. (4.12) for the case of a constant heating rate, ϕ, the expression is obtained

$$g(\alpha) = \frac{ZE}{R\phi}\left[p\left(\frac{E}{RT}\right) - p\left(\frac{E}{RT_{eq}}\right)\right] \tag{4.22}$$

where Z, E, R and ϕ are the temperature-independent constants and T_{eq} is the equilibrium temperature for the process. For $T \gg T_{eq}$, the second term in the square brackets is negligible with respect to the preceding term and eqn. (4.22) is simplified to Doyle's equation[20]

$$g(\alpha) = \frac{ZE}{R\phi}\,p\left(\frac{E}{RT}\right). \tag{4.23}$$

Other cases of non-linear heating have been developed for the study of the ageing of insulating materials[14,16]*.

---

*A general case of non-programmed temperature variation is exponential-like. $T = T_{fin} - (T_{fin} - T_0)\exp(-qt)$, where T_0 and T_{fin} are the starting (0) and final (fin) temperatures. This course of temperature is often met in the first period of isothermal experiments[17] or in the investigation of electrical insulators[14,16]. Hence, the heating rate between the start of heating, T_0, and the onset of the final

4.1.2.2. Empirical kinetics (choice and integration of simplified model relations). If only a formal description of the process is the aim of the investigations then it is satisfactory to fulfil the mathematical requirement of eqn. (4.12) by a simple function $f(\alpha)$[1], in the most simple form[17],

$$f(\alpha) = (1-\alpha)^n \tag{4.24}$$

where n is the exponential factor, sometimes called the reaction order, in analogy with homogeneous kinetics. This factor has a purely empirical significance and is by no means a universal constant for heterogeneous reactions[1,50]. In contrast to homogeneous-like kinetics, fractional or even negative reaction orders, n, are often observed. However, this concept has proven useful as a means of classifying a limited number of solid state reactions (phase-boundary controlled processes where $n = 0$, $1/2$, $1/3$ and 1) and so may serve as preliminary information to the reaction kinetics[1]. Furthermore, it is found suitable for obtaining a measure of the change in the kinetic processes when comparing a series of experiments conducted under different conditions which is usually the case with engineering investigations.

The above form of the function, $f(\alpha)$, cannot describe the kinetics of diffusion or nucleation and or nuclei growth. The latter can be fitted by the Johanson–Mehl–Avrami–Yerofeyev–Koglomorov equation[41],

$$g(\alpha) = -\ln(1-\alpha) = kt^r \tag{4.25}$$

The function, $f(\alpha)$, can be derived from eqn. (4.25), or

$$f(\alpha) = (1-\alpha)\,(-\ln(1-\alpha))^p = k^*t \tag{4.26}$$

where $k^* = rk^{(1/r)}$ and $p = 1-(1/r)$. This equation contains the polynomial character of the expression. Upon expansion, eqn. (4.26) may be transformed into the form[42–44]

$$(1-\alpha)\,(-\ln(1-\alpha))^p \cong (a_0 + a_1\alpha + a_2\alpha^2 + \ldots)\,(b_0\alpha^p + b_1\alpha^{p+1} + b_2\alpha^{p+2} + \ldots) \tag{4.27}$$

and finally rearranged as

$$= c_0\alpha^p + c_1\alpha^{p+1} + c_2\alpha^{p+2} + \ldots \cong \alpha^m(1-\alpha)^n \tag{4.28}$$

where a, b and c are constants and the values of the exponent-factors p and n are given in Fig. 4.1. These two-exponent type equations (4.27) and (4.28) demonstrate well the similarity of different kinds of mathematical description and the unnecessary use of any more complicated (e.g., three-exponent) expressions[44]. They represent a more generalized form of eqn. (4.24) by adding the function α^m.

---

required temperature, T_{fin}, is given by $d \ln T/dt = q = \text{const.}$ (m in eqn. (4.11) is equal to one). The integration of the rate equation, after the substitution for the function variable, gives

$$u = \frac{E}{T_{\text{fin}} - (T_{\text{fin}} - T_0)} \exp\left(\frac{-qt}{R}\right).$$

An exponential integral in the form

$$E_i(-x) - \exp(-x_{\text{fin}})\,E_i(x_{\text{fin}} - x)$$

for $x = E/RT$ and $x_{\text{fin}} = E/RT_{\text{fin}}$ is then obtained.

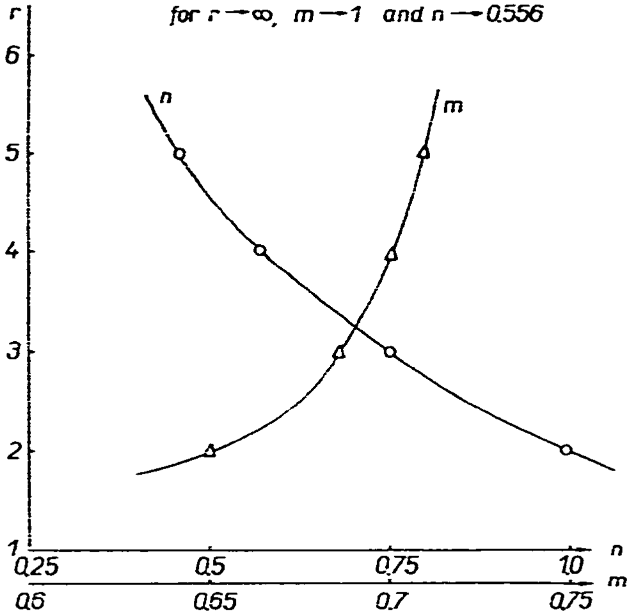


Fig. 4.1. Plot for determination of exponent factors n and m from known value of r.

This generalization can also be made by introducing a function of time $f^{+}(t)$, as a multiple to the simple function, $f(\alpha)$, in eqn. (4.24). It was found empirically that an equation of the following form is mathematically suitable to describe a variety of reactions[45]

$$\frac{d\alpha}{dt} = k^{+} t^{r-1}(1-\alpha)^{n} = k^{+} f(\alpha)\, f^{+}(t) \tag{4.29}$$

It should be noted however, that k^{+} is not a true rate constant because it is defined inconsistently by an equation involving both variables α and t. Therefore, such an expression is not capable of yielding comparable values of kinetic parameters unless eqn. (4.29) is mathematically transformed into the dependence on either variable, α or t. It may by accomplished, for example, by dropping the so-called impingement factor, $(1-\alpha)$, from eqn. (4.29) to give[41]

$$d\alpha/dt \cong t^{r-1} \text{ and therefore } \alpha = t^{r}/r \tag{4.30}$$

hence,

$$d\alpha/dt \cong \alpha^{[1-(1/r)]} = \alpha^{m} \tag{4.31}$$

It is plausible that eqn. (4.28) also applies to the case described by eqn. (4.29) by reintroducing $(1-\alpha)^{n}$ into eqn. (4.30).

The following alternative rate equation[46] is of more general utility

$$\frac{d\alpha}{dt} = k\alpha^{m}(1-\alpha)^{n}(-\ln(1-\alpha))^{p} \tag{4.32}$$

where m, n and p are empirically obtained exponent factors, one of them being always zero[43,44,46].

In some cases it is more favorable to express the function $f(\alpha)$ in the form of a polynomial with a suitable number of terms, as given by eqns. (4.27) and (4.28), and to determine the individual constants (c's) by fitting the experimental data. This is useful when a numerical derivation is needed[17] and/or in polymer chemistry[19] to describe various types of depolymerizations, e.g., $6(\alpha^{1/2}-\alpha)$;

$$-\frac{60}{31}\left(\alpha^{3/2}+\alpha-\frac{7\alpha^{1/2}}{4}-\frac{1}{4}\right)$$

and/or

$$-\frac{24}{13}\left(\alpha^{3}+\alpha^{2}-\frac{7\alpha}{4}-\frac{1}{4}\right).$$

A more exact approach, which enables the determination of the most probable rate-controlling processes, is based on fitting experimental data with a known model relation, $g(\alpha)$ (ref. 47) (see Chapter 3). The most suitable function, $g(\alpha)$, is found by a trial and error method from a set of case-models corresponding to the appropriate reaction mechanisms[1,46–49]. This is perhaps the best method for obtaining the reaction path because such data provide the first information to direct the consequent experimental study in order to explain the detailed reaction kinetics and mechanism. For details of this approach, see section 4.2.3.

4.1.3. Influence of kinetic parameters on the shape of non-isothermal curves

The shape of non-isothermal curves is affected by both the model relation, $g(\alpha)$,

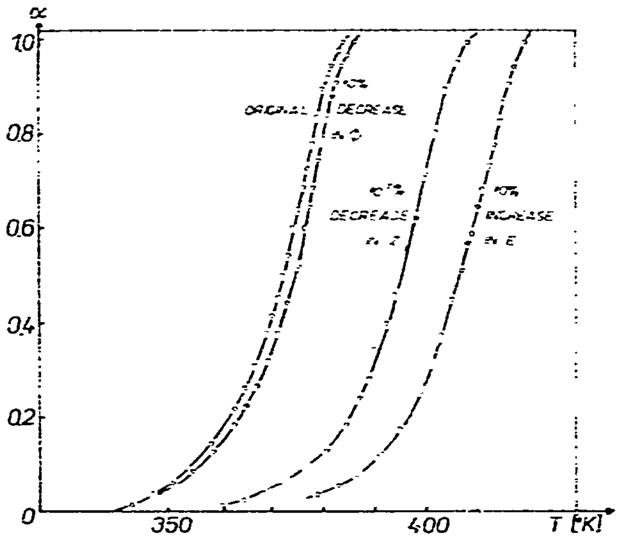


Fig. 4.2. Effect of the change of individual kinetic parameters on the shape of the original non-isothermal curve[51], where $E = 27\times10^3$ cal mole^{-1}, $Z = 10^{10}$ s^{-1}, $\phi = 3.18$ °C/min, $f(\alpha) = (1-\alpha)^{1/2}$ (see text).

reflecting the reaction mechanism and the kinetic parameters. E and Z, characterizing the temperature dependence of the reaction rate. The term, $g(\alpha)$, reaches the value of unity for α approaching one (or for $\alpha = 0.5$, $g(\alpha) \cong 10^{-1}$) and therefore, the right-hand side of eqn. (4.23) must also be of this magnitude. The effect of these phenomena on the so-called integral curves is graphically demonstrated in Fig. 4.2, assuming a simple process propagating far above its equilibrium temperature. The constructions of TG curves by Doyle[20] and Šatava[21] was discussed first by Flynn and Wall[19], Šesták[51], Ozawa[52], and later by others[40,53–56]. Mathematically, the changes in eqn. (4.23) may be induced by[51]:

(a) the change in the multiplying constant, $EZ/\phi R$,

(b) the change in the function, $p(E/RT)$,

(c) the change of model relation, $g(\alpha)$.

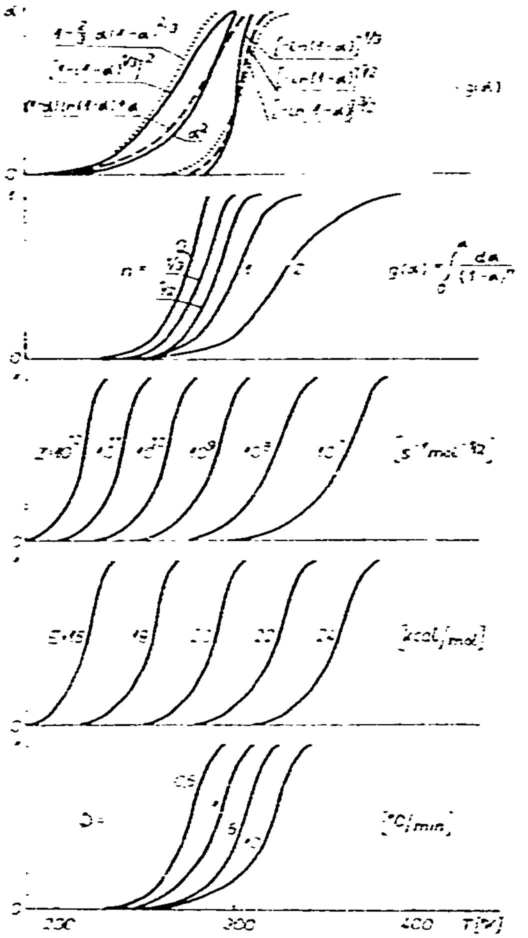


Fig. 4.3. Graphical demonstration of the influence of the individual kinetic parameters on shape and position of TG curves, where $E = 2 \times 10^4$ cal mole^{-1}; $Z = 1 \times 10^9$; $\phi = 1$ °C/min. $g(\alpha) = 1-(1-\alpha)^{1/2}$ if not specified differently.

For the first point, maintaining a constant value for g(α) ($\cong 1$), if Z is decreased by one order of magnitude, then the value of the function, p(E/RT), must accordingly increase by one order of magnitude to maintain the required balance between the left and right hand sides of eqn. (4.23). This is only possible by the shift, $E/RT \rightarrow E/R(T+\Delta T)$. Alternatively, the change in E by ten per cent does not greatly affect the multiplying constant, $EZ/R\phi$, but it substantially changes the value of the function, p(E/RT). This variable must be compensated thus: $E/RT = (E+\Delta E)/R(T+\Delta T)$ (see Fig. 4.3). It can be seen that the changes in the kinetic parameters, E and Z, are closely related and mutually supported and may be compared to the correlation between the pre-exponential, entropy-like term, and the exponential, energy-barrier term, in the original Arrhenius rate constant (see section 3.2).

In an opposite manner, a similar procedure can be adapted to enumerate the effect of operational variables[51] (changes in the measured temperature and heating rate) on the value of calculated kinetic parameters. Since the temperature detected experimentally is usually higher than that inside the reacting sample, higher values of the kinetic parameters are to be expected, or, $T+\Delta T \equiv\ > E+\Delta E$ and/or $T+\Delta T \equiv\ > Z+\Delta Z$ (accompanied also with a slight increase of E). Consequently, the deviation in the heating rate, ϕ, by ten per cent influences the multiplication constant only to a small degree but brings a comparatively larger change in the p(x) function and increases the curve slope and curvature (see Fig. 4.3). Uncertainties in the measurement of T and ϕ, together with a possible error in α, are essential for the *accuracy* with which the kinetic parameters, E and Z, are determined. On the other hand, the appropriate choice of the function g(α), see point (*3*) (as well as the function k(T) in eqn. (4.1)) determines the *correctness* of the kinetic parameters (i.e., whether these kinetic constants are attributed to the true rate-controlling process).

The effect of kinetic parameters on the shape of differential curves was calculated by Jüntgen and van Heek[55] using the equation,

$$\frac{\mathrm{d}V}{\mathrm{d}T} = \frac{Z}{\phi}\exp\left(\frac{-E}{RT}\right)(V_\infty - V)^n \tag{4.33}$$

where V is the volume of gaseous product liberated in time t and V_∞ is volume of the product finally obtained. After integration of eqn. (4.33), and introduction of the p(x) function, the following set of equations is obtained for the discrete values of reaction order, n,

$$n = 0, \quad \mathrm{d}V/\mathrm{d}t = A \tag{4.34}$$

$$n = \tfrac{1}{2}, \quad \frac{\mathrm{d}V}{\mathrm{d}t} = A\left[V_\infty^{1/2} - \frac{Z}{2\phi}\,p\left(\frac{E}{RT}\right)\right]^{-1/2} \tag{4.35}$$

$$n = 1, \quad \frac{\mathrm{d}V}{\mathrm{d}t} = AV_\infty \exp\left[-\frac{Z}{\phi}\,p\left(\frac{E}{RT}\right)\right] \tag{4.36}$$

$$n = 2, \quad \frac{\mathrm{d}V}{\mathrm{d}t} = A\left[\frac{1}{V_\infty^{1/2}} + \frac{Z}{2\phi}\,p\left(\frac{E}{RT}\right)\right]^{-2} \tag{4.37}$$

where A is a constant. The diagramatic representation of the above equations is given in Fig. 4.4. Similar calculations were made for DTA curves[62] first by Reed et al.[142] and recently also correlated with regard to the kind of rate-controlling processes[61] (see section 4.4, Fig. 4.21).

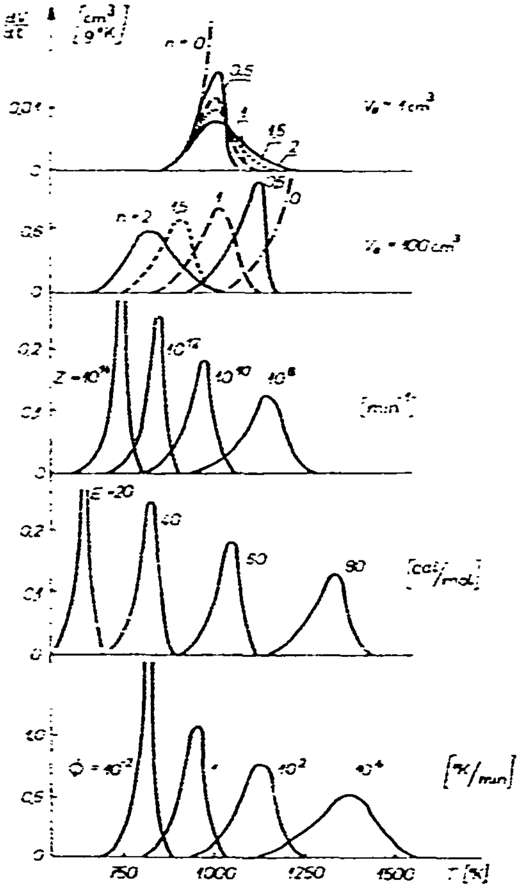


Fig. 4.4. Graphical demonstration of the effect of individual kinetic parameters on the shape and position of effluent analyses (i.e., derivative) curves, where $V_0 = 20\ \mathrm{cm}^3$, $E = 5 \times 10^4$ cal mole^{-1}, $Z = 10^{10}\ \mathrm{cm}^{3(1-n)}\ \mathrm{min}^{-1}$, $\phi = 3\ ^\circ\mathrm{C/min}$ and $f(\alpha) = (1-\alpha)^n$ for $n = 1$ if not specified differently (according to Jüntgen and Van Heek[55]).

4.1.4. *Experimental conditions and significance of calculated kinetic data*

The most important problem arising in the study of heterogeneous process kinetics is the precise definition of both the initial state of the system and the conditions under which the experiment is conducted. For exactly determined conditions, the path between the initial and the final state of the system is given only by the properties of the material investigated. If the goal of the investigation is a technological application of the process studied, then the initial state and experimental conditions duplicate the actual operational conditions. Such a case may be a pilot-plant type reactor so that the laboratory determined time course of the process corresponds to that to be expected in an actual plant process. The main interest is probably directed to the energy consumption and not to the elucidation of the reaction mechanism. In general, kinetic studies are usually intended to verify theoretical assumptions about the physico-chemical nature of the process and to find a reaction mechanism which holds for constant conditions influencing the reaction rate (pressure, temperature, concentration, etc.). Using TA methods, the characteristic elevation of the temperature brings into consideration the problem of holding constant experimental conditions within a certain temperature interval. For transitions in condensed systems, the required conditions are readily put into use, as shown in Fig. 4.5a. In the case of gaseous products, the simplest method is given in Fig. 4.5b which is also suitable for multicomponent systems forming no solid solutions (decomposition of carbonates, metal salt hydrates, etc.).

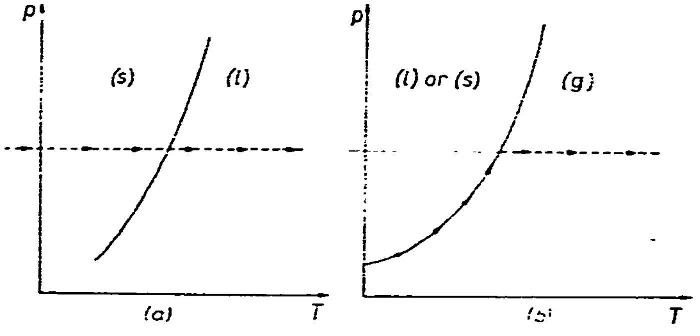


Fig. 4.5. Graphical representation of conditions of a process accomplishment.

In the case of the formation of solid solutions and/or new chemical compounds in multicomponent systems, the relations become quite complicated[67,67a]. The corresponding non-isothermal fractional conversion, λ, is then composed of two com-

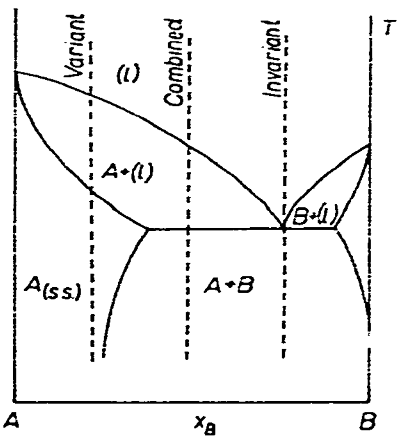


Fig. 4.6. Three possible types of processes differing in their temperature dependence for a binary system[8].

ponents. The first component relates to the entire kinetic process and equals the normal fractional conversion of the corresponding invariant process, α. The second component, λ_{eq}, reflects the propagation of equilibrium (the shift of the final state) with a temperature increase. The non-isothermal degree of conversion for variant processes, λ, and the equilibrium advancement for the process, λ_{eq}, can be defined by the relationship introduced by Holba and Šesták[8].

$$\lambda = \alpha\lambda_{eq}. \tag{4.38}$$

It can be applied to the case of melting in binary phase diagrams, (Fig. 4.6) where components A and B form a solid solution (s.s). Three typical processes may be distinguished, according to Fig. 4.7. The normalized change of the equilibrium

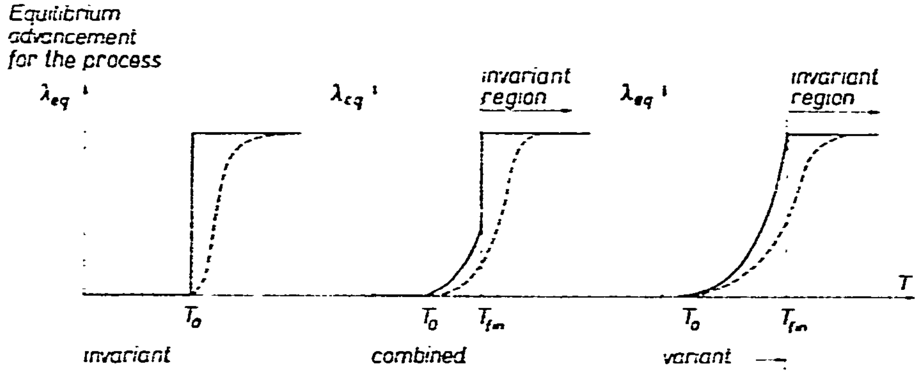


Fig. 4.7. Diagramatic representation for the course of the degree of conversion on temperature for three systems. The full line represents conditions of an infinitesimally slow heating (equilibrium curve), the dashed line represents conditions of a definite heating rate (real curve).

advancement, λ_{eq}, quantitatively describe each of them using the lever rule[8]. It is evident that only those processes may be described by the normal kinetic equation which have an invariant character (a temperature-invariant final state), or for which the variant temperature region is small and so the onset of the kinetic investigation lies at a temperature above this region. In all other cases a knowledge of the temperature dependence of λ_{eq} is required in order to satisfy the universal non-isothermal kinetic equation,

$$\frac{d\xi}{dt} = \frac{1}{\lambda_{eq}}\left(\frac{d\lambda}{dt} - \lambda\phi\frac{d\ln\lambda_{eq}}{dT}\right) = k(T)\,f(\alpha) \tag{4.39}$$

given by Holba and Šesták[8]. This expression is valid for the case where f(α) represents a process mechanism, which is independent of temperature, and where the left-hand side of eqn. (4.39) signifies the modified rate of the process, $d\xi/dt$. In a practical sense, it is applicable to the processes of dissociation and oxidation of quenched oxides and alloys.

In the case of coexistence in time of processes which develop within a wide temperature interval, it is clear that a superposition of processes is to be expected. If the conditions of the experiment are precisely defined the corresponding plot of λ_{eq} vs. T can be realized even for such a combination. It should be emphasized that owing to insufficient choice, definition, and constancy of experimental conditions during an experiment, an unwanted superposition of processes may be created. As an example, the combined process of evaporation and boiling of water in Fig. 4.7b. The plot of λ_{eq} vs. T may be of assistance in separating simple processes by a suitable modification of experimental conditions. It is important for the physical meaning of the kinetic parameters subsequently evaluated since these relate only to simple processes.

The determination of the function, g(α) and/or f(α), requires certain assumptions pertaining to the character of the initial system. The experimental set-up of the system investigated should comply with the hypothetical-case-model, for example, the Jander equation for three dimensional diffusion (section 3.4.4) is valid only in the case when the particles of one reacting component of a powder mixture are at least 10–100 times larger than the particles of the second component. Besides these geometrical requirements, the hydrodynamic conditions on the reacting interfaces are of great importance (section 3.6.1). The transport of matter and/or energy may become the rate-controlling process or at least a part of the slowest process. By a suitable choice of experimental conditions it is possible to investigate the individual regions where an elementary process has the most determining character. Practically, the tendency is to exclude the transport processes by means of thin layers of solid samples[51,59] in good contact with large heat reservoirs in order to facilitate the heat exchange between the sample and its holder and also to minimize self-heating and/or self-cooling phenomena[59,60].

The mass transport in the surrounding fluid phase may also serve as an effective impedance factor. High velocities of flowing gases and/or low, well-defined pressures are thus desirable. The latter method is more convenient in TG experiments because of the difficulty in obtaining well-defined conditions of a gas stream along the solid sample surface. From this viewpoint, the recommended method of studying processes on phase boundaries is a continuous gas evolution analysis of a fluid-bed sample.

Another problem is the real physical meaning of the calculated kinetic parameters. Beside the requirement of a known mechanism, the best examples of kinetic constants comprising individual rate determining processes may be the case of the complex activation energy for nucleation and crystal growth (see section 3.4.3 and Table 3.6). The latter is composed of two thermodynamic work terms associated with the formation of new phase stable domains and with the accomodation of product species in the growing lattice and of the terms arising from the kinetic barrier to transport. Relatively high values of such activation energies determined for crystallization processes in glasses (about 100 kcal/mol) may be basically explained by the large contribution of the activation energy for diffusion[63]. The activation energy of glass ionic (d.c.) conductivity determined just below the crystallization region may be of assistance in further analysis.

In some instances it is of value to compare the results obtained under isothermal and non-isothermal conditions[64–66]. Although the former techniques involve the difficulty connected with the precise determination of onset temperature, in comparison with a non-isothermal method, it provides more information necessary for a detailed determination of the reaction mechanism. Assuming a constant function $g(\alpha)$, the correlation between these two techniques was made by Doyle[24] and later improved by Szako[58] who estimated the isothermal data from thermogravimetric data. If samples of the same geometry and degree of subdivision are subjected to isothermal and non-isothermal TG measurements under otherwise identical experimental conditions, then identical values of α and $g(\alpha)$ are obtained. The isothermal ageing time, t_j, and the absolute TG temperature T_j, at which the same value of α occurs are related by

$$\log t_j = \log \frac{E}{\phi R} + \frac{0.434 E}{R T_{\mathrm{ISO}}} + \log p \frac{E}{R T_j} \tag{4.40}$$

where T_{ISO} is the absolute ageing temperature.

Generally there has been good agreement between the parameters calculated by both methods[43a,64–66,131,131a], under comparable experimental conditions.

Schneider[68,69] has treated the interdependence between the observed effect of the degree of conversion and the heating rate on the apparent activation energy of polymer thermal degradation reactions using TG methods. It was shown that complex chain reactions, which occur in non-stationary TG conditions, always display such influences. By extrapolation of the obtained apparent activation energies it is possible to deduce the activation energy of initiation while the values corresponding to the maximum reaction rate lead to the activation energy for quasi-stationary reaction, comparable with that obtained under isothermal reaction conditions.

4.2. Methods of kinetic data evaluation

The determination of kinetic parameters and model relations is made from one of the experimental expressions: $\dot{\alpha} = Z \exp(-E/RT)\, f(\alpha)$ or $g(\alpha) = (ZE/R\phi)\, p(E/RT)$. The first methods are called differential types while the second are integral. Such a classification is not completely consistent because some of the methods of evaluation use combinations of both approaches.

4.2.1. Historical development of applied non-isothermal kinetics

In spite of a surprisingly extensive literature prior to 1960 on non-isothermal methods of kinetic data evaluations, this field was long ignored by chemical kineticists[92]. Accordingly, the pioneering work in non-isothermal kinetics remained relatively unknown. The first attention to the neglected literature was given by Flynn[70]; due to the large amount of work by many authors, attention is called to the following reviews[17,19,70,71].

The use of thermal analysis to measure reaction rates dates to the work of Bruylants in 1911. A major contribution was made by Akahira in 1925 who also was the first to publish tables to evaluate the p(x)-like function. Urbach (1930) introduced an equation for the maximum of the glow curve derived to evaluate the first order kinetics from inflection points. In 1932, Škramovský pointed out some advantages of non-isothermal methods. Vallet (1935), Sherman (1936) and Brietmann (1937) dealt with the temperature dependence of the reaction rate by improving the use of the p(x)-like function. In 1948, Randall–Wilkins and Garlich–Gibbson developed a theory of glow curves while Harton used the numerical approximation of p(x)-like functions. Segawa was the first to calculate activation energies from the following equation (where j is an arbitrary point)

$$\log k_j = \log\left[\frac{(\mathrm{d}\alpha/\mathrm{d}T)_j}{f(\alpha)_j}\right] = \log\frac{Z}{\phi} - \frac{E}{2.3\,R}\left(\frac{1}{T_j}\right). \tag{4.41}$$

In 1951, Van Krevelen, Van Heerden and Hutjens made a comprehensive analysis of integral methods and published nomograms for kinetic data evaluation. Richter and Vallet (1953) applied non-isothermal kinetics to the $CaCO_3$ decomposition, while Bohun (1953) was the first to evaluate the activation energy from the variation of the maximum temperature with the heating rate. The most extensive development took place in the next ten years, for example: 1955 (Boersma; Murray and White; Baur, Bridges and Frassel; Gaensslen and Mackenzie); 1957 (Borchardt and Daniels; Berg; Frentz; Koftsad; Jongi; Tsuzuki and Nagasawa); 1958 (Freeman and Carroll; Daneš and Ponec; Smith and Arranof; Hoogenstraaten); 1959 (Barrer and Bratt; Whitman; Lumme; Anderson; Kissinger; Vallet; Blumberg); 1960 (Murgulescu and Segal; Newkirk); 1961 (Doyle; Garn; Markowitz and Boryta; Šatava; Jaque, Guichon and Gendzel; Wendlandt); 1962 (Flynn; Wall; Lukaszewski; Franck and Sizmann; Turner, Schnitzer and Hoffmann; Reich; Berlin and Robinson; Kwong-Hwa; Proks; Redhead); 1963 (Horowitz and Metzger; Anderson; Friedman; Šesták; Haber, Rosický and Škramovský; Lee and Levi); 1964 (Piloyan; Coats and Redfern; Magnusson; Fuoss, Sayler and Willson; Savin; Rezniczenko; Ingraham and Marier; Tratore; Rabovkyi; Nikolayev; Schneider; Szekely); 1965 (Brindley, Achar and Sharp; Hughes; Szako, Chaterjee; Jüntgens and Peters; Fatu; Rogers and Smith; Lutter and Gerbach; Osawa; Bohon; Reed, Weber and Gottfried; Heide); plus other numerous titles in the recent literature. The first comprehensive reviews in non-isothermal methods of kinetic data evaluation were published about the same time (1966/67) by Flynn and Wall (general treatment of the thermogravimetry of polymers), Šesták (methods of kinetic data evaluations from isothermal and non-isothermal TG curves) and Murgulescu and Segal (study of the kinetics of heterogeneous reactions by thermogravimetry).

4.2.2. *Differential methods*

Differential methods are based on the use of the dependence of the instantaneous reaction rates, ($\mathrm{d}\alpha/\mathrm{d}t$), on the temperature, T. This application seems to be simple and, in some cases, is able to circumvent difficulties found in many of the so-called "integral" methods where the direct dependence of the fractional conversion on temperature is used. However, they suffer from an inherent weakness such as the magnification of experimental scatter due to differentiation which thus produces the necessity of very precise and tedious recording. Many differential methods assume the existence of a single reaction order, n, as an empirical constant [see eqn. (4.24)]. The most widely used method of this kinetic analysis of TG data is the difference-differential method first introduced by Freeman and Carroll[73,74], on the basis of $f(\alpha) = (1-\alpha)^n$.

$$\Delta \log \frac{d\alpha}{dT} = n\Delta \log(1-\alpha) - \frac{E}{2.3R}\Delta\left(\frac{1}{T}\right) \tag{4.42}$$

which can be rearranged in two different ways[19]:

$$(1) \quad \left[\frac{\Delta \log d\alpha/dT}{\Delta \log(1-\alpha)}\right] = -\frac{E}{2.3R}\left[\frac{\Delta(1/T)}{\Delta \log(1-\alpha)}\right] + n \tag{4.43}$$

$$(2) \quad \left[\frac{\Delta \log d\alpha/dT}{\Delta(1/T)}\right] = n\left[\frac{\Delta \log(1-\alpha)}{\Delta(1/T)}\right] - \frac{E}{2.3R}. \tag{4.44}$$

These equations have been employed to determine the kinetic parameters, E and n, from TG curves with a reported success not only for the degradation of polymers but also for simple inorganic decomposition reactions. However, at the same time, they have been subjected to much criticism[74]. It is obvious that the magnitude of errors depends on the position of the point j, on which the kinetic analysis is being performed[17,19]. Considering an approximately constant experimental scatter, the determination both at low and high conversions will be quite erroneous. The disadvantage of this method, the usual graphical determination of rates, may be improved by numerical solutions such as[17]:

$$\left(\frac{d\alpha}{dt}\right)_0 = \frac{1}{Q}\left[\frac{\Delta_0+\Delta_{-1}}{2} - \frac{\Delta^3_{-1}+\Delta^3_{-2}}{12} + \frac{\Delta^5_{-2}+\Delta^5_{-3}}{60}\cdots\right]. \tag{4.45}$$

Where Q is the constant time or temperature interval of scanning and Δ^k_j is the difference between j and $j+1$ points of k order. On introducing eqn. (4.45) to eqn. (4.42) and neglecting terms higher than first order, there is obtained the expression

$$\left[\log\frac{w_{j+2}-w_j}{w_{j+1}-w_{j-1}}\right] = n\left[\log\frac{w_\infty-w_{j+1}}{w_\infty-w_j}\right] - \frac{E}{2.3R}\left[\frac{T_{j+1}-T_j}{T_{j+1}T_j}\right]. \tag{4.46}$$

This is suitable for the simple numerical method of thermogravimetric data where w_j and w_∞ are the instantaneous (j) and the final (∞) measured weight loss. For a precise determination, the electronic or polynomial derivatives are required. Flynn and Wall[19] pointed out, however, that the difference-differential method gives only a procedural n and E, particularly where an additional competitive or independent reaction takes place, and treatment of each linear-like range independently does little to improve the results (see section 4.3).

This disadvantage may, of course, be improved by direct use of a less formal case-model. In the case of nucleation and crystal growth, the general function is given by eqn. (4.26), i.e., $f(\alpha) = (1-\alpha)(-\ln(1-\alpha))^p$ and then[43,43a,44]

$$\left[\frac{\Delta \log\left[(\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)\right]}{\Delta \log(-\ln(1-\alpha))}\right] = -\frac{E}{2.3R}\left[\frac{\Delta(1/T)}{\Delta \log(-\ln(1-\alpha))}\right] + p \tag{4.47}$$

Generally, the f(α)-function is determined by two exponents, n, m or p [see eqns. (4.28) and (4.32)]: for the simultaneous determination of three kinetic parameters (E, n, m, or p), it becomes necessary to resort to a numerical method of calculation. For example, the equation*

$$\Delta \log\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = -\frac{E}{2.3R}(\Delta 1/T) + m\Delta \log \alpha + n\Delta \log(1-\alpha) \tag{4.48}$$

and/or

$$\Delta \log\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = -\frac{E}{2.3R}(\Delta 1/T) + n\Delta \log(1-\alpha) + p\Delta \log(-\ln(1-\alpha)) \tag{4.49}$$

forms a set of non-homogeneous linear equations for different values of α and T scanned at equidistant points.

A radical simplification includes the assumption[77] that the reaction rate, $\mathrm{d}\alpha/\mathrm{d}t$, is influenced more by the change in the temperature-dependent constant than by the change in the function f(α). In such a case the reaction mechanism is not important and E can be roughly calculated by the equation:

$$\log\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \frac{E}{2.3R}(1/T) + [\log Zf(\alpha)] \cong \frac{E}{2.3R}(1/T) + \text{const.} \tag{4.50}$$

This is believed to be true when working in the initial part $(0.2<\alpha<0.5)$ of the sigmoidally shaped curves of α vs. T, (or close to the maximum values of $\mathrm{d}^2\alpha/\mathrm{d}t^2$). A comparison of kinetic data thus calculated for the thermal decomposition of $KMnO_4$ is given[44] in Fig. 4.8 using eqns. (4.41), (4.43), and (4.50).

For a kinetic analysis which utilizes the detection of the volume of volatilized reaction products (or products in an inert gas, as for gas chromatography or mass

---

*The exponent factor m in eqn. (4.48) may also be determined in analogy with the above simple difference-differential methods. After differentiating with respect to $\log \alpha$ and rearrangement it gives

$$\left[\frac{\mathrm{d}(\log(\mathrm{d}\alpha/\mathrm{d}t))}{\mathrm{d}\log \alpha} + n\frac{\alpha}{1-\alpha}\right] = -\frac{E}{2.3R}\left[\frac{\mathrm{d}(1/T)}{\mathrm{d}\log \alpha}\right] + m$$

for fixed values of n equal to, e.g., 2, 1 and 1/2. We notice once more that E and m are procedural values and it is unnecessary to assume them to be constant in the whole reaction region. But, in fact, any observed variation of m would have to be quite large to be significant enough. For detailed mathematical analysis of formal descriptions used in non-isothermal kinetics see ref. 43.

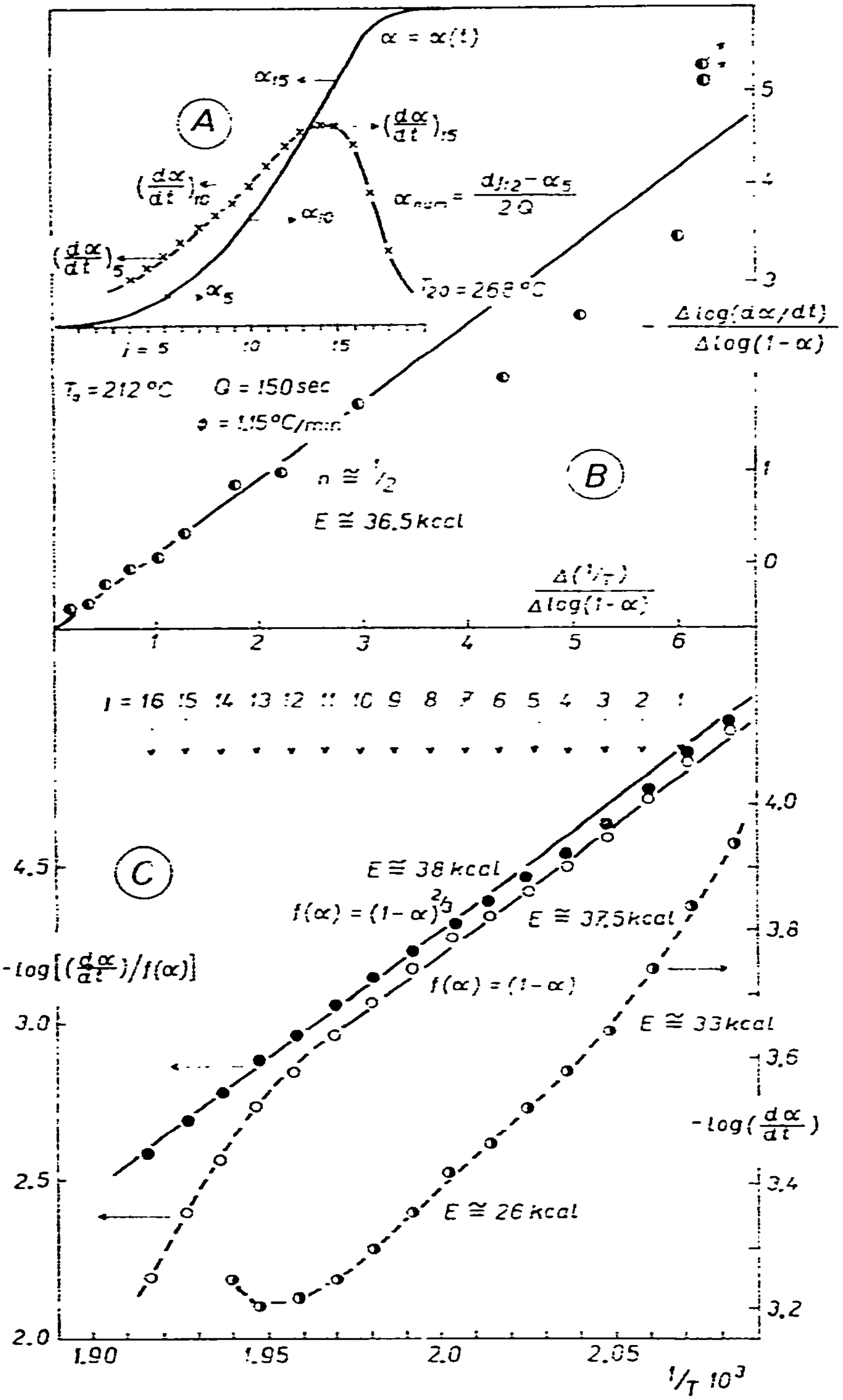


Fig. 4.8. Example of the manual evaluation of a TG curve[44]. (A) for the decomposition of freshly powdered $KMnO_4$ using differential (C) and difference-differential (B) methods (see text). The most linear plot is obtained assuming phase-boundary reaction as the rate controlling process.

spectrometry) the differential method was used by Jüntgen and Van Heek[55,76,92]. Assuming a model relation of n-th order with regard to the volatile product, the set of equations given in eqns. (4.34) to (4.37) is obtained (see section 4.1.3). The reaction order is then determined either by a method similar to Kissinger[75], which is based on peak assymetry, or from the position of the maximum reaction rate, similar to the method of Horowitz and Metzger[78]. Calculation of E and Z is made from the half-width of the peak and from the corresponding temperature at the maximum rate. Nomogramatic evaluations were also used by Van Krevelen et al.[81].

Generally, the plots of rates vs. temperatures exhibit a maximum $(d\alpha/dT)_{max}$, except when the reaction order is equal to zero. In such a case, the second derivative of the kinetic equation must be equal to zero, or

$$\left(\frac{d^2\alpha}{dT^2}\right)_{max} = 0 = \left(\frac{d\alpha}{dT}\right)_{max}\left[\frac{E}{RT_{max}} - \frac{Z}{\phi}\exp\left(-\frac{E}{RT_{max}}\right)n(1-\alpha)^{n-1}_{max}\right] \qquad (4.51)$$

Kissinger[75], and Horowitz and Metzger[78] have shown that the term, $(1-\alpha)_{max}$, is a constant for a given value of n. On taking logs, and rearranging the equation is obtained,

$$\log\frac{\phi}{T^2_{max}} = -\frac{E}{R}\left(\frac{1}{T_{max}}\right) \qquad (4.52)$$

which was used for DTA measurements by Kissinger[75] and Reich[83]. These equations were first derived for first order reactions by Murray and White[80] and Tsuzuki and Nagasawa[79]. Van Krevelen et al.[81] plotted families of curves for various T_{max}, for $\log(T(d\alpha/dT))_{max}$ and $\log(\Delta T/T)_{max}$ vs. $\log(E/R)$ for first order reactions (where ΔT is the half-width of the differential curve for easy E-scanning). Turner et al.[82] later refined these relations correlating E/R to T_{max} and ΔT for $n = 1$ and 3/2. Kissinger[75] developed a shape index, s, defined as the absolute value of the ratio of the tangents to the differential curves at the inflection points, and related them to the reaction order by the equation, $n = 1.26s^{1/2}$. Fuoss et al.[84] suggested the determination of three maximum values, T_{max}, $(d\alpha/dT)_{max}$ and $(1-\alpha)_{max}$ from the inflection point of the integral curve for the consequent evaluation of the activation energy by

$$\left(\frac{d\alpha}{dT}\right)_{max} = \frac{E(1-\alpha)_{max}}{nRT^2_{max}}. \qquad (4.53)$$

However, $(1-\alpha)_{max}$ is relatively independent of the heating rate, ϕ, and may be expressed by means of n[75,78] because of $\ln(1-\alpha)_{max} = (1/(1-n))\ln(n)$. Introducing it back to eqn. (4.53)

$$E \cong \left(\frac{d\alpha}{dT}\right)_{max} RT^2_{max}n^{n/(n-1)}. \qquad (4.54)$$

Flynn and Wall[19] pointed out that if $(1-\alpha)_{max}$ is independent of ϕ, then $T_{max}(d\alpha/dT)_{max}$

must also be independent and eqn. (4.52) may be transformed to

$$\Delta \log \phi \left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\max} = -\frac{E}{R}\Delta\left(\frac{1}{T_{\max}}\right). \tag{4.55}$$

Similarly, Farmer[85] developed an equation for $T_{1/2}$, the temperature at which the conversion reaches 0.5, using

$$\ln(1-\alpha)_{\max} = \frac{1}{1-n}\left[\frac{1-n}{n} r_x + 1\right],$$

where r_x is a function of E/RT.

A mathematically simple differential method for determining kinetic parameters is a modified Arrhenius plot given by eqn. (4.41). Magnusson[72], Kofstand[86], Barrer and Bratt[87], Newkirk[88], Ingraham and Marrier[89], and Carroll and Manche[96], employed this equation on the basis of the reaction order, n. Others[43a,97,98] have suggested the use of eqn. (4.41) by testing different model relations of $f(\alpha)$ to remove the order of reaction. Andersen[90] solved three simultaneous equations for eqn. (4.41) at three different ϕ values computing the parameters, Z, n and E at a series of constant $(1-\alpha)$ values. Friedman[91] applied the general form of eqn. (4.41) to the terms, $(\mathrm{d}\alpha/\mathrm{d}T)$ and T[95]. A plot of $\log(\mathrm{d}\alpha/\mathrm{d}T)$ vs. $(1/T)$ gave a slope of $E/2.3R$ and an intercept of $\log[Z\,f(\alpha)]$. This method has the most general use in computing. Doyle[20] substituted $Z/\phi = \exp(E/RT)\,f(\alpha)/(\mathrm{d}\alpha/\mathrm{d}T)$ into eqn. (4.41) and together with a one term approximation of the $p(x)$ function, obtained

$$E = \frac{T_j^2 R(\mathrm{d}\alpha/\mathrm{d}T)_j}{[f(\alpha)_j\, g(\alpha)_j]}. \tag{4.56}$$

This method is suitable to obtain a rough value of E from a single point j. The error in E depends on the value of E/RT and lies within 4 to 16 relative percent (for $E/RT = 10$ and 50, respectively).

Flynn and Wall[19] suggested on the basis of Chatterjee[93], the working equation

$$\underset{[\text{const } W]}{\frac{\Delta \ln(\mathrm{d}w/\mathrm{d}t)}{\Delta(1/T)}} = \frac{E}{R} = \underset{[\text{const d}W/\mathrm{d}t]}{\frac{\Delta \ln Z\,f(w)}{\Delta \ln(1/T)}} \tag{4.57}$$

which is applicable to two or more runs at different initial sample weights during TG measurements. They recommended[94] also the calculation of an approximate E from initial rates even where $f(\alpha)$ is unknown because all well-behaved reactions approach zero order at $\alpha \to 0$. This is only possible for non-isothermal techniques because the beginning of the experiment is precisely characterized. In isothermal studies, an inevitable time-lag in reading the experimental temperature is always present. In general, $(\mathrm{d}\alpha/\mathrm{d}T)$ vs. α plots remain linear to higher conversions ($\cong 0.03$) than do $\log(\mathrm{d}\alpha/\mathrm{d}T)$ vs. $1/T$ ($\cong 0.01$). The best procedure appears to be to plot $\mathrm{d}\alpha/\mathrm{d}(1/T)$

[$= T^2$ $(\mathrm{d}\alpha/\mathrm{d}T)$] vs. α having the slope, $E/R + 2\overline{T}$, where $E/R \gg 2\overline{T}$. The term $\overline{T}$ is the average temperature over which the slope is being determined. In practice

$$E = \frac{RT_j^2(\mathrm{d}\alpha/\mathrm{d}T)_j}{\alpha_j - 2R\overline{T}} \qquad (\text{at } \alpha \to 0). \tag{4.58}$$

The curves, $\mathrm{d}\alpha/\mathrm{d}T$ vs. α, are shown in Fig. 4.9.

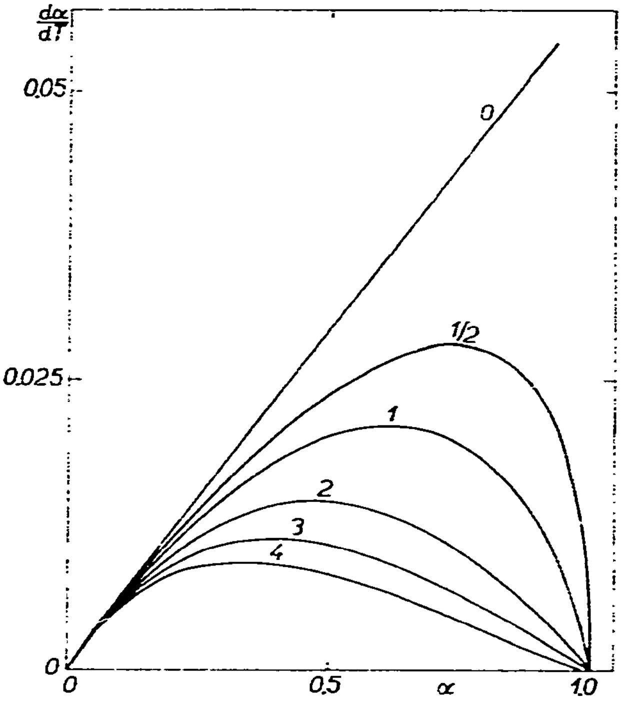


Fig. 4.9. Plot of rate of a process vs. fractional conversion for different reaction orders[19].

4.2.3. *Integral methods*

The integral methods are simpler than the differential methods as they do not involve the determination of rates even though they are complicated by the integration of the rate constant. Some difficulty, however, may arise from the cumulative character of the values[19] evaluated by an integral method, particularly in the case of the existence of a temperature dependent induction period: differential methods, which give instantaneous values for these parameters, are not so affected.

The integral methods may further be divided into two groups: (*1*) *approximate*, which employ for the rate constant integration an approximation related usually to a particular experimentally determined value such as the inflection point; and (*2*) *based on the p(x) function* (see section 4.1.2) both expressed by a limited number of terms in an expansion series or tabulated.

In the first serious treatment of thermogravimetric data, Van Krevelen et al.[81] used the approximation, $T = T_i + \delta$, where δ is the characteristic temperature deviation of the instantaneous reaction temperature, T, from the temperature of the inflection point, T_i, (equal to T_{max} scanned in the corresponding derivative curves; see section 4.2.2). These authors approximated the exponential integral by substituting

$$\exp\left(-\frac{E}{RT}\right) = [\exp(-T_i/T)]^{E/RT_i} = [0.368\,T/T_i]^{E/RT_i} \tag{4.59}$$

which is valid in the region, $0.9\,T_i < T < 1.1\,T_i$. Through an approximation of the rate constant and integration of the kinetic equation, they obtained

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{Z}{\phi}\left[\frac{0.368}{T_i}\right]^{E/RT_i} \frac{T^{(E/RT_i+1)}}{E/RT_i+1} \tag{4.60}$$

which may be transferred into logarithmic form

$$\log g(\alpha) = \log C_{61} - [(A/T_i)+1]\log T \tag{4.61}$$

The constant, C_{61}, is given in eqn. (4.60). Eqn. (4.61) can be tested for linearity by plotting $\log T$ vs. $\log g(\alpha)$ for various model relations of $g(\alpha)$.

Horowitz and Metzger[78] simplified the exponential integral with an approximation similar to but simpler than that of Van Krevelen et al.[81] (see eqn. (4.59)). They defined a characteristic temperature deviation, δ, through the equation

$$\frac{1}{T} = \frac{1}{T_i+\delta} = \frac{1}{T_i(1+\delta/T_i)} = \frac{1}{T_i} + \frac{\delta}{T_i^2} \tag{4.62}$$

After substituting and integration, the expression is obtained

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{ZRT_i^2}{\phi E}\exp\left[-\frac{E}{RT_i}\left(1-\frac{\delta}{T_i}\right)\right]. \tag{4.63}$$

Assuming the validity of order, n, the multiplication term, E/RT^2, can be replaced through the second derivative [given by eqn. (4.51)] yielding in the logarithmic form

$$(\text{for } n \neq 1):\quad \log[1-(1-\alpha)^{1-n}] = \log(1-n) - E/(2.3\,RT_i^2) \times \delta \tag{4.64a}$$

$$(\text{for } n = 1):\quad \log[-\log(1-\alpha)] = -\log 2.3 - E/(2.3\,RT_i^2) \times \delta \tag{4.64b}$$

where the relationship between values of order, n, and residual fraction, $(1-\alpha)$, is given in Table 4.1. Gyulai and Greenhow[26b] recommended the use of an improved form $(1-\alpha)_i = 1.062n^{1/(1-n)}$.

This kinetic method of evaluation was also used by Logvinenko et al.[99] in chromatography. They also derived an equation for a rough calculation of E from two points, T and α (= partial to total peak area), obtained by plotting a line parallel to time axis at 0.632 times the height of the peak, or

$$E = \frac{nRT_1T_2\log[(1-\alpha_1)/(1-\alpha_2)]}{T_2-T_1} \tag{4.65}$$

This expression, unfortunately, has little practical use. These authors further

TABLE 4.1

DATA FOR INFLECTION POINTS OF TG CURVES FOR VARIOUS REACTION ORDERS, n

n	$(1-\alpha)_i = n^{1/(1-n)}$	n	$(1-\alpha)_i = n^{1/(1-n)}$
0	0	2	0.5
1/3	0.192	3	0.576
1/2	0.250	4	0.63
2/3	0.298	5	0.669
1	0.368 (= 1/e)	10	0.919
3/2	0.444	∞	1

investigated the applicability[100,101] of the Horowitz and Metzger[18] method for the use of more general kinetic equation [Johanson–Mehl–Avrami–Yerofeyef–Koglomorov eqn. (4.25)] and found that a plot of $\log[-\log(1-\alpha)]$ vs. $(T-T_i)/(TT_i)$ gave a straight line with a slope of $E/2.3\,R$ holding a fixed order of $n = 1$. They noticed that the calculation with the fixed exponent, n, decreased the value of the activation energy, if $n > 1$, and increased this value, if $n < 1$. Dharwadkar and Karkhanavala[102] pointed out the change of T_i with sample size and the rate of heating. Hence, they assumed T_i not to be representative enough for the actual sample temperature. Due to self-cooling the temperature deviation from the true value is a maximum just when the reaction rate reaches its maximum. Therefore, they invented instead the temperature of the inflection point, T_i, the temperature of the inception of the process, T_{in} (where $T = T_{in} + \varphi$), and derived the modified form of eqn. (4.64), or

$$\log[-\log(1-\alpha)] = \frac{E}{2.3\,RT_{in}^2} - \frac{100}{(T_{fin}-T_{in})}\,\varphi + C_{66} \tag{4.66}$$

T_{fin} is the temperature of the process termination. This equation is reported to give a satisfactorily correct value for E. This is in contrast to the original equation (4.64), particularly because both values, α and $\bar{\varphi}$ $(100\varphi/(T_{fin}-T_{in}))$, are used in a normalized form.

Using a two-term approximation for the p(x) function, Flynn and Wall[19] also suggested an improved version of eqn. (4.64), or

$$\log[-\log(1-\alpha)] = \frac{1.052\,E}{2.3\,RT_{st}^2}\,\delta + C_{67} \tag{4.67}$$

where T_{st} is any reference temperature. The numerical constant, 1.052, may be improved by means of the tabulated p(x) function.

Reich[103] pointed out that at a very small and nearly constant ΔT, the integration of the rate constant may be roughly carried out by taking the exponent as a constant and replacing dt by $\Delta T/\Phi$, which then yields

$$\log g(\alpha) \cong -\frac{E}{2.3\,RT} + \log\frac{Z}{\phi}\,\Delta T. \tag{4.68}$$

(It is interesting to compare eqn. (4.68) with eqn. (4.74).)

On considering constant weight loss points for two different heating rates*

$$E \cong 4.6 \frac{\log(\phi_2/\phi_1)(T_1/T_2)^2}{1/T_1 - 1/T_2} \tag{4.69}$$

Flynn and Wall[94] derived a simpler equation in comparison to eqn. (4.69) using Doyle's approximation for the p(x) function of eqn. (4.21)

$$E = -4.35 \frac{\Delta \log \phi}{\Delta (1/T)} \quad (\text{for } (1-\alpha) = \text{const.}) \tag{4.70}$$

(see also Fig. 4.18).

Activation energies may be quite accurately and simply obtained by successive approximations from tables of log p(x) and Δ log p(x) for various $x = E/RT$. Ozawa[52] also derived eqn. (4.70) but employed it without further refinement to calculate E at several α values and to construct theoretical masters-curve similar to the work of Doyle[20] and Šatava[21]. A more accurate experimental master curve is obtained by superimposing the curves of log ϕ vs. $1/T$ at several heating rates by displacement along the abcissa (see also Fig. 4.16). Flynn and Wall[94] considered this method to be one of the best and most generally applicable[96];

The expression is:

$$\log g(\alpha) = \log \frac{ZE}{R} - \log \phi - 2.315 - 0.457 \frac{E}{RT} \tag{4.71}$$

From the slopes of plots of log α vs. $1/T$ at constant α, log g(α) vs. $1/T$ at constant ϕ, and for log g(α) vs. log ϕ at constant T, there is obtained

$$\underset{[\alpha = \text{const.}]}{\frac{\Delta \log \phi}{\Delta (1/T)}} \cong -0.457 \frac{E}{R} = \underset{[\phi = \text{const.}]}{\frac{\Delta \log g(\alpha)}{\Delta (1/T)}} \tag{4.72a}$$

and

$$\underset{[T = \text{const.}]}{\frac{\Delta \log g(\alpha)}{\Delta \log \phi}} = 1 \quad (= \text{horizontal plot}) \tag{4.72b}$$

The right-hand side of eqn. (4.72) may also be applied to a single thermogravimetric curve and has some advantages over the methods of Farmer[85] and Coats and Redfern[108] (eqn. 4.73). The use of the MacCallum and Tanner approximation[48] for

---

*Doyle[106] corrected another similar equation invented by Reich and Levi[105] to the form, $E = 2.3 \log (A_2/A_1)/(1/T_1 - 1/T_2) R$, where A_2/A_1 is the ratio of two corresponding initial areas at T_1 and T_2. This equation shows a lack of sensitivity.

$\log p(x)$ equal to $0.4828\,E^{0.4351}+(449+217E)/T$ gives a similar result[46], i.e., $[\Delta \log \phi/\Delta(1/T)]_\alpha \cong -(450+220E)$.

Coats and Redfern[108,109] used the approximation for the p(x) function as $\exp(-x)[(1/x)-(2/x^2)]$ and obtained

$$\log\left(\frac{g(\alpha)}{T^2}\right) = \log\frac{ZR}{\phi E}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.3RT} \tag{4.73}$$

where the first term on the right-hand side of eqn. (4.73) is a slowly changing function of the temperature and may be considered as being constant in a narrow temperature interval. Hence, a plot of $\log(g(\alpha)/T^2)$ vs. $(1/T)$ appears to give a straight line when the model relation, $g(\alpha)$, is known or is being tested for a linearity. This equation may be applied for low level conversion data as well[109], assuming all reactions behave as zero order ($\alpha \rightarrow 0$). Hence, the plot of $\log(\alpha/T^2)$ vs. $(1/T)$ should give a straight line for α not exceeding 0.1.

In the recent literature, attention has focused back to eqn. (4.23), $g(\alpha) = ZE/R\phi \times p(x)$ (assuming the $p(x_0)$-term negligible), first suggested by Doyle[20] as a trial-and-error curve-fitting method for the determination of activation energy. Zsako[37] attempted to simplify this method by using this equation in the logarithmic form

$$\log\frac{ZE}{R\phi} = \log(g(\alpha))-\log(p(x)) = \text{const.} \tag{4.74}$$

where the constant, $\log(Z(E/R)\phi)$, depends only upon the nature of the material studied and the heating rate but not upon the temperature. This constancy suggests a quantitative method of testing different model relations, $g(\alpha)$, by means of the trial-and-error method to determine the apparent activation energy consistent with a

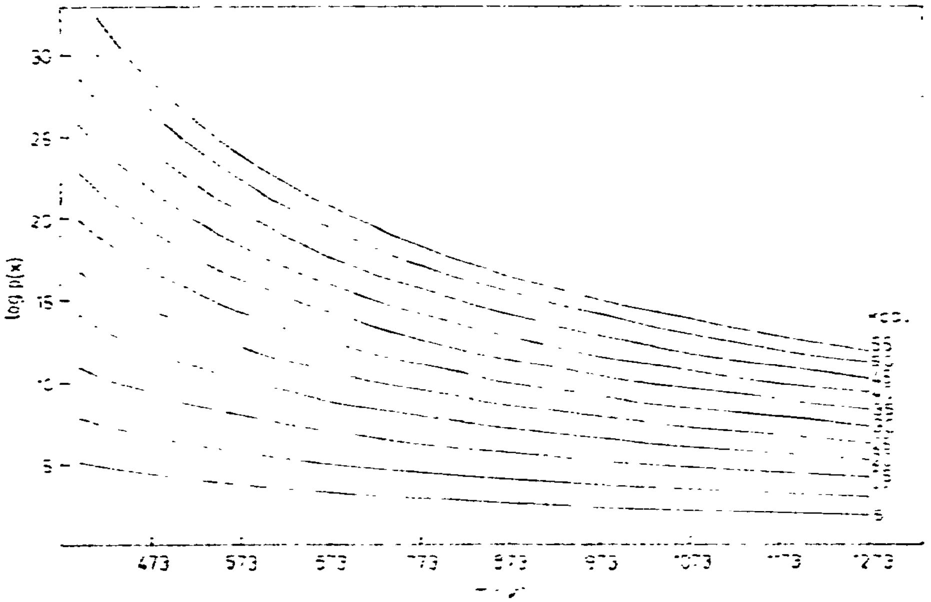


Fig. 4.10. Plot of log p(x) vs. absolute temperature[40].

chosen function of $g(\alpha)$. Šatava and Škvára[40] went even further to simplify the tedious procedure[37] and suggested a graphical comparison of log $(g(\alpha))$ and log$(p(x))$ by means of nomograms. The log $(g(\alpha))$-values for various rate processes are plotted vs. the corresponding T values on transparent paper on the same scale as the standard plot of $-\log(p(x))$ vs. T. The plot of log $g(\alpha)$ is placed on top of the log $(p(x))$ diagram so that the temperature scales coincide and it is then shifted along the coordinate until one of the log $g(\alpha)$ curves fits one of the log $(p(x))$ curves. From this log $(p(x))$ function, the corresponding activation energy, E, can then be obtained (see Fig. 4.10).

Later Zsako[58], improved Doyle's isothermal method[24] of deriving activation energies from theoretical curves by an iterative procedure, suggested that log $(p(x))$ may, to the first approximation, be a linear function of reciprocal absolute temperature. MacCallum and Tanner[48] and Šatava[49] assumed further that if the difference between functions of log $(g(\alpha))$ and log $(p(x))$ does not depend upon the temperature, and if log $(p(x))$ is a linear function of $1/T$, then log $(g(\alpha))$ must also be a linear function of $1/T$ (see Fig. 4.11). This property of log $(g(\alpha))$ can be used for the determination of the probable reaction mechanism with regard to both the reaction order concept[48], or more accurately, the particular model relation for a heterogeneous process[49]. It is evident that a plot of log $(g(\alpha))$ vs. $(1/T)$ calculated from the experimentally obtained data, α and T, becomes linear only for such a $g(\alpha)$ function which corresponds to the most probable rate-controlling process (see Fig. 4.12). This is true

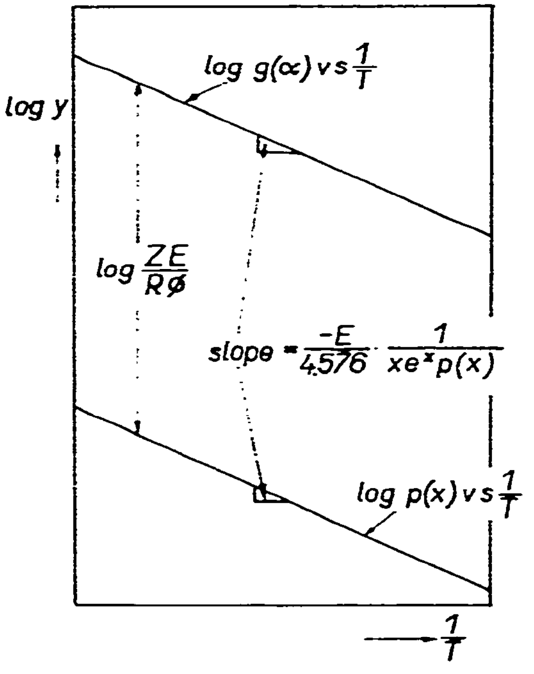


Fig. 4.11. Diagramatic representation[65] of eqn. (4.74).

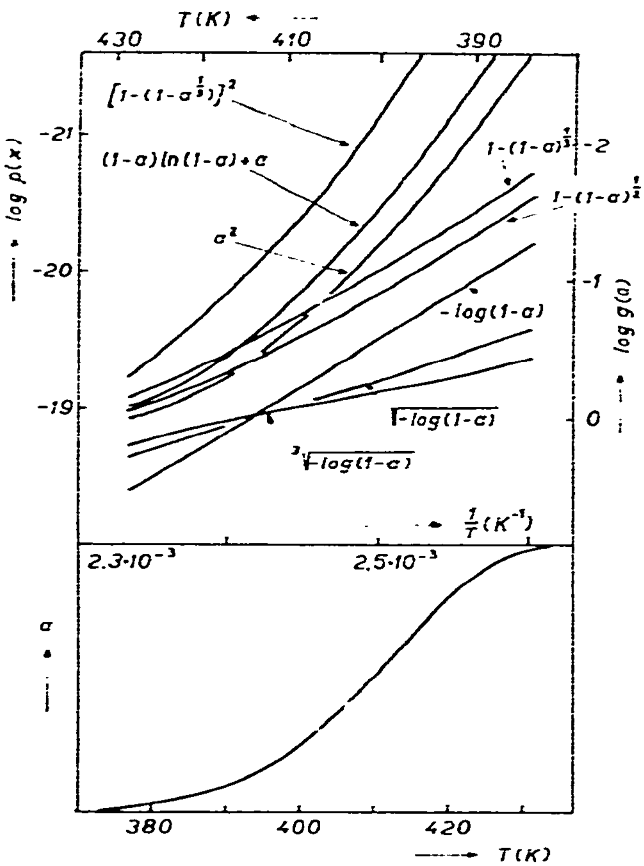


Fig. 4.12. Procedure for the evaluation of TG curves[49]. Lower curve complies with kinetic equation, $g(\alpha) = -\log(1-\alpha)$, $E = 30$ kcal mole^{-1}, $Z = 10^{13}\,\text{s}^{-1}\,\text{mol}^{-1}$, $\phi = 1$ °C/min. Upper curves are plots of $\log g(\alpha)$ vs. $1/T\alpha$ calculated from TG curve for various kinetic equations (see Table 4.1). The straight line corresponding to the kinetic equation of random nucleation coincides with the plot of $-p \log p(x)$ vs. $1/T$, for $p = 1$ slope with $E = 30$ kcal.

for the temperature interval of process duration not exceeding 100 °C, as shown by Šesták[18]. From the slope, $\text{tg}\,\beta$, of the straight line the corresponding activation energy can be calculated as follows:

(1) As a root of the derived quadratic equation employing the first two terms of the expansion series[49]

$$E = \frac{1.987}{2}\left(-\text{tg}\,\beta + (\text{tg}^2\beta + 8\,\text{tg}\,\beta \times \bar{T})^{1/2}\right) \tag{4.75}$$

where $\bar{T}$ is the mean temperature of the process.

(2) Using a derivative with respect to the reciprocal temperature in the approximate equations, $\log p(x) = -2.315 - (0.4567E/RT)$, and/or $= -482.8E^{0.4361} - -(449+217E)/T$, which gives[18] $E = -[449+\text{tg}\,\beta/2.3]/217$.

(3) By an iteration procedure[65] where E, to a first approximation, is intro-

duced by the equation, $E = (4.567\ \mathrm{tg}\,\beta - 2R\bar{T})$, and then substituted into $x = E/R\bar{T}$ where $\bar{T}$ is the mean temperature. This is used as input data for the equation[18,49,65]

$$E = R\,e^{x}x^{2}p(x)\,\mathrm{tg}\,\beta = R\,\mathrm{tg}\left(1 - \frac{2!}{x} + \frac{3!}{x^{2}} - \ldots + \frac{(-1)^{n}n!}{x^{n}}\right) \qquad (4.76)$$

where one iteration loop is usually sufficient to yield E with a high enough accuracy.

The value of the pre-exponential factor is then obtained[64] by introducing the values of E, ϕ, $\log(g(\alpha))$, and $\log(p(x))$ with appropriate values of ϕ and T, into the modified eqn (4.74).

$$\log Z = \log\frac{R\phi}{E} + \log g(\alpha) - \log p(x) \qquad (4.77)$$

A similar procedure of kinetic rate determination was suggested by others[107,114,115]; particularly, the use of dilatometric measurements in sintering investigations should be noted[114].

It is clear that owing to the small differences between the values of the individual case-model functions, the determination of the rate-controlling process is not completely unambiguous[44,49,63,131a]. This, of course, applies to all methods which employ a test of linearity, e.g., eqns. (4.61), (4.64), (4.73)*. Besides the difficulty due to small deviations from the linearity (see Fig. 4.12), there arises another problem connected with the direct determination of the value of the exponent-factor, r, for the function, $(-\ln(1-\alpha))^{1/r}$ [eqn. (4.25)]. Double logarithmization gives the least sensitive function but it cannot provide any further information about the exponent, r, from the plots of $(1/r)\log(-\ln(1-\alpha))$ vs. $1/T$ because the slope contains the value of a multiplying constant[63] as well. It applies also to the case of the exponent 2, if comparing[112] Jander's equation for diffusion, $[1-(1-\alpha)^{1/3}]^{2}$, with the phase-boundary equation, $[1-(1-\alpha)^{1/3}]$, both of which are valid under spherical symmetry. An additional criterion is needed for a correct decision about the rate-determining process. It may be, for example, the value of the pre-exponential factor which, for most simple decompositions, should not differ from 10^{12} by more than two orders of magnitude.

Another source of information may be the comparison of results obtained through the differential and integral methods, as noted by Šesták[63]. Assuming a simple form of the rate constant, k, in the original form of the Johanson–Mehl–Avrami–Yerofeyev–Koglomorov method, eqn. (4.25), then the algebraic manipulation necessary to obtain the functions, $g(\alpha)$ and $f(\alpha)$, changes its value to $k' = rk^{1/r}$ (or $E' = E/r$). This last value takes part in the $p(x)$-function, i.e., $p(x) = p(E/r\,RT)$. The difference-differential method[44] (eqn. (4.47)] gives the procedural slope of $E/4.57r$ while Šatava's integral method[49], on plotting $\log(-\ln(1-\alpha))$ vs. $1/T$, yields the procedural slope of $rE/4.57r = E/4.57$. Therefore, the ratio of these two slopes may provide an estimate of the exponent factor, r. The same meaning was obtained by Nikolayev et al.[101] that the only comparable values of the activation energies are those

---

*See *Note added in proof* on p. 500.

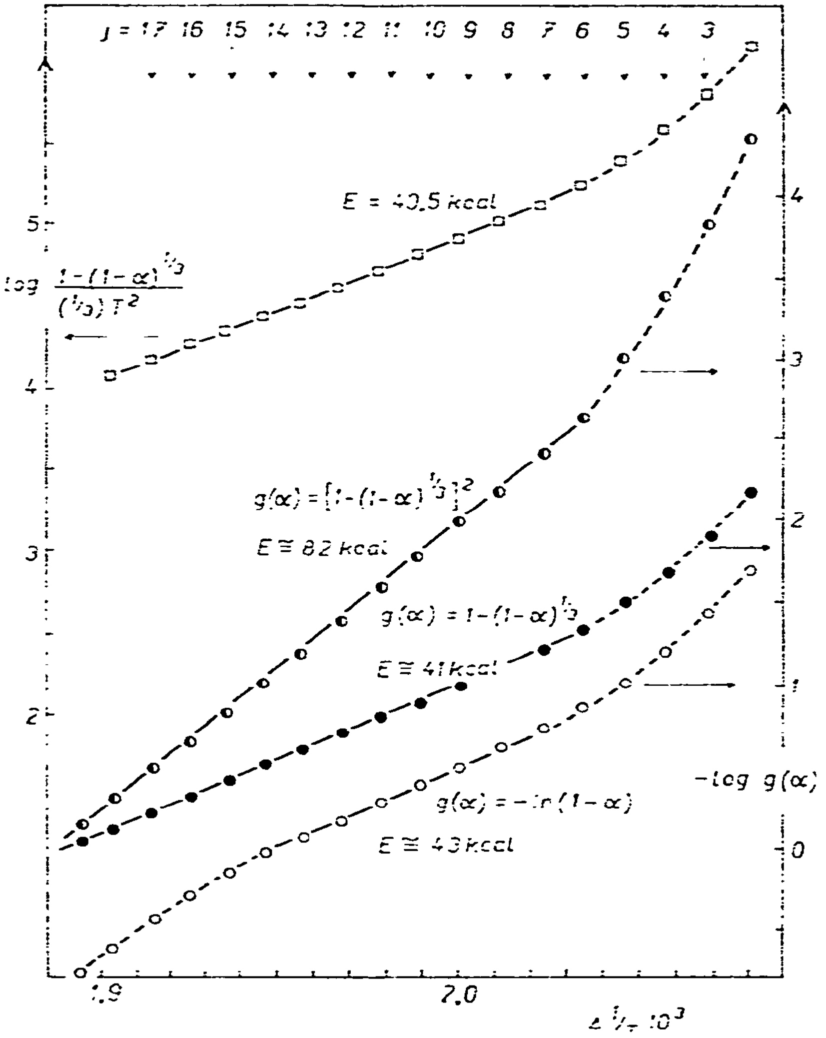


Fig. 4.13. Integral methods for manual TG curve evaluation[44]. Compare with Fig. 4.8 and the following table, obtained by the least squares computer evaluation using Škvára's program[191] for the required accuracy of 10 percent in the calculated linearity region.

Case-model	*Interval of linearity* (*in α*)	*E* (*in Kcal*)	*Z*	*Standard deviation*
$[1-(1-\alpha)^{1/3}]$	84% 0.1–0.93)	40.8	9.0×10^{13}	0.028
$[1-(1-\alpha)^{1/3}]^2$	84% (0.1–0.93)	83.5	9.3×10^{31}	0.028
$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$	84% (0.1–0.93)	77.2	1.4×10^{29}	0.051
$[1-(1-\alpha)^{1/2}]$	77% (0.1–0.86)	39.0	2.1×10^{13}	0.06
$(1-\alpha)\ln(1-\alpha)+\alpha$	63% (0.13–0.76)	74.2	2.7×10^{28}	0.058
$[-\ln(1-\alpha)]^{1/2}$	52% (0.06–0.57)	22.8	3.5×10^{6}	0.023
$[-\ln(1-\alpha)]$	52% (0.06-0.57)	47.5	2.7×10^{17}	0.023

obtained with an identical value of exponent factors or calculated to the same value*, conveniently equal to one.

The actual use of integral methods for kinetic data calculations is shown in Fig. 4.13 for the thermal decomposition[44] of $KMnO^4$ employing the methods of Šatava[49] (eqn. 4.74) and Coats and Redfern[108] (eqn. 4.73).

4.3. Special cases of evaluation

4.3.1. Reversible reactions and proximity to equilibrium

In reality, every process can be assumed as being reversible and the overall reaction rate may then be expressed as the difference of both of the opposite rates

$$r = r_{\text{for}} - r_{\text{rev}} = r_{\text{for}}[1-\exp(\Delta G/RT)] \tag{4.78}$$

where r_{for} is the rate of the forward reaction and r_{rev} is rate of the reverse reaction. This was actually derived by Bradley[116] for transformations passing through the vapor phase and satisfactorily applied to describe various heterogeneous processes. The term, ΔG, is the driving force which, in the case of chemical reactions, may be expressed as $\Delta G = RT \ln (X/K)$, where K is the equilibrium constant and X is the product of activities of all components. The change of the Gibbs free energy, ΔG, for a reaction reaches large negative values for the stages distant from equilibrium ($\Delta G \rightarrow -\infty$ and $\exp(\Delta G/RT) \rightarrow 0$), i.e., the total reaction rate is independent of the driving force, $r = r_{\text{for}}$. In the vicinity of equilibrium ($\Delta G \rightarrow 0$), the expression, $(1-\exp(\Delta G/RT))$, may be expanded according to the Taylor series so that $r = r_{\text{for}}(\Delta G/RT)$ when neglecting the terms of higher orders. Considering the opposite processes as obeying the same rate controlling process (diffusion for reactions in a condensed system) eqn. (4.78) may be rewritten as

$$d\alpha/dt = k_{\text{for}}\,f(\alpha) - k_{\text{rev}}\,f(\alpha) = k_{\text{for}}\,f(\alpha)\,[1-\exp(\Delta G/RT)] \tag{4.78a}$$

Such a corrected kinetic equation has a logical justification in the activation energy diagram (see chapter 2, Fig. 2.1) and can also be derived by means of thermodynamics of irreversible processes. Under non-isothermal conditions the integration of eqn. (4.78) yields

$$g(\alpha) = \frac{ZE}{R\phi}[p(x)-p(x_{\text{eq}})] - \frac{Z(\Delta G - E)}{R\phi}[p(y-x)-p(y_{\text{eq}}-x_{\text{eq}})] \tag{4.79}$$

where x, x_{eq}, y and y_{eq} are E/RT, E/RT_{eq}, $\Delta G/RT$ and $\Delta G/RT_{\text{eq}}$, respectively. Because $\Delta G = \Delta H - T\Delta S$ and assuming that ΔH and ΔS are temperature independent,

---

*Upon using Van 't Hoff relation these authors[101] also derived following equation for the correlation of activation energies

$$E\,\frac{1-\alpha_i}{n\alpha_i} = \frac{n^{1/(1-n)}}{n(1-n)^{1/(1-n)}}\,E = \xi E = \Delta H$$

where coefficient ξ has value 0.708; 0.667; 0.583; 0.5 and 0.453 for $n = 1/3$; $1/2$; 1; 2 and 3 respectively. The term ΔH is the heat of reaction and i designates the inflection point.

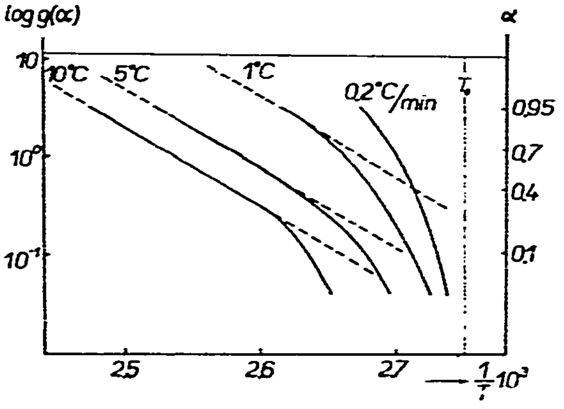


Fig. 4.14. Effect of the heating rate, ϕ, on the dehydration of α-$CaSO_4\cdot\frac{1}{2}H_2O$ at $p_{H_2O} = 0.025$ atm.[65]. Extrapolated linear parts corresponds to $E = 30$ kcal $mole^{-1}$, for $g(\alpha) = -\ln(1-\alpha)$.

then $\Delta S \cong \Delta H/T_{eq}$ where T_{eq} is the temperature of equilibrium. After rearrangement

$$g(\alpha) = \frac{ZE}{R\phi}[p(x)-p(x_{eq})] - \exp(\Delta H/T_{eq})\frac{ZE'}{R\phi}[p(x')-p(x'_{eq})] \tag{4.80}$$

where $E' = E-\Delta H$, $x' = E'/RT$ and $x_{eq} = E'/RT_{eq}$. If E' is small the second term on the right-hand side of eqn. (4.80) can be neglected and the term, $(\log g(\alpha) - \log [p(x) - p(x_{eq})]$, is a constant. However, in comparison with the previously given evaluation method (see Fig. 4.11) neither $\log [p(x)-p(x_{eq})]$ nor $g(\alpha)$ are linear functions of $1/T$. This can be demonstrated[65] in the case of $CaSO_4\cdot\frac{1}{2}H_2O$ dehydration which proceeds close to the equilibrium temperature. It is evident that the $g(\alpha)$ function then requires the same curvature as $\log [p(x)-p(x_{eq})]$ and the difference between both curves depends only on the value of the heating rate applied, ϕ. The direct determination of $g(\alpha)$, E and Z would thus be almost impossible but, with a sufficiently high heating rate, the curve of $\log(g(\alpha))$ vs. $1/T$ approaches a straight line suitable for a simple treatment (see eqn. 4.74), as shown by Šatava and Šesták[65]. Thus, it is evident that the proper choice of a sufficiently high heating rate is essential for kinetic data calculations because at too low a heating rate the process is completed in the vicinity of the equilibrium temperature, T_{eq} (in the curved part of the plot). Kinetic data calculated under such conditions are erroneous and the apparent E is larger than the true E.

4.3.2. *Simple parallel and consecutive processes*

If multiple reactions take place in a process, the experimentally measured curve represents the sum of the individual contributions, as was shown by Flynn and Wall[19] and Jüntgen and Van Heek[55]. For a proper analysis it is necessary to determine the partial steps, N, and to find a method for the direct study of $(N-1)$ processes and to compare the partial curves with the sum of the curves. It is evident that the complex value of parameters characterizing the summation curve cannot be attached to a particular physical meaning. An illustrative case was given by Jüntgen and Van Heek[5];

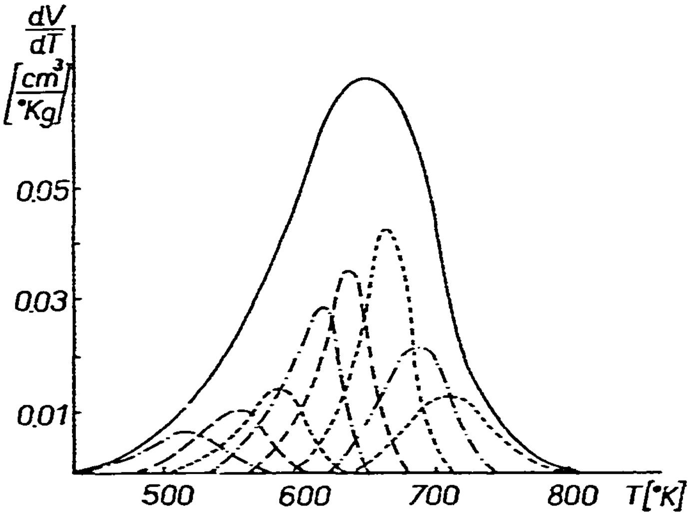


Fig. 4.15. Overall effluent gas curve calculated for given composite case. Individual parallel reactions (dashed lines) are for first order with E from 48 to 62 kcal/mole, $Z = 1 \times 10^{15}$ min^{-1}, $\Sigma V_0 = 9.6$ cm^3 g^{-1}. Resulting peak corresponds to $E = 20$ kcal $Z = 1 \times 10^4$ min^{-1}, $V_0 = 10$ cm^3 g^{-1} and $\phi = 1$ °C/min (according to Jüntgen and Van Heek[55]).

and is reproduced in Fig. 4.15. The summation curve is composed of eight partial processes the activation energies of which lay within the region of $E = 48 - 62$ kcal mole^{-1} ($Z = 10^{15}$). An analysis of the summation curve leads to an apparent activation energy value which is equal to 20 kcal mole^{-1} ($Z = 10^4$). Flynn and Wall[19] reported that two parallel processes could be separated by a suitable choice of the heating rate so that the kinetic parameters of each process could be calculated from the corresponding part of the summation curve. A necessary condition is that their activation energies be different[19,55]. Flynn and Wall[19] also showed an example of two parallel independent reactions where a fraction of reactant, A_1, volatilizes by first order kinetics (the Arrhenius parameters, Z_1 and E_1). Similarly the reactant remainder, $(1 - A_1)$, possesses the parameters, Z_1 and E_1. After the integration procedure, the equation is

$$(1-\alpha) = A_1\left[\exp\left(-\frac{Z_1E_1}{\phi R}\,\mathrm{p}(x_1)\right)\right] + (1-A_1)\left[\exp\left(-\frac{Z_2E_2}{\phi R}\,\mathrm{p}(x_2)\right)\right] \qquad (4.81)$$

where $\mathrm{p}(x_0)$ is neglected.

Another case is exhibited[19] by two consecutive reactions where the initial reactant may be volatilized by two alternative paths of competitive character, each having a rate proportional (accordingly to eqn. (4.81)) to the first power of remaining volatilizable polymer (Z_1, E_1 and Z_2, E_2), or

$$(1-\alpha) = \exp\left[-\frac{Z_1E_1}{\phi R}\,\mathrm{p}(x_1) - \frac{Z_2E_2}{\phi R}\,\mathrm{p}(x_2)\right]. \qquad (4.82)$$

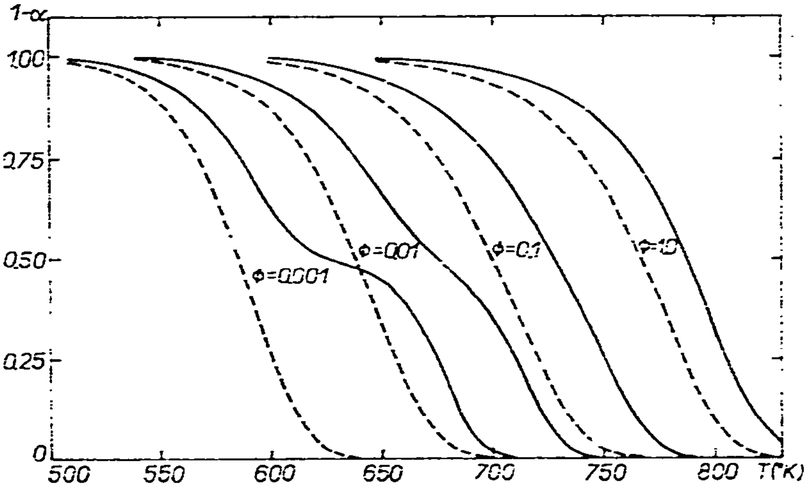


Fig. 4.16. Effect of heating rate on residual fraction vs. temperature for composite cases, where full line corresponds to independent first-order reactions ($E = 30$ kcal mole^{-1}, $Z = 4.458 \times 10^{6}$ sec^{-1}), dashed line competitive first-order reactions ($E = 60$ kcal mole^{-1}, $Z = 1 \times 10^{15}$ sec^{-1}) (according to Flynn and Wall[19]).

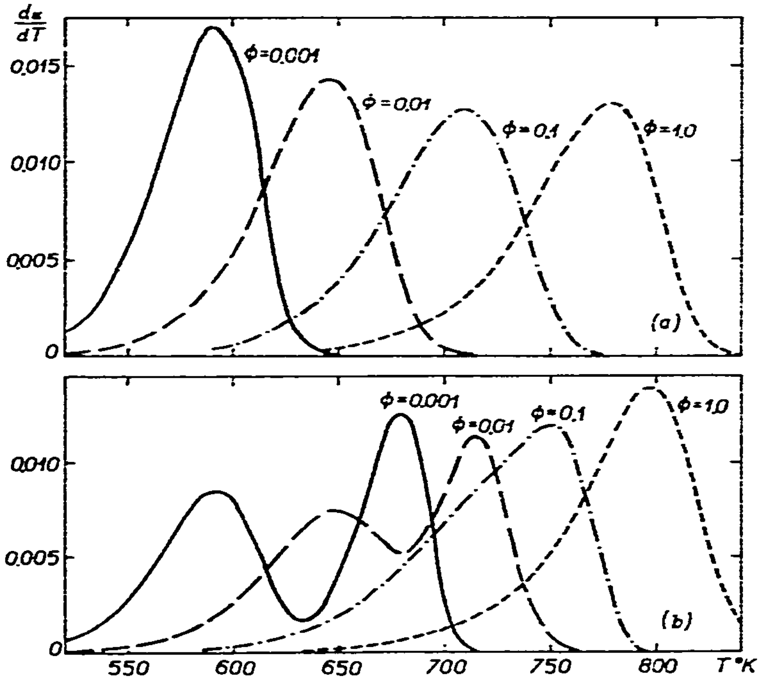


Fig. 4.17. Effect of heating rate on the thermogravimetric rate vs. temperature for composite cases, see Fig. 4.16. *Case* (*a*), competitive; *case* (*b*), independent reactions[19].

These two cases may be separated by applying various heating rates, as is shown in Fig. 4.16 (the effect of heating rate on the residual fraction) and Fig. 4.17 (the effect of heating rate on the overall reaction rate). Independent reactions give at higher heating rates the appearance of one single curve as these two reactions broadly overlap each other. At decreasing heating rate, the curve tends to flatten as the two reactions begin to separate until two peaks are obtained in the differential curve. On the other hand, for two competitive reactions, the low activation energy reaction takes over almost completely at low temperatures and heating rates. At the higher heating rate, this reaction takes place only during the first third of the curve while the high-energy reaction considerably modifies the latter portion of it. The high-energy reaction causes a temporary increase $(\mathrm{d}\alpha/\mathrm{d}T)_{\max}$ with increasing ϕ while in a simple reaction the maximum rate decreases upon increasing ϕ and $T_{\max}$. For equal activation energies these two consecutive first order reactions appear as a simple first order reaction with no regard to the difference in pre-exponential factors. For evaluation of this effect, the Flynn and Wall[19] method, eqn. (4.70) is perhaps the best method to distinguish them, as is demonstrated in Fig. 4.18. In general, employing very low heating rates will best isolate competing reactions while fast heating rates are best for independent reactions.

4.3.3. *Non-uniform and cyclic heatings*

Under actual experimental conditions it is almost impossible to attain a per-

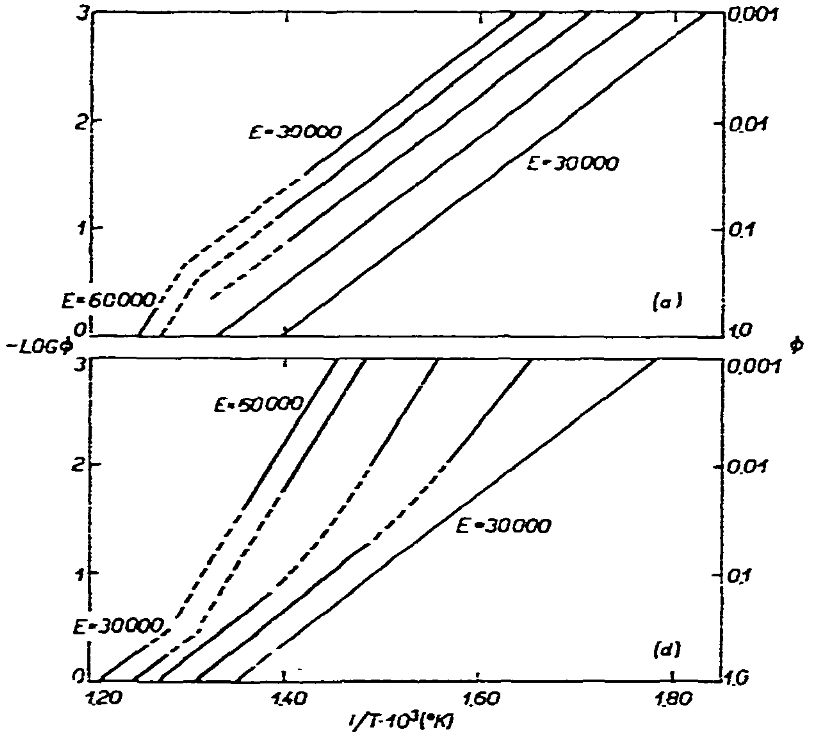


Fig. 4.18. Calculation of kinetic data according to Flynn and Wall[19] (eqn. 4.70). The logarithm of heating rate is plotted vs. absolute temperature for curves in Fig. 4.17. Each line constructed for multiple values of α.

fectly linear increase of temperature with time. There are two probable sources of error, namely, the heat evolved or absorbed in the process (self-cooling or self-heating of sample[51,59,60]) and the failure of the temperature control equipment to respond linearly to the temperature (as for example, thermocouple voltage not strictly proportional to the temperature). Such departures from linearity do not necessarily lead to fundamental errors of observation but a correction of the measurement that corresponds to a linear temperature vs time relationship is essential. The correction is ideally made by introduction of the proper monotonic form of the function, $T = \bar{T}(t)$. Alternatively, it may be more practical to obtain the departure from the linearity in the T vs. t curve in the form of either an experimental set of points or polynomial fitting with a computer. The correction of the measured thermal property is then straight forward. Szekely[117,118] et al. and Vachuška and Vobořil[119] employed second derivates in the ordinary differential equation to calculate the instantaneous values of kinetic parameters from the instantaneous value of the heating rate, $\phi_{\text{inst}} = (\mathrm{d}T/\mathrm{d}t)_{\text{measured}}$. Hence,

$$\left[\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}\,\frac{T^2}{\left(\dfrac{\mathrm{d}\alpha}{\mathrm{d}t}\,\phi_{\text{inst}}\right)}\right] = \frac{\mathrm{f}'(\alpha)}{\mathrm{f}(\alpha)}\left[\frac{T^2(\mathrm{d}\alpha/\mathrm{d}t)}{\phi_{\text{inst}}}\right] + \frac{E}{R} \tag{4.83}$$

which can be treated as a linear equation by plotting the contents of the square brackets against each other; the slope is $\mathrm{f}'(\alpha)/\mathrm{f}(\alpha)$ (in the case of order, equal to n) and the intercept, E/R.

Flynn[70] claimed that the kinetic parameters are best determined under isoconversional conditions if the temperature was changed rapidly from T_j to T_{j+1}, as can be seen in Fig. 4.19. The rates may be extrapolated to the same degree of conversion of different temperatures according to

$$\frac{E}{R} = \frac{\ln\,(\mathrm{d}\alpha/\mathrm{d}t)_j/\ln\,(\mathrm{d}\alpha/\mathrm{d}t)_{j+1}}{\dfrac{1}{T_{j+1}} - \dfrac{1}{T_j}} \qquad [\alpha = \text{const.}]\,. \tag{4.84}$$

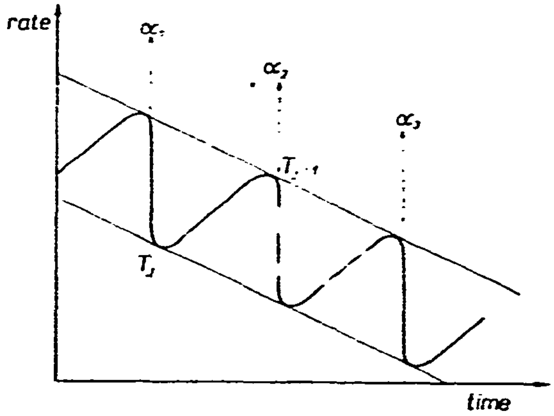


Fig. 4.19. Method by Flynn[70].

If the temperature is varied in a slow harmonic cycle, $T = T_0 + T \sin \omega t$ (as shown in Fig. 4.19), the rates at the temperatures, $T_j = T_0 + T_A$ and $T_{j+1} = T_0 - T_A$, may be obtained at the constant conversion from the upper and lower parts of the curve. These methods have the advantage that there is no sample variation and that they give instantaneous values of the parameters. Practical considerations require T to be small, but other sets of temperature may be tested at a number of conversions in this manner. The constancy of the rate constant, $k_j = Z \exp(-E/RT_j)$ may also be tested at various constant conversions by several runs at different heating rates. A similar method was used by Reich et al.[103–105,120].

4.3.4. *Heat transfer as the rate-determining step*

A quite different situation arises when the experimental arrangement is so designed that the heat transfer between the source of heat and the reacting interface becomes the rate-controlling process. Assuming steady-state conditions, then

$$\frac{d\alpha}{dt} = \frac{1}{V_0 \Delta H} \frac{dq}{dt} = \frac{\tau S_A (T - T_R)}{V_0 \Delta H} \tag{4.85}$$

where $d\alpha/dt$ is the rate of a process related to the reaction volume, V_0; dq/dt is the rate of heat supply, τ is the overall heat transfer coefficient, S_A is the reacting surface, ΔH is the heat of reaction, T is the temperature of sample surroundings (equal to that on the sample outer surface) which increases linearly with time, t, and T_R is the temperature of reaction under which the reaction is assumed to proceed on the sample reacting surface S_A. For spherical symmetry of the sample bulk, S_A may be expressed

$$S_A = 4\pi (r_0 - y)^2 = 4\pi r_0^2 (1 - \alpha)^{2/3} \tag{4.86}$$

where r_0 is the initial radius of the sample and y is the thickness of the product layer. Combining eqns. (4.85) and (4.86)

$$d\alpha/dt = 3\tau (T - T_R)(1 - \alpha)^{2/3} / \Delta H r_0 . \tag{4.87}$$

After the integration, using $t = (T - T_R)/\phi$,

$$1 - (1 - \alpha)^{1/3} = \frac{\tau}{2 \Delta H r_0 \phi} (T - T_R)^2 = \frac{\tau}{2 \Delta H r_0} t^2 \tag{4.88}$$

Such cases were considered by Draper[3,121] as "non-activated processes". In general, eqn. (4.88) holds for voluminous samples[46,113] with well-defined outer geometry. For more details see the work of Narsimham[122] who assumed interface behavior and steady-state heat and mass flow conditions. The resulting equation agreed with experimental data reported by Satterfield and Feakes[123] for the decomposition of $CaCO_3$. Similarly, the detailed work of Hills[124] treated this decomposition from the engineering point of view assuming the rate-controlling steps to be both the transfer of heat to the reaction zone and the transport of carbon dioxide away from it.

The opposite case can be met under the assumption of adiabatic conditions for an exothermic reaction, or

$$\frac{d\alpha}{dt} = \frac{C_p(dT/dt)}{V_0 \Delta H} \tag{4.89}$$

where C_p is the average heat capacity. Such conditions are suitable for investigations of the thermal stability of compounds in continuous, stirred systems[125]. In practice, the reaction rate term is replaced by the rate equation $Z \exp(-E/RT)(1-\alpha)^n$. If the fractional conversion is eliminated, then

$$\frac{dT}{dt} = C_{90}(T_m - T)^n \exp\left(\frac{-E}{RT}\right). \tag{4.90}$$

This equation is usually employed in a logarithmic form. The term, C_{90}, is a constant given by the limiting conditions, T_0 and T_m, the initial and the maximum adiabatic temperatures, respectively. The general case of a non-adiabatic system exchanging heat with the surroundings is given by the combination of eqns. (4.85) and (4.89)[125]

$$\frac{d\alpha}{dt} = \frac{C_p}{V_0 \Delta H}\frac{dT}{dt} - \frac{\tau S_A(T - T_R)}{V_0 \Delta H} \tag{4.91}$$

which, however, is difficult to solve analytically[125,126]. For a detailed integral solution, see Dammers et al.[125].

4.3.5. Searching for an adequate kinetic description

The major purpose of the above methods of kinetic data evaluation is to reach as close a description of the path of the process as possible under the given experimental conditions. Besides the ordinary splitting of case-models due to a simplifying homogeneous-like approach[110,111,113] all heterogeneous processes can always be broken down into three basic steps[1,41,46,49,131]; (*1*) transport of matter; (*2*) nucleation and nuclei growth and (*3*) phase-boundary reactions. The not yet considered adsorption process can also play a significant role as discussed for non-isothermal conditions in the review by Cvetanovic and Amenoniya[128] and others[129]. Generally, there are no absolute methods of selecting a proper case-model but there exist preliminary linearity tests which employ single predetermined isothermal runs. Literally, it is a plot of the functions,

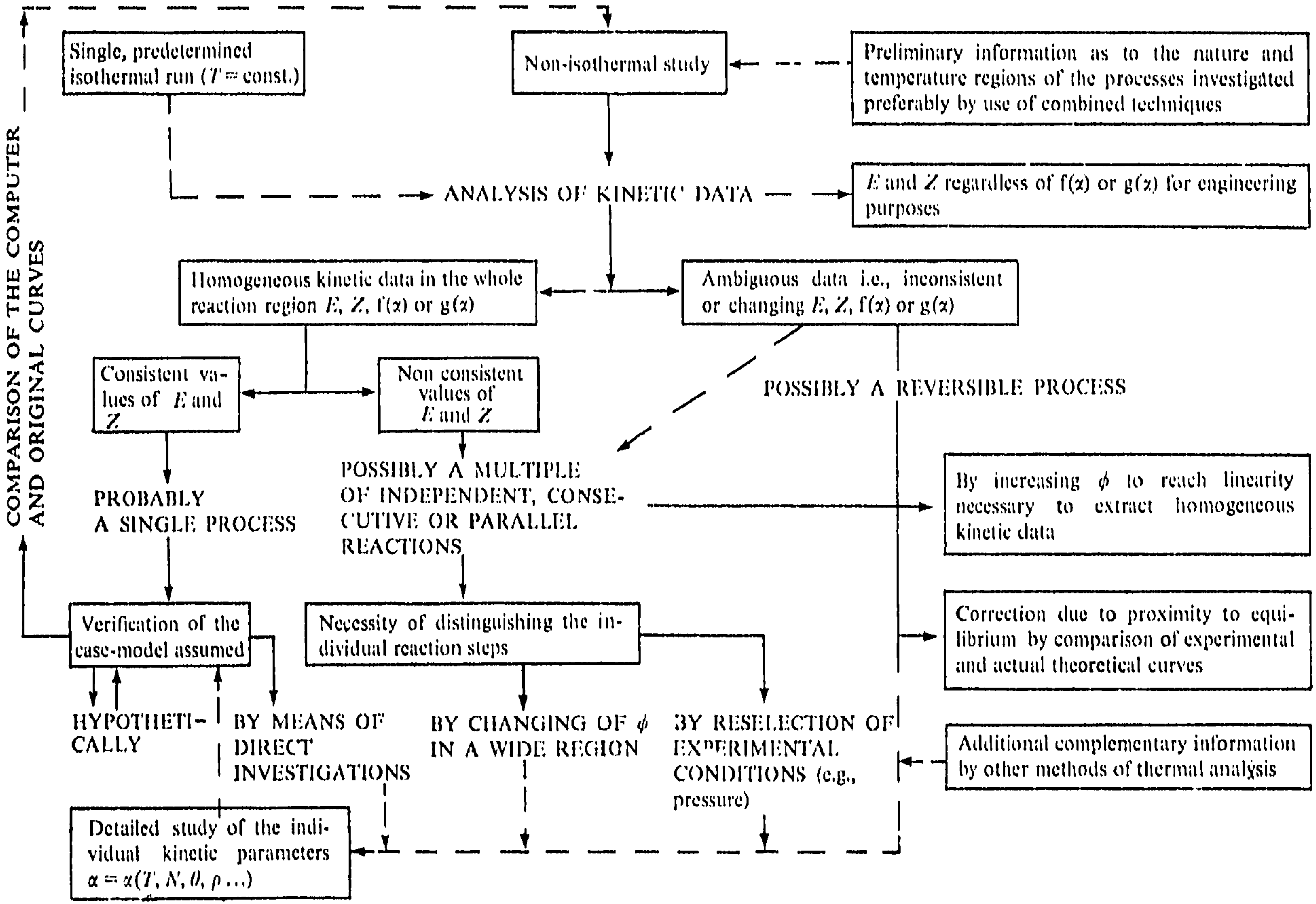
$\log[-\ln(1-\alpha)]$ vs. (time) and/or
$\log[d\alpha/dt]$ vs. $\log(1-\alpha)$

to determine the value of the exponent-factors for nucleation and nuclei growth models and/or phase-boundary models, respectively.

Accordingly, a more general test for isothermal data can be adopted according to the method of Hancock and Sharp[130] who employed a formal function in the form

TABLE 4.2

KINETIC ANALYSIS SCHEME



of $-\log(\ln(1-\alpha)) = m \ln t + \ln k$. By plotting

$$-\log(\ln(1-\alpha)) \text{ vs. } \log(\text{time})$$

a straight line is obtained having the slope, m, the value of which falls within 0.57 to 0.62 for simple diffusion, 1.0 to 1.15 for nuclei growth and within 1.25 to 3.00 for phase-boundary reactions. A possible scheme of steps for non-isothermal kinetic analyses is outlined in Table 4.2.

4.4. Kinetic parameters by differential thermal measurements

The usefulness of thermal measurements as a TA method of monitoring and defining thermal effects associated with chemical changes and structural transformations has been shown in section 2.2. In principle, DTA curves can be used for both enthalpy change determinations (proportional to the DTA peak area) and investigation of reaction kinetics (influencing the shape and the position of DTA peak in the temperature scale, see section 4.1.3). The success of kinetic data evaluations, however, has been limited by the difficulties in formalizing the factors responsible for the curve. The shape of the DTA peak has been shown to be a function not only of the reaction kinetics[61] but also of the geometry and thermal diffusivity within furnace, sample and thermocouple assembly[132,147]. The calibration procedure widely used in the determination of heats of reaction is of little actual use in the study of reaction kinetics. Because of the fact that accurate calorimetric measurements are difficult to obtain by means of DTA, reliable kinetic results should not be expected either[133]. The design of an energy proportioning DSC technique substantially corrected difficulties in the conventional DTA system. Despite all of these factors, a large number of articles have been published dealing with the kinetic appraisal of DTA peaks.

The most simple and widely used approach is that derived by Borchardt and Daniels[134,135]. They assumed experimental conditions under which no temperature gradient occurs in either the sample or standard and that the thermal diffusivities of sample and reference were identical and independent of temperature and reaction progress. In such a case, where heat loss is being neglected, the heat balance for the rate of reaction gives

$$\frac{\mathrm{d}\bar{m}}{\mathrm{d}t} = \frac{\bar{m}_0}{A}\left(C_\mathrm{p}\frac{\mathrm{d}\Delta T}{\mathrm{d}t} + \tau\Delta T\right) = \frac{\mathrm{d}\alpha}{\mathrm{d}t}\frac{1}{\bar{m}_0} \tag{4.92}$$

where $\bar{m}$ and $\bar{m}_0$ are the numbers of moles of the reactant at time $t = t$ and $t = 0$, respectively; A is the total area under the peak, ΔH is the reaction heat and $\mathrm{d}\Delta H = \mathrm{d}\bar{m}$, C_p is the heat capacity of the sample, ΔT is the temperature difference recorded and τ is the heat transfer coefficient. After integration

$$\frac{\bar{m}_0 - \bar{m}}{\bar{m}_0} = \alpha = \frac{1}{A}\frac{C_\mathrm{p}\Delta T}{\tau} + A_\mathrm{a} \tag{4.93}$$

where A_a is the peak area to time t. The values of A can be determined from the DTA peak by means of graphical, numerical, disc and/or analog integration methods. The value of C_p/τ may be established from the cooling curve of the system as shown by Baumgartner and Duhaut[136] who also determined the kinetic parameters, E, Z, and order, n, by means of an integral method.

For the processes which actually follow the reaction order kinetics, Freeman and Carroll[73] modified eqn. (4.93) into the difference-differential form

$$\frac{\Delta \log \left(C_p \dfrac{\mathrm{d}\Delta T}{\mathrm{d}t} + \tau \Delta T \right)}{\Delta \log \left[\tau (A - A_a) - C_p \Delta T \right]} = -E \frac{\Delta (1/T)}{2.3 R \log \left[\tau (A - A_a) - C_p \Delta T \right]} + n \,. \tag{4.94}$$

By neglecting comparatively small values in eqn. (4.94) a simplified form can be established[133,137]

$$\frac{\Delta \log \Delta T}{\Delta \log (A - A_a)} = -E \frac{\Delta (1/T)}{2.3 R \Delta \log (A - A_a)} + n \,. \tag{4.95}$$

Another method was introduced by Wendlandt[138,139] using the equation

$$\log \frac{\Delta T}{A - A_a} = \frac{E}{2.3 R} \Delta \left(\frac{1}{T} \right) \tag{4.96}$$

A number of methods have been proposed for extracting kinetic parameters from multiple DTA runs. Especially prominent is the Kissinger method[75,140] for determining E, which was independently developed by Murray and White[80] and Daneš and Ponec[141], on the basis of the following equation (see also section 4.2.2)

$$\log (\phi / T_{\max}^2) = -E/2.3 R (1/T_{\max}) \tag{4.97}$$

where $T_{\max}$ is the temperature at the maximum rate developed during the process. Reed et al.[142] considered the DTA thermal resistance problems and concluded that eqn. (4.97) would be inaccurate if $T_{\max}$ were applied as the temperature at the maximum of the DTA peak, particularly for voluminous samples (preferably a micro-DTA system should be used). Rogers and Smith[143] pointed out that the assumed constant value of $(1-x)_{\max}$, which develops at the maximum rate (see section 4.2.2), may vary with $T_{\max}$ at different heating rates applied for more complex processes. Reich[144] developed a different equation on the basis of the Borchardt simplification[135] that $C_p(\mathrm{d}\Delta T/\mathrm{d}t) \ll \Delta T$, or

$$\log \left(\frac{\phi \Delta T}{A} \right) = n C_{98} \log \left(\frac{A - A_a}{A} \right) - \frac{E}{2.3 R} \frac{1}{T} \tag{4.98}$$

which requires at least two DTA curves obtained at two different heating rates. Reaction order, n, is then determined by the equation

$$\log \left(\frac{\Delta T}{A} \right) = n \Delta \log \left(\frac{A - A_a}{A} \right) + \log \phi \,. \tag{4.99}$$

These methods, however, share the disadvantage of all isothermal measurements where multiple runs are needed. In addition, it is also rather difficult to reproduce precisely the identical conditions for individual experimental runs[133].

All of the above methods using the simplifying assumption of Borchardt and Daniels[134,135] can be rigorously applied only to stirred systems, the theory of which was critized by Reed et al.[142]. However, it should be noticed that a variety of workers, on using the same simplifying assumption, reached satisfactory results even in analysing DTA curves for the thermal decomposition of solids[145-154][*].

Another method of DTA kinetic evaluation was introduced by Rabovskiy et al.[145]. The method of Ellerstein[127] was used to calculate the kinetics of glass transitions. The crystallization of glasses was studied by combined methods[63,155,156] as well as the decomposition of various inorganic compounds[137,151,153,154] and dissolution of solids in liquids[162]. Kinetics of explosive materials[157] and polymers[62,144,158] were also investigated. Solving basic DTA equations, Bae[164] presented a new method for determining the kinetic parameters from a single run. The determination of the probable reaction mechanism of heterogeneous reactions was attempted by Škvára and Šatava[61]. Influence of the individual analytical form of model relations, $g(\alpha)$, introduced into eqn. (4.93) instead of order n, is demonstrated in Fig. 4.20.

Akita and Kase[159,160] solved basic DTA equations for an infinite cylindrical

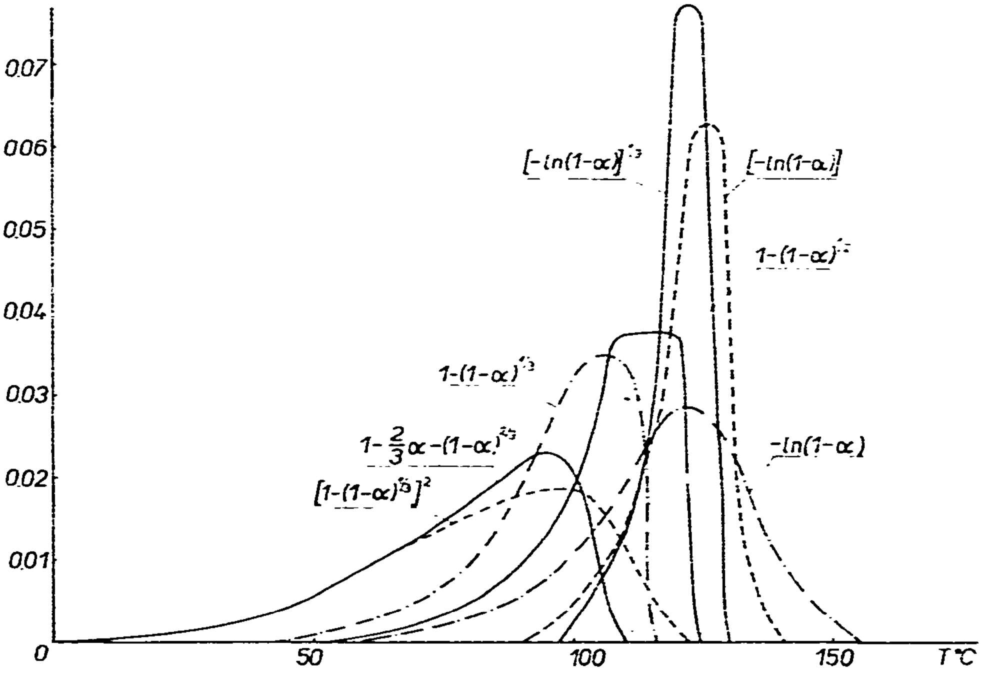


Fig. 4.20. Effect of the individual rate controlling process on the shape of the DTA peak[61].

---

[*] For a critical examination see review by Garn, CRC Critical Reviews, *Anal. Chem.*, Sept. 1972, p. 65, which also presents a thorough discussion of non-isothermal kinetic analysis.

sample with the first[159] and later n-th order[160] reactions by Laplace transformations (similar to the work of Tateno[161]) and by Green's function, under the boundary condition of a linear rise of temperature of the outer cylinder surface with time. The change of thermal properties of the sample material due to chemical reaction is neglected. From these results it was concluded that the peak temperature of the DTA curve and the temperature of the inflection point of the TG curve agreed with each other within a certain limit of experimental conditions, i.e., heating rate, cell size and kinetic properties of reactant. Some useful diagrams, permitting judgement of the coincidence of experimental conditions, were also devised[159,160]. Thus, these results may explain the apparent agreements obtained for the solid-state kinetics. The necessary condition, however, is to hold the thermal properties of the sample unchanged during the entire interval of the process. This may be achieved by mixing the reactant with an inert, well-conducting substance (corundum, noble metal powders such as Ag. Au, Pt, etc.) which act, in fact, as a diluting agent to average the thermal properties before and after the reaction. Tratore[163] investigated approximations used for the description of the temperature difference curves of heterogeneous reactions in a detailed way, including the accuracy and limits of the DTA method for the determination of kinetic parameters and heat of transformations. Borman and Olson[57] also discussed DTA kinetics.

A different approach of DTA peak evaluation is based on utilization of the initial part of the reaction progress where the change in the sample properties is small. One of the most popular methods is that of Piloyan et al.[71,165] where the combination of Borchardt's approximation[135] and the general form of the differential rate equation is used,

$$\log\left(\frac{d\alpha}{dt}\right) \cong \log \Delta T = \underbrace{[\log(ZA) + \log f(\alpha)]}_{\cong\ \text{constant}} - \frac{E}{2.3\,R'}(1/T). \tag{4.100}$$

The entire procedure is illustrated graphically in Fig. 4.21.

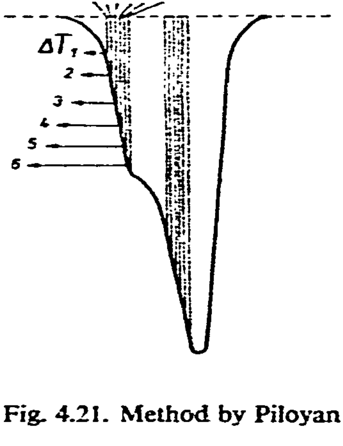


Fig. 4.21. Method by Piloyan[77,133].

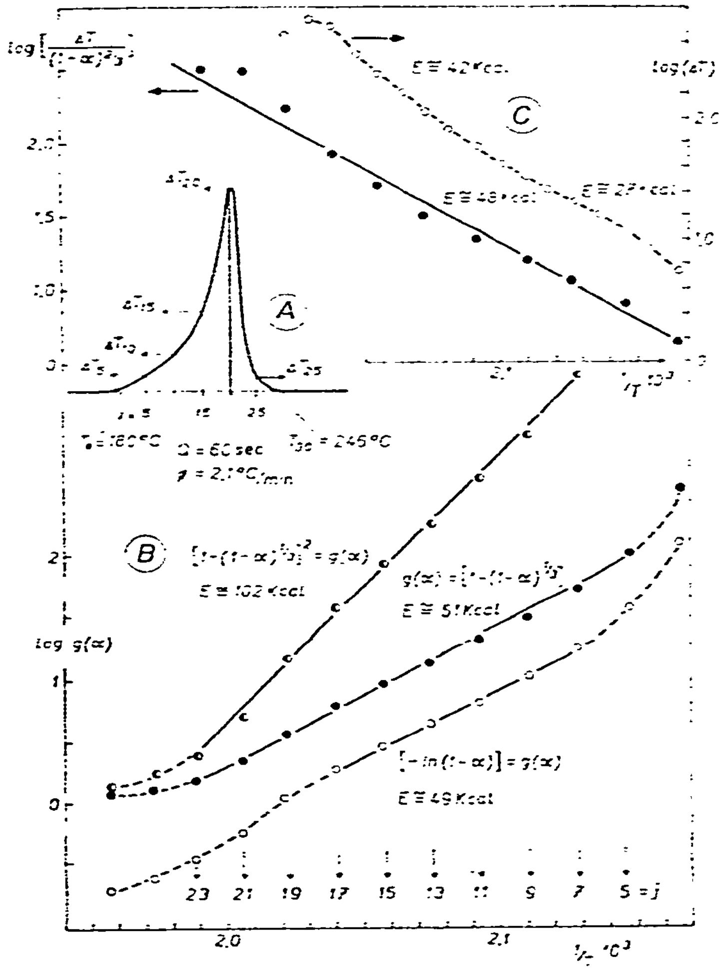


Fig. 4.22. Graphical representation of manual evaluation of DTA[44]. Curve (*A*) for the decomposition of freshly powdered $KMnO_4$ (compare Fig. 4.8 and 4.13). (*B*) Integral method using the plot of log g(α) vs. (1/*T*) assuming different rate controlling processes. (*C*) Differential method assuming validity of $\Delta T \cong d\alpha/dt$. Compare with the following table obtained by least squares computer evaluation using Škvára's program[191] for the required accuracy of 10 percent in the calculated linearity region.

Case-model	*Interval of linearity (in α)*	*E (in Kcal)*	*Z*	*Standard deviation*
$[1-(1-\alpha)^{1/3}]$	94% (0.01–0.95)	53.8	5.6×10^{20}	0.015
$[1-(1-\alpha)^{1/3}]^2$	94% (0.01–0.95)	109.6	1.3×10^{45}	0.015
$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}$	80% (0.03–0.83)	97.9	6.9×10^{39}	0.035
$(1-\alpha)\ln(1-\alpha)+\alpha$	80% (0.03–0.83)	95.6	2.6×10^{39}	0.074
$[-\ln(1-\alpha)]^{1/2}$	59% (0.01–0.59)	29.2	1.3×10^{10}	0.081
$[-\ln(1-\alpha)]$	59% (0.01–0.59)	60.2	1.4×10^{24}	0.081
$[1-(1-\alpha)^{1/2}]$	57% (0.03–0.59)	48.4	2.7×10^{18}	0.044

In the case that $f(\alpha)$ is small with regard to E/RT and is a well-behaved function[133] (temperature effect on the term E/RT is greater than that induced in $f(\alpha)$ under a suitably chosen heating rate) then the modified Arrhenius plot of $\log \Delta T$ vs. $1/T$ is linear with a slope of $E/2.3\,R$. It can be directly derived from the advancing edge of the DTA peak in the region of about $0.1<\alpha<0.4$. The agreement between the results produced in this way and those obtained from more conventional methods was reported to be excellent[137,154–156].

Girgis[167] has subjected Piloyan's method and others to severe criticism because of deviations found in the calculated kinetic parameters exceeding ±ten percent (he also made a comparison with isothermal DTA methods). It can be shown[63] that the reliability of Piloyan's method depends on the kind of model relation employed. The function, $(1-\alpha)^n$, is the least suitable while the functions describing nucleation, crystal growth and/or diffusion give quite satisfactory results. The best example supporting the validity of Piloyan's method is the work of Rasmunsen[166] who recently reported the theory of DTA based investigations of diffusional growth of particles. He made an analysis[166] of pseudo-exothermal base line drift associated with the agglomeration process of NiO fine particles dispersed in a Ni metal matrix. Following the Kissinger approach[75,140], the direct proportionality, C_R, between the changes in both the DTA curve, $d\Delta T$, and the thermal resistance, d_R, can be established. Assuming the product of thermal resistance, R, and the average cross section of particles, $1-\eta^{2/3}\pi r^2$, to be constant for a fixed number of equal sized spheres, it can be derived that

$$dR = R_0\eta^{2/3}d(r^2) \tag{4.101}$$

where η is the number of voids per volume unit and R_0 is a constant. Considering further growth of particles as controlled by volume diffusion (parabolic law $r = C_D\sqrt{Dt}$ where r is the radius and D is the diffusion coefficient) the term, $d(r^2)$, can be equated to $C_D^2\,d(Dt)$ yielding

$$dR = R_0\eta^{2/3}C_D^2\,d(Dt) = C_{102}\,d(Dt) \tag{4.102}$$

together with the equation, $d\Delta T = C_R dR$, and after integration

$$\Delta T = C_{103}\,(Dt - D_0 t_0) \tag{4.103}$$

In order to eliminate the constant C_{103}, the logarithmic form of eqn. (4.103) for two different time-limits is taken and simplified by iterations utilizing $D = D_0\exp(-E/RT)$ so that

$$\ln\frac{\Delta T_2}{\Delta T_1} = -\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) + \ln\frac{t_2}{t_1} \overset{(t_2\to t_1)}{\cong} -\frac{E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right). \tag{4.104}$$

This is identical with the Piloyan eqn. (4.100). The activation energy so calculated[166], 37 kcal/mol, corresponds to the activation energy for the diffusion of oxygen in nickel metal (literature value of 39.5 kcal/mol).

A typical example of DTA evaluation is given in Fig. 4.22 in comparison with the previously described methods[44].

The use of DSC substantially simplifies the kinetic data evaluation because the

DSC curve is a direct record of the rate of heat evolution, dq/dt, which is directly proportional to the reaction rate (see section 2.2.4). The major contribution to DSC kinetics methods has been made by Rogers and his coworkers[143,152,168]. The simplest method utilizes the equation[152]

$$E = -2.3\,R\,\frac{\Delta \log \bar{d}}{\Delta(1/T)} \tag{4.105}$$

where $\bar{d}$ is the deflection (analogous to ΔT) from the baseline at the associated absolute temperature, T. For simple decompositions which follow the reaction-order concept, E can be determined from the curve peak maximum using a predetermined value of n (ref. 143).

$$E = \frac{RT_{\max}^2\, n\bar{d}}{\phi(1-\alpha_{\max})\, C_{106}} \tag{4.106}$$

where C_{106} is the proportionality constant including the heat of reaction, ΔH. Rogers and Smith[168] extended this method to evaluate Z as

$$Z = \frac{E\phi \exp\,(E/RT_{\max})}{RT_{\max}^2}\,. \tag{4.107}$$

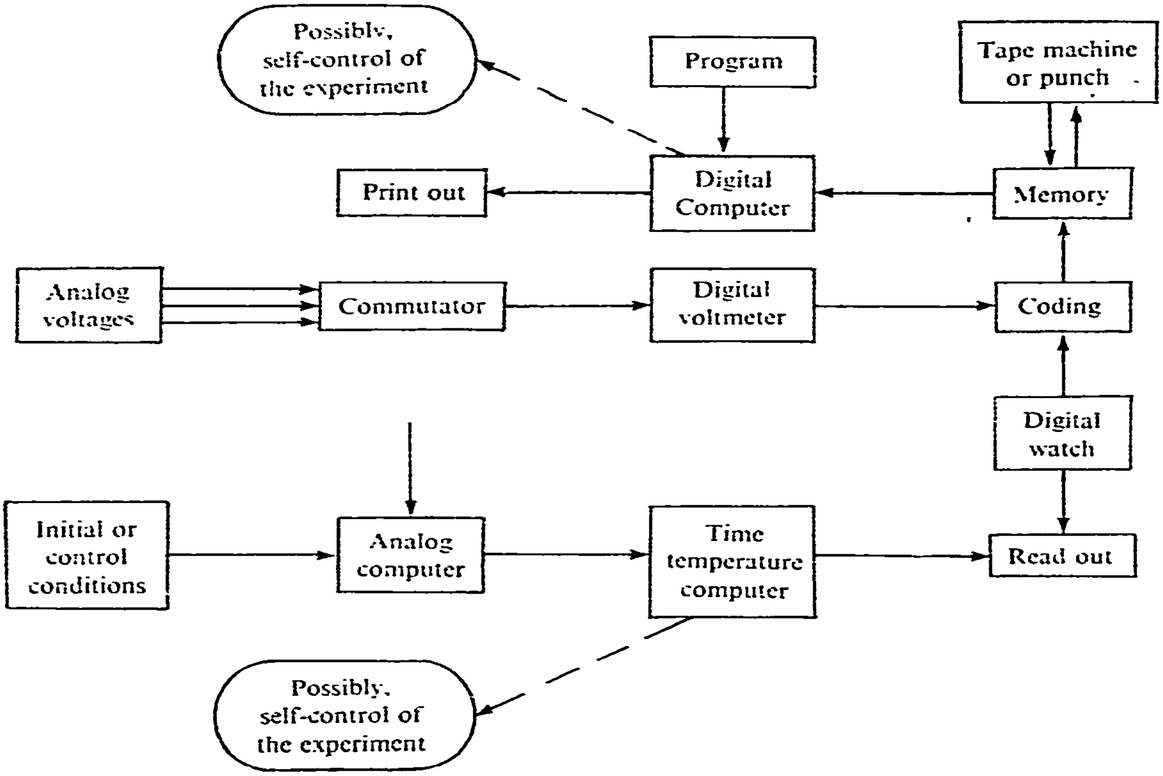
There are other DSC based kinetic investigations[167–172].

4.5. *Use of computers*

An accumulation of recorder charts is the characteristic result of present TA experiments. Owing to the practice of manual data logging the choice of a suitable chart is somewhat arbitrary. However, two alternative types of input data are possible, $\alpha = \hat{\alpha}(T)$ and/or $\dot{\alpha} = \hat{\dot{\alpha}}(T)$. Such data, scanned, and then assembled for calculation sometimes require a numerical method for obtaining a reliable derivative curve. The uncertainties inherent in such methods of data collecting will be reflected in the final results. A more reliable and time-saving approach is to use a digital voltmeter combined with a direct data logging system. The commutator selects the impulses in a suitable order and transmits them to the voltmeter, which converts the analog voltage into digital form. The on-line coupled coder then transmits the information together with a time base to the digital computer system. Another way may be the direct combination of TA output with an analogous computer system. The principle of on-line systems is shown in the flow chart in Table 4.3.

In general,[176,178] for an electronic analog computer the physical variables are time and voltage, corresponding mathematically to an independent variable and dependent variable, respectively. The value of the physical variable is taken to be proportional to the mathematical variable of the equations that the computers present. Programming requires only the coupling of the appropriate operations by wires to form the equation desired and the solution may than be displayed visually on an oscilloscope. However, this method presents many problems which are difficult to solve, such as those encountered in partial differential equations or matrix calculus.

TABLE 4.3
FLOW CHART FOR ON-LINE EVALUATION OF EXPERIMENTAL DATA



The advantage of this method is found particularly in the study of chemical reactions by stopped flow or relaxation procedures where a large quantity of data is collected in a short period of time[172].

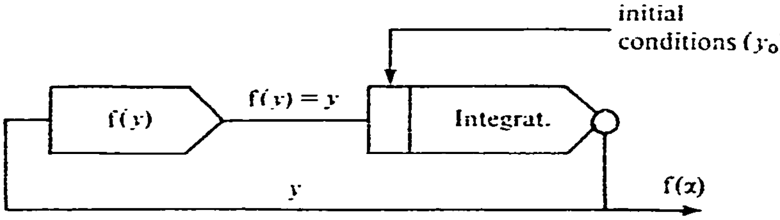
The principle of digital computer operation is simply that of fully automated counting on an abacus using a set of basic elements each of them representing the number zero in the closed and the number one in the open state. Thus the input data must be combined with a suitable program to control the calculation of desired information. The advantage of this method is the ability to calculate stored data in any time and with an advanced program to direct the calculation to match the desired accuracy.

Hesitation to calculate kinetic parameters from non-isothermal measurements probably originated in the rather complicated mathematical operations necessary for extracting the desired information. The main contribution of machine computation to heterogeneous reaction kinetics may be classified as follows:

(1) Automated monitoring of experimental data,
(2) Predicting the experimental course from known kinetic parameters,
(3) Kinetic appraisal of the experimental curves.

The first task does not necessarily require fully automated computers as the primary purpose is to establish a suitable record of experimental data such as $\alpha = \hat{\alpha}(T)$ and/or $\dot{\alpha} = \hat{\dot{\alpha}}(T)$, and the accurate calculation of peak areas, derivatives, etc. In such cases, a desk-computer containing some logic operations, conditional instructions and sufficient memory will save time in comparison with normal graphical methods[187–189]. All of the necessary corrections for experimental data normalization (e.g., thermocouple voltage-temperature dependance)[182,192,193], can be made also. The second point finds use in engineering problems such as reactor design and the control of experimental conditions by comparing the actual reaction course with that predicted theoretically from optimum kinetic data; it may also serve as a check of the quality of the calculated data. The last point presents the task of the actual calculation of the kinetics and the mechanisms of processes and is based on the mathematical methods reviewed in section 4.2. The analysis may be accomplished either directly, yielding the individual parameters, E, Z and $f(\alpha)$ (preferably by means of digital computers), or relatively, by comparing the experimental curve with a set of curves of a known description (by means of an analog computer).

Examples of the latter are: Maclean and Tranter[172], who used a two-stage logarithmic amplifier; Wilburn et al.[132,147] employed a system to simulate the equation for the center temperature in an infinite cylinder; James and Pardue[174] used an analog system for linear and non-linear response curves; Gayle and Egger[173] for heating rate curves programming; and Hughes and Hart[175] used the following patch diagram to integrate the equation, $\dot{y} = \phi \exp(-E/RT)(E/RT^2)$



using the generated, $y = \exp(-E/RT)$ and $f(y)$. The output, $df(\alpha)/dt$, gives upon integration the function $f(\alpha)$.

Probably the first to use a digital computer in non-isothermal kinetics was Anderson[90] who solved three simultaneous equations of the general form to yield E and Z for three multiple runs with different ϕ. Mc Crackin[177] used a series of weights, w_j, and temperatures, T_j, to feed the computer for the evaluation of $(1-\alpha)_j$ and $g(\alpha)_j$ for each point, j, assuming the validity of reaction order, n, i.e., $g(\alpha)_j = (Z/\phi)(E/R)\,\Gamma_{-1}(E/RT)$ where Γ_{-1} is the incomplete gamma function of minus first order. Assuming the error in α_j to be only experimental and independent of its value, $g(\alpha)_j$ will have a constant variance so that the best estimate for Z/ϕ is given by

$$\frac{\left[\sum_j \left(\frac{E}{R}\right)\Gamma_{-1}\left(\frac{E}{R}\right) g(\alpha)_j (1-\alpha)_j^{2n}\right]}{\left[\sum \left\{\left(\frac{E}{R}\right)\Gamma_{-1}\left(\frac{E}{R}\right)\right\}^2 (1-\alpha)_j^{2n}\right]}.$$

The procedure is carried out for various values of n and E. The values that give the smallest standard error are then chosen. Beech[180] used the equation, $\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln Z + n\ln(1-\alpha) - E/RT$, with a FORTRAN II computer program. A relative error least-squares procedure was used with a regression method to solve kinetic parameters assuming that the proportionality between $\mathrm{d}\alpha/\mathrm{d}t$ and $\mathrm{d}\Delta H/\mathrm{d}t$ is equal to $M\bar{d}\xi/(\Delta H\omega_0 \mathrm{C})$, where M is the molecular weight, $\bar{d}$ the pen reflection, ξ the sensitivity, ΔH the heat of reaction, ω_0 the in-weight of the sample and C the width of the chart, respectively. The term, α, is the ordinary fractional conversion established from the ratio of the partial to the total peak area which is convenient in DSC measurements. Gwinup[179] wrote a FORTRAN IV program to employ data from either a DTA or DSC peak. The DTA calculation is accomplished by Borchardt and Daniel's method. In DSC methods the function, $f(\alpha) = \alpha^m(1-\alpha)^n$, is used to calculate the specific rate constant, k, according to $(\mathrm{d}\Delta H/\mathrm{d}t) = (\mathrm{A}/\mathrm{Aa})^{-m} \times (1-\mathrm{A}/\mathrm{Aa})^{-n}$.

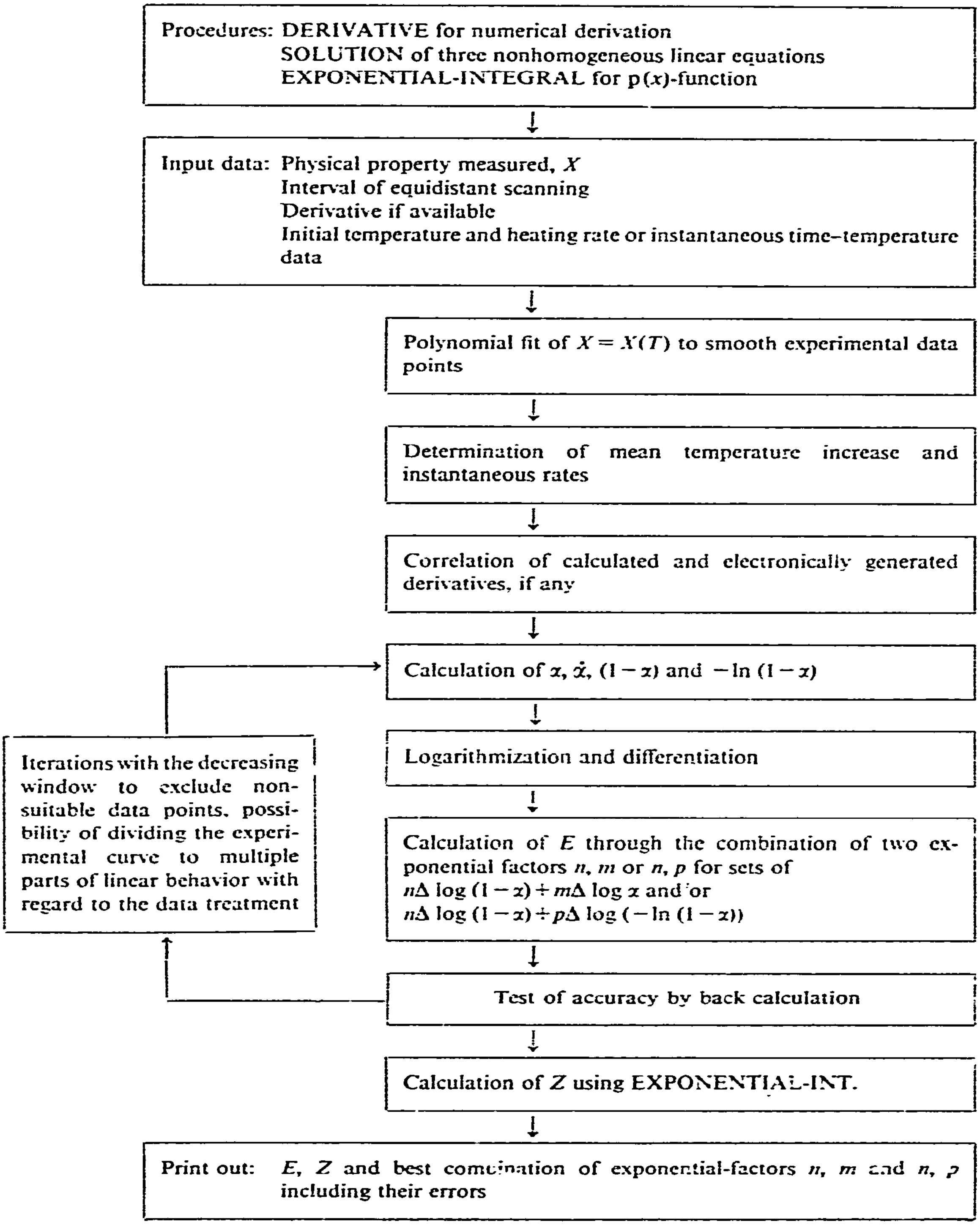
The method of Schempf et al.[181] is written in FORTRAN II and is applicable only to first order kinetics. The method utilizes a least squares polynomial fit of a TG curve with a j-th order polynomial ($\alpha = \mathrm{A}_0 + \mathrm{A}_1 x + \mathrm{A}_2 x^2 + \ldots + \mathrm{A}_j x^j$), where j is about 13 and A_j are constants received from the least square fit of sample weight–time data necessary for obtaining the correct derivative curves. The rate constant, k, is established for each temperature and the corresponding kinetic parameters, E and Z, are then evaluated.

The algorithmization method of Šesták et al.[183] proposed the use of numerical derivation to obtain a derivative of an observed TG curve,

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_j = \left[\frac{\dfrac{(w_{j+1}-w_{j-1})}{2} - \ldots + \ldots \dfrac{(w_{j+3}-4w_{j+2}+5w_{j+1}-5w_{j-1}+4w_{j-2}-w_{j-3})}{60}}{W_{\max} Q}\right]$$

where Q is the constant time interval of scanning and W and $W_{\max}$ are the instantaneous and final weight losses, respectively. Using a least squares method, the parallel evaluation of the kinetic parameters, E and n, is made by means of the simple difference-differential method. The constant Z is calculated from the original curve. The program is written in ALGOL and errors in the data evaluation are computed at various stages to indicate the level of accuracy attained. Because of the experimental uncertainty and necessity of a precise re-reading of the weight loss data inherent in all derivative methods, this algorithmization was improved[184] by smoothing the numerical derivative obtained by Gaussian curve fit. An iterative least-squares refinement of linear coefficients was applied to exclude points which lie outside the permitted level. A test of order, n, obtained by a derivative procedure is then made through the integral method of Coats and Redfern[108] checking the neighboring values of n until the least relative error in the straight line is achieved. A test of the calculated parameters by re-evaluation of the weight loss curve is also possible. To extend the applicability of this program, an improved method was proposed based on matrix evaluation of the

TABLE 4.4
FLOW CHART FOR KINETIC ANALYSIS I



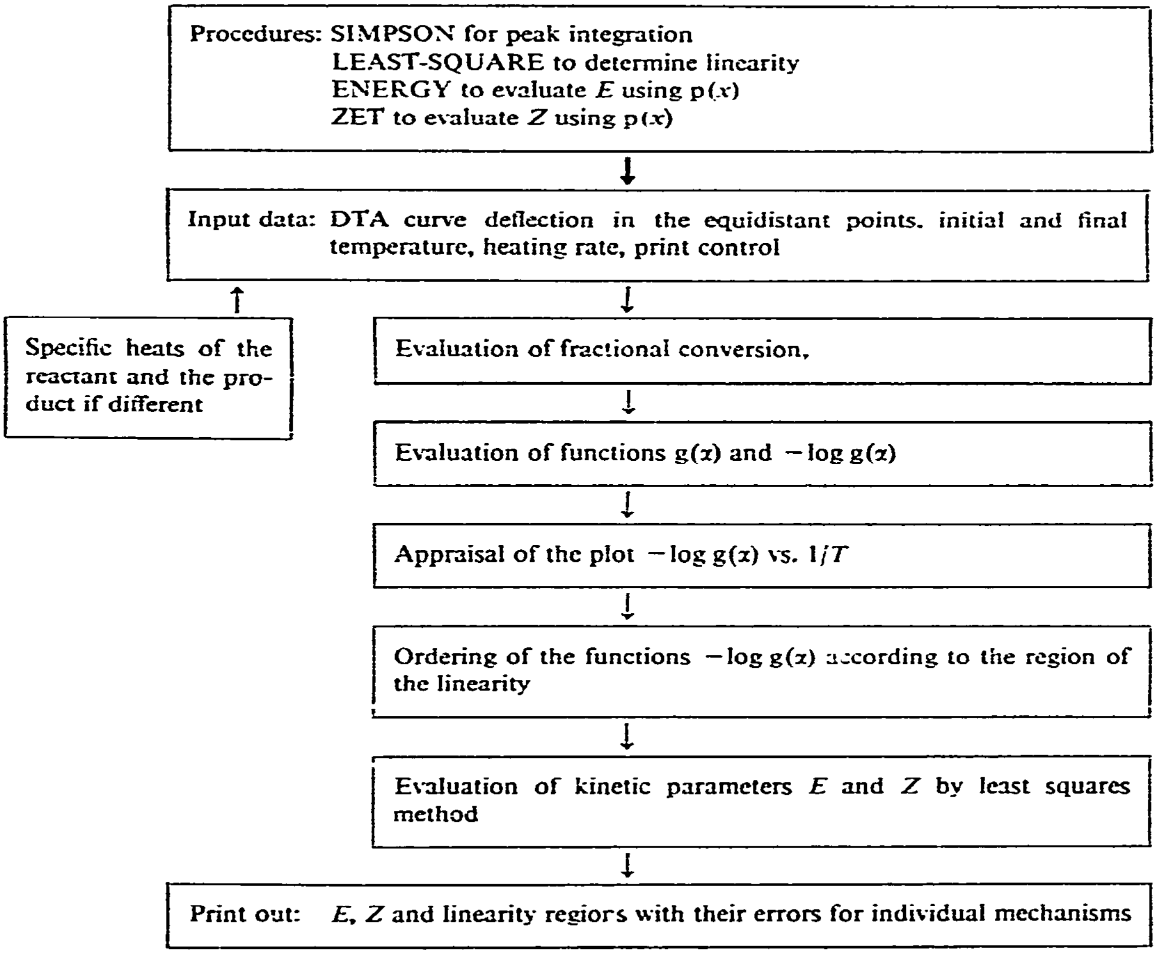
general, but formal kinetic equation, $d\alpha/dt = k\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p$, using its difference-logarithmic form as shown in the flowchart in Table 4.4.

Recently Nolan and Lemay[201] studied a systematic variation of the three parameters *m*, *n* and *p* and found eqn. (4.32) useful for a preliminary appraisal of reaction mechanism or as a means for checking isothermal results. The program is written in FORTRAN IV and performs the DSC peak area integration by Simpson's rule and the linear least-squares analysis of the Arrhenius plot including a t-test to indicate the degree of linearity. The possible rate equation is limited by considering those cases which have a relatively small range of *m*, *n* or *p* and/or which yield a limited range of activation energies as the range of α is varied.

Šatava and Škvára[61] used ALGOL 60 language and Borchardt and Daniel's method to facilitate calculations of the fraction decomposed and kinetic parameters from a DTA peak. The improved program of Škvára[191] is similar to the procedure used in the conventional estimation of reaction mechanism from isothermal measurements, as was recently demonstrated by Johnson and Gallagher[186]. The latter method

TABLE 4.5

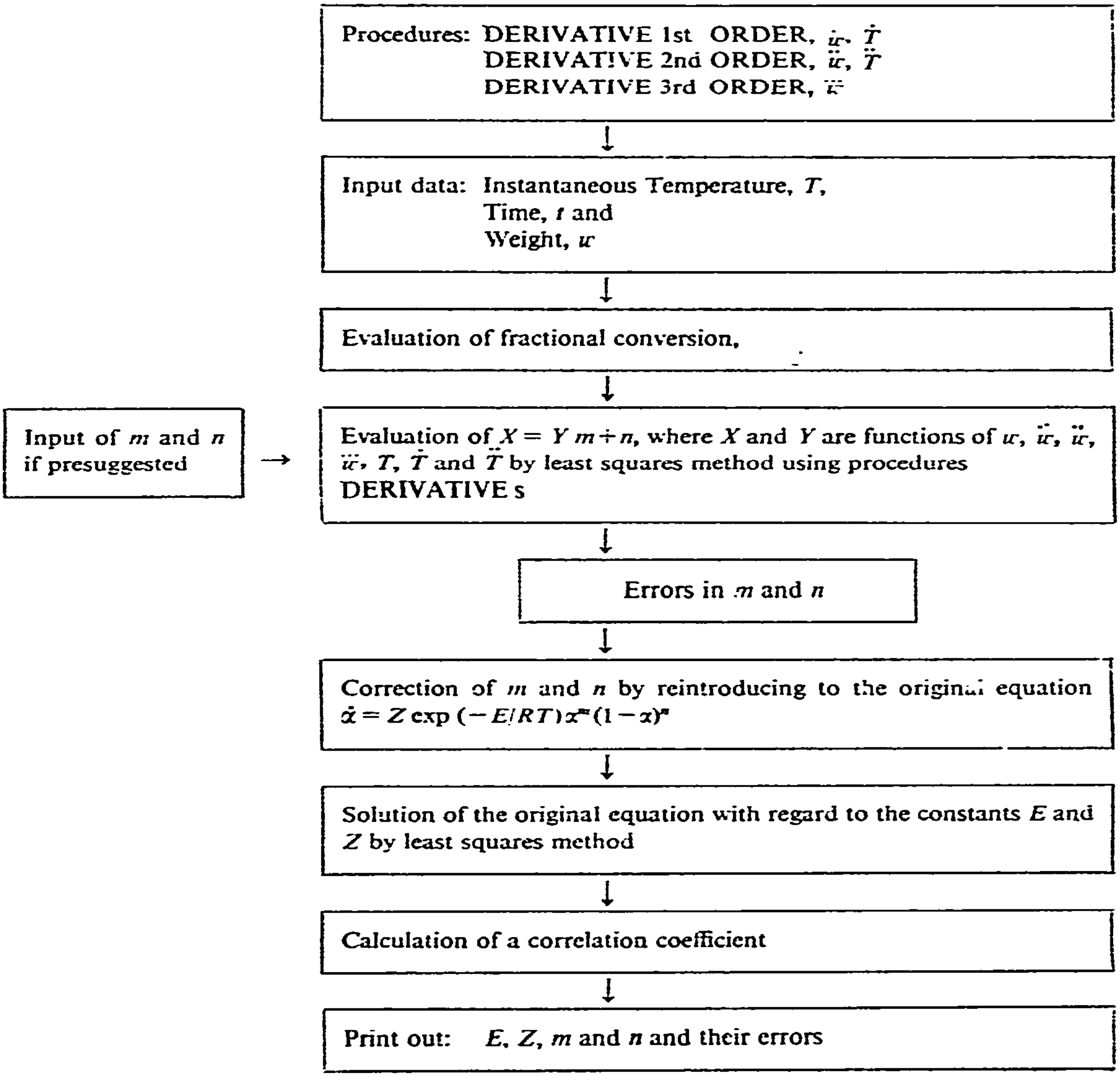
FLOW CHART FOR KINETIC ANALYSIS II



is written in FORTRAN IV and based on Šatava's method[49] for the estimation of model relation from the linear fit of log $(g(\alpha))$ vs. $1/T$. A least-squares method is used throughout the treatment which is based on comparing different reaction mechanisms to achieve the greatest region of linearity. Kinetic parameters are evaluated by the numerical solution of the series for the $p(x)$-function using iterative successions, as shown in the flow chart of Table 4.5. A universal program combining flow charts in Tables 4.4 and 4.5 is in preparation[185].

Vachuška and Vobořil[119] described a program in ALGOL to evaluate kinetic parameters from the derivative form of the logarithm of the rate equation to enable the solution for a non-linear temperature rise during the heating of a sample. The equation

TABLE 4.6
FLOW CHART FOR KINETIC ANALYSIS III



of a straight line is solved with regard to E and n using input data of instantaneous values of weight, w, temperature, T, and time, t. The temperature rise and the first- and second-order derivatives are computed numerically. This program is now being improved[190] to utilise a polynomial fit throughout the experimental points. It is possible to make a direct solution of derivatives, even of the third order, required to extend the calculation in order to obtain the values of the two exponential factors, m and n (see Table 4.6): See also the work of Zsekely[118].

There are, of course, many more applications of computer techniques[200] to non-isothermal kinetics such as polymers[169–171,165–196], near-equilibrium experimental conditions[197], heat transfer effects[194], calorimetry[198,199]; and their number increases continuously. The computer technique has been a welcome tool to facilitate experimental data processing[188–189]. It should be kept in mind that for advanced physical investigations, only a very sophisticated program may give a reliable result. The high sensitivity to random errors and lead-in misinformation is troublesome and may often be misleading particularly when relating the final considerations to the numerical print out. Hence, the manual evaluation still is of great use because the mistakes introduced or generated can be continuously corrected by logical considerations.

Note added in proof

These equations predict straight lines when $\log(-\ln(1-\alpha))$ is plotted against $\ln T$, T and $1/T$, respectively, and E is computed as $(4.567\, RT_i \operatorname{tg} \beta)$, $(4.567\, RT^2 \operatorname{tg} \beta)$ and $(4.567 \operatorname{tg} \beta - 2R\overline{T})$, respectively. The precision of these approximations has recently been illustrated by Broido and Williams (*Thermochim. Acta*, 6 (1973) 245) who found that a higher degree of linearity is given by eqn. (4.73), i.e. the last of above-mentioned plots is about twice as good as the plot to the second approximation than the first (justified on the basis of an asymptotic expansion with a non-dimensional activation energy as the large parameter). It also explains the deviations obtained in the E values when using different methods of kinetic data calculation (see refs. 51, 66, 113).

REFERENCES

1 J. Šesták, Plenary lecture, Non-Isothermal Kinetics, IIIrd ICTA, Davos, in H. G. Wiedemann (editor), *Thermal Analysis*, Vol. 2, Birkhäuser Verlag, Basel, 1972, p. 3.
2 J. R. MacCallum and J. Tanner, *Nature*, 225 (1970) 1127.
3 A. L. Draper, in H. G. McAdie (editor), *Proceedings of 3rd Toronto Symposium on Thermal Analyses*, Toronto, CIC, Canada, 1970, p. 63.
4 J. R. MacCallum, *Nature, Phys. Sci.*, 232 (1971) 41.
5 R. A. W. Hill, *Nature*, 227 (1970) 703.
6 R. M. Felder and E. P. Stehel, *Nature*, 228 (1970) 1085.
7 J. M. Gilles and H. Tompa, *Nature, Phys. Sci.*, 229 (1971) 57.
8 P. Holba and J. Šesták, *Z. Phys. Chem. (Frankfurt am Main)*, 80 (1972) 1.
9 E. L. Simmous and W. W. Wendlandt, *Thermochim. Acta*, 3 (1972) 498.
9a V. M. Gorbatchev and V. A. Logvinenko, *J. Thermal Anal.*, 4 (1972) 475.
9b G. Gyula and J. Greenhow, *Thermochim. Acta*, 5 (1973) 481.
10 J. Šesták and J. Kratochvil, *Plenary lecture, Rational Approach to Constitutive Equations in Isothermal and Non-isothermal Kinetics*, presented at Round Table Discussions on Thermal

Analysis, Budapest, Hungary 1972, *J. Thermal Anal.*, 5 (1973) 193.

11 C. Truesdell, *Rational Thermodynamics*, McGraw-Hill, New York, 1969.

12 J. Szako, *J. Thermal Anal.*, 2 (1970) 141.

13 J. Simon and E. Debreczeny, *J. Thermal Anal.*, 3 (1971) 301.

14 H. Y. Frentz, *Electrotechnische Z.*, A 78 (1957) 156.

15 D. Fatu and E. Segal, *Rev. Roum. Chim.*, 16 (1971) 343.

16 T. Akahira, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, 9 (1928) 165, and Table No. 3, (1929) 181–215.

17 J. Šesták, *Silikáty*, 11 (1967) 153.

18 J. Šesták, *Thermochim. Acta*, 3 (1971) 150.

19 J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 70 A (1966) 487.

20 C. D. Doyle, *J. Appl. Polym. Sci.*, 5 (1961) 285.

21 V. Šatava, *Silikáty*, 5 (1961) 68.

22 P. Vallet, *C. R. Acad. Sci.*, 249 (1959) 823; and *Integration of Ratio Constants with Respect to Temperature*, Gauthier–Villars et Cie, Paris, 1961.

23 O. Schlönmilch, *Vorlesungen über hohere Analysis, Vol. II.*, Braunschweig, 1874, p. 269.

24 C. D. Doyle, *J. Appl. Polym. Sci.*, 6 (1962) 639.

25 C. D. Doyle, *Nature*, 207 (1965) 290.

26 S. R. Biegen and A. W. Czandera, *J. Therm. Anal.*, 4 (1972) 39.

26b G. Gyulai and E. J. Greenhow, *Thermochim. Acta*, 6 (1973) 239 and 254.

27 F. E. Harris, *Math. Tables Aids Comp.*, 11 (1957) 9.

28 J. Miller and R. P. Hurst, *Math. Tables Aid Comp.*, 12 (1958) 187.

29 I. W. Glaischer and R. F. Caylay, *Phil. Trans. Roy. Soc. London*, 160 (1970) 367.

30 E. Jahnke and F. Embde, *Tables of Higher Functions*, Leipzig, 1960 and E. Jahnke, F. Embde and F. Losch *Tables of Higher Functions*, 6th Edition, McGraw Hill, New York, 1960, p. 18.

31 M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, New York, 1965.

32 *Tables of Definite Integral Functions*, Publ. House of Acad. Sci. USSR, Moscow, 1954.

33 *Tables of Sine, Cosine and Exponential-integrals*, Vols. 1 and 2, Federal Works Agency, WPA of New York, 1940.

34 *Tables of Exponential-integrals for Complex Arguments, Applied Mathematics Series*, 51, U.S. NBS, Washington D.C. 1958, p. 590.

35 *Ibid.*, Series 55, *Handbook of Mathematical functions*, 1964, p. 248.

36 S. Oberländer, *Tabellen von exp- und integralfunktionen zur Thermodynamik und Gaskinetic*, Akademie-Verlag, Berlin, 1959.

37 M. Zsako, *J. Phys. Chem.*, 72 (1968) 2406.

38 A. W. Smith and S. Aranoff, *J. Phys. Chem.*, 62 (1958) 684.

39 P. A. Redhead, *Vacuum*, 12 (1962) 203.

40 V. Šatava and F. Škvára, *J. Amer. Ceram. Soc.*, 52 (1966) 591.

40a F. Škvára and J. Šesták, *Proc. 6th Czech. Conf. Thermal Anal., SVŠT, Bratislava*, 1973, pp. P11–P17.

41 J. Burke, *The Kinetics of Phase Transformations in Metals*, Pergamon Press, New York, 1965.

42 B. V. Yerofeyev, *Dokl. Ross. Akad. Nauk, Ser. A*, 52 (1946) 511; and *Reactivity of Solids*, Elsevier, Amsterdam, 1961, p. 273.

43 E. Segal, *Rev. Roumain. Chim.*, (1973), in press.

43a D. W. Johnson and P. K. Gallagher, *J. Phys. Chem.*, 76 (1972) 1474.

44 J. Šesták and V. Šatava, unpublished results.

45 E. Jona, V. Jeseňák and T. Šramko, *Chem. Zvesti*, 23 (1969) 420.

46 J. Šesták and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.

47 J. H. Sharp, G. W. Brindley and B. N. N. Achar, *J. Amer. Ceram. Soc.*, 49 (1966) 379.

48 J. R. MacCallum and J. Tanner, *Europ. Polym. J.*, 6 (1970) 1033.

49 V. Šatava, *Thermochim. Acta*, 2 (1971) 423.

50 G. W. Brindley, J. H. Sharp and B. N. N. Achar, in J. P. Redfern (editor), *Thermal Analysis 1965*, MacMillan, London 1965, p. 180; *Proceedings Inter. Clay Conf.*, Jerusalem, 1966, p. 67.

51 J. Šesták, *Talanta*, 13 (1966) 567.

52 T. Ozawa, *Bull. Chem. Soc. Jap.*, 38 (1965) 1881.

53 B. Lengyel and T. Szekely, *Monatsh. Chem.*, 103 (1972) 24.

54 A. Franck and R. Sizman, *Chem. Ztg., Chem. App.*, *Part I* 86 (1962) 174 up to *Part IV* 87 (1963) 1.

55 H. Jüntgen and K. H. van Heek, *Fortschr. Chem. Forsch.*, B, (3/4). Springer, 1967.

56 M. M. Pavlyuchenko, *Heterogeneous Chemical Kinetics*, Nauka i Technika, Minsk, 1965.

57 B. M. Borman and F. A. Olson, *Thermochim. Acta*, 6 (1973) 345.

58 J. Szako, *J. Thermal Anal.*, 2 (1970) 145.

59 J. Šesták, *Silikáty*, 7 (1963) 125.

60 P. Gray and M. Y. Harper, *Reactivity of Solids*, Elsevier, Amsterdam, 1961, p. 283.

61 F. Škvára and V. Šatava, *J. Thermal. Anal.*, 2 (1970) 325.

62 T. Ozawa, *J. Thermal. Anal.*, 2 (1970) 301.

63 J. Šesták, *Phys Chem. Glasses*, (Dec. 1973) in press.

64 V. Šatava and J. Šesták, *Silikaty*, 8 (1964) 134.

65 V. Šatava and J. Šesták, *Anal. Chem.*, 45 (1973) 154.

66 R. Andebert and C. Aubineau, *J. Chim. Phys.*, 67 (1970) 617; and *Europ. Polym. J.*, 6 (1970) 965.

67 L. Böhm and M. Kahlweit, *Z. Phys. Chem. (Frankfurt am Main)*, 49 (1966) 147.

67a D. M. Popov, *Zh. Prikl. Khim. (Leningrad)*, 39 (1966) 2484.

68 I. A. Schneider, *Makromol. Chem.*, 125 (1969) 201; 108 (1967) 182.

69 I. A. Schneider, *Rev. Roum. Chim.*, 17 (1972) 1.

70 J. H. Flynn, in J. R. Schwenker and P. D. Garn (editors), *Thermal Analysis*, Vol. 2, Plenum Press, New York 1969, p. 1111.

71 J. G. Murgulescu and E. Segal, *St. Cerc. Chim. Tom. (Bucharest)*, 15 (1967) 261.

72 J. A. Magnusson, *Anal. Chem.*, 36 (1964) 1807.

73 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.

74 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 73 (1969) 751.

75 H. E. Kissinger, *Anal. Chem.*, 29 (1959) 1702.

76 K. H. van Heek and H. Jüntgen, *J. Phys. Chem.*, 35 (1963) 1464.

77 F. O. Piloyan, I. O. Ryabchikov and O. S. Novikova, *Nature*, 5067 (1966) 1229.

78 H. H. Horowitz and G. Metzger, *Anal. Chem.*, 35 (1963) 1464.

79 Y. Tsuzuki and K. Nagasawa, *J. Earth Sci., Nagoya Univ.*, 5 (1957) 153.

80 P. Murray and J. White, *Trans. Brit. Ceram. Soc.*, 54 (1955) 204.

81 D. W. Van Krevelen, C. Van Beerden and F. J. Hutjens, *Fuel*, 30 (1951) 253.

82 R. S. Turner, J. Hoffman and M. Schnitzer, *Soil Sci.*, 93 (1962) 225; *Can. J. Chem.*, 41 (1963) 243.

83 L. Reich, *Polym. Lett.*, 2 (1964) 621.

84 R. M. Fuoss, O. Sayler and H. S. Wilson, *J. Polym. Sci.*, 2 (1964) 3147.

85 R. W. Farmer, *Aeronautical Syst. Div. Tech. Doc. Rep.* ASD–TDR–62–1043, *Part I*, 1963.

86 P. Kofstand, *Nature*, 179 (1957) 1362.

87 R. M. Barrer and G. C. Bratt, *J. Phys. Chem. Solids*, 12 (1959) 130.

88 A. E. Newkirk, *Anal. Chem.*, 32 (1960) 1558; and in H. G. MacAdie (editor), *Proceedings of First Toronto Symp. on Thermal Anal.*, CIC, Canada, 1965, p. 29.

89 T. R. Ingraham and P. Marrier, *Can. J. Chem. Eng.*, (1964) 161.

90 H. C. Anderson, *J. Polym. Sci.*, 6 (1963) 175.

91 H. L. Friedman, *J. Polym. Sci.*, 6 (1963) 183.

92 H. B. Palmer, *Int. J. Chem. Kinetics*, 2 (1970) 77.

93 P. K. Chatterjee, *J. Polymer. Sci.*, 3A (1965) 4253.

94 J. H. Flynn and L. A. Wall, *Polym. Lett.*, 4 (1966) 323; 5 (1967) 191.

95 A. Berlin and R. J. Robinson, *Anal. Chim. Acta*, 27 (1962) 50.

96 B. Carroll and E. P. Manche, *Thermochim. Acta*, 3 (1972) 449.

97 B. Carroll and E. P. Manche, *Anal. Chem.*, 42 (1970) 1296.

98 J. H. Sharp and S. A. Wentworth, *Anal. Chem.*, 41 (1969) 2060.

99 V. A. Logvinenko, V. M. Gorbatchov, G. F. Nikitchenko, L. I. Myachina and A. V. Nikolaev, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 5 (1970) 11; and B. M. Gorbatchov and V. A. Logvinenko, *ibid.*, 5 (1970) 14.

100 V. B. Gorbatchov, V. A. Logvinenko, G. F. Nikitchenko and L. I. Myachina, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 3 (7) (1970) 28.

101 A. V. Nikolayev, V. A. Logvinenko, V. M. Gorbatchov, L. I. Myachina and N. N. Kuyazeva, in H. G. Wiedemann (editor), *Thermal Analysis*, Vol. 2, Birkhäuser, Basel, 1972, p. 611.

102 R. S. Dharwadkar and M. D. Karkhanavala, in G. F. Schwenker and P. D. Garn (editors), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1049.

103 L. Reich, *Polym. Lett.*, 3 (1965) 231.

104 L. Reich and D. W. Levi, *Makromol. Chem.*, 66 (1963) 102.
105 L. Reich and D. W. Levi, *Polym. Lett.*, 2 (1963) 1109.
106 C. D. Doyle, *Makromol. Chem.*, 80 (1965) 220.
107 V. Pai Verneker, M. MacCarty and J. N. Maycock, in H. G. Wiedemann (editor), *Thermal Analysis*, Vol. 1, Birkhäuser, Basel, 1972, p. 355.
108 A. W. Coats and J. P. Redfern, *Nature*, 29 (1964) 88.
109 A. W. Coats and J. P. Redfern, *Polym. Lett.*, 3 (1965) 917.
110 M. D. Judd and M. I. Pope, *J. Thermal Anal.*, 4 (1972) 31.
111 M. D. Judd, *Proceedings of the Round table Discussion on Thermal Anal.*, Budapest, 1972, *J. Thermal Anal.*, 5 (1973) 179.
112 V. Šatava, *ibid.*, ref. 111, p. 217; and ref. 40a, pp. V13–V17.
113 J. Simon, *ibid.*, p. 271; and J. Simon and E. Debreczeny, *Period. Polytech., Chem. Eng.*, in press.
114 I. B. Cutler, *J. Amer. Ceram. Soc.*, 52 (1969) 14.
115 D. A. Venkatu and D. L. Johnson, *J. Amer. Ceram. Soc.*, 54 (1971) 641.
116 R. S. Bradley, *J. Phys. Chem.*, 72 (1968) 2406.
117 T. Szekely, *Chim. Ind. Genie Chim.*, 104 (1971) 945.
118 T. Szekely, F. Till and G. Borossay, *Kinetics and Mechanisms of Polyreactions*, IUPAC, 1969, V, p. 403.
119 J. Vachuška and M. Vobořil, *Thermochim. Acta*, 2 (1971) 315.
120 L. Reich, H. T. Lee and D. W. Levi, *J. Polym. Sci.*, 9 (1965) 351.
121 A. L. Draper and L. K. Sveum, *Thermochim. Acta*, 1 (1970) 345.
122 G. Narsimham, *Chem. Eng. Sci.*, 16 (1961) 7.
123 C. N. Satterfield and F. Feakes, *AI Chem. Eng. J.*, 5 (1959) 115.
124 A. W. D. Hills, *Chem. Eng. Sci.*, 23 (1968) 297.
125 W. R. Dammers, W. Frankvoort and M. Tels, *Thermochim. Acta*, 3 (1972) 133.
126 O. T. Hanna and R. S. Kapner, *Ind. Eng. Chem. Fundam.*, 6 (1967) 116.
127 S. M. Ellerstein, *J. Phys. Chem.*, 69 (1965) 2471.
128 R. J. Cvetanovic and Y. Amenoniya, *Advan. Catal. Relat. Subj.*, 17 (1967) 103.
129 G. K. Boreskov (editor), *The Porous Structure of Catalysts and Transport Processes in Heterogeneous Catalysis* (*4th Int. Cong. on Catalysis, Novosibirsk, 1968*), Akademiai Kiado Publ., Budapest.
130 J. D. Hancock and J. H. Sharp, *J. Amer. Ceram. Soc.*, 55 (1972) 74.
131 D. W. Johnson and P. R. Gallagher, *Thermochim. Acta*, 4 (1972) 283; 6 (1973) 67.
131a B. K. Speronello, C. J. Brinkers and W. R. Ott, *Thermochim. Acta*, 6 (1973) 85.
132 F. W. Wilburn, J. R. Hesford and J. R. Flower, *Anal. Chem.*, 40 (1968) 777.
133 J. Šesták and G. Berggren, *Chem. Listy*, 64 (1970) 695.
134 H. J. Borchardt and F. J. Daniels, *J. Amer. Chem. Soc.*, 79 (1957) 41.
135 H. J. Borchardt, *J. Inorg. Nucl. Chem.*, 12 (1960) 257.
136 P. Baumgartner and P. Duhaut, *Bull. Soc. Chim. Fr.*, (1960) 1187.
137 D. Fátu, *J. Thermal Anal.*, 1 (1969) 285.
138 W. W. Wendlandt, *J. Chem. Educ.*, 38 (1961) 571.
139 W. W. Wendlandt and J. K. Fisher, *J. Inorg. Nucl. Chem.*, 24 (1962) 1685.
140 H. E. Kissinger, *J. Res. Nat. Bur. Stand.*, 57 (1956) 217.
141 V. Daneš and P. Ponec, *Collect. Czech. Chem. Commun.*, 23 (1958) 848.
142 R. L. Reed, L. Weber and B. S. Gottfried, *Ind. & Eng. Chem. Fundam.*, 4 (1965) 38.
143 R. N. Rogers and L. C. Smith, *Thermochim. Acta*, 1 (1970) 1.
144 L. Reich, *J. Inorg. Nucl. Chem.*, 28 (1966) 1329.
145 B. G. Rabovskiy, V. M. Kogan and A. A. Furman, *Zh. Fiz. Khim.*, 38 (1964) 2895.
146 L. J. Taylor and S. W. Watson, *Anal. Chem.*, 42 (1970) 297.
147 R. Melling, F. W. Wilburn and R. M. McIntosh, *Anal. Chem.*, 41 (1969) 1275.
148 G. J. Jong, *J. Amer. Ceram. Soc.*, 40 (1957) 4.
149 T. A. Klarke, E. L. Evans and K. G. Robinson, *Chem. Commun.*, 6 (1969) 266.
150 E. Koch, *Chem.-Ing. Techn.*, 37 (1965) 1004.
151 K. Heide, *Silikattechnik*, 17 (1966) 447.
152 R. N. Rogers and E. D. Harris, *Anal. Chem.*, 38 (1966) 412.
153 R. P. Agarwala and M. C. Naik, *Anal. Chim. Acta*, 24 (1961) 128.
154 G. Berggren, *J. Thermal. Anal.*, 1 (1969) 265.

155 D. Clinton, R. A. Mercer and R. P. Miller, *J. Mater. Sci.*, 5 (1970) 171.
156 J. Šesták, *Application of DTA to the Study of Devitrification Processes in Glass, AB Progress* AE–RKP–120, Studsvik (Sweden) 1969.
157 G. Krein, *Explosivstoffe*, 13 (1965) 205.
158 L. Reich, *Makromol. Chem.*, 105 (1967) 223.
159 K. Akita and M. Kase, *J. Polym. Sci.*, 5 (1967) 833.
160 K. Akita and M. Kase, *J. Phys. Chem.*, 72 (1968) 906.
161 J. Tateno, *Trans. Faraday Soc.*, 62 (1966) 1885.
162 A. A. Blumberg, *J. Phys. Chem.*, 63 (1959) 1129.
163 K. Tratore, *J. Thermal Anal.*, 4 (1972) 19; 4 (1972) 135.
164 J. H. Bae, *J. Thermal Anal.*, 4 (1972) 261.
165 G. O. Piloyan and O. S. Novikova, *Zh. Neorg. Khim.*, 12 (1967) 313.
166 J. G. Rasmunssen, in H. G. Wiedemann (editor), *Thermal Analysis*, Vol. 1, Birkhäuser, Basel, 1972, p. 379.
167 B. S. Girgis, *Trans. Brit. Ceram. Soc.*, 71 (1972) 177.
168 R. N. Rogers and L. C. Smith, *Anal. Chem.*, 39 (1967) 1024.
168a T. Ozawa, *J. Polym. Sci.*, 12 (1971) 150.
169 E. A. Dorko and R. W. Crossley, *J. Phys. Chem.*, 76 (1972) 2253.
170 R. W. Crossley, E. A. Dorko and R. L. Diggs, *Analytical Calorimetry*, Vol. 2, Plenum Press, New York, 1970, p. 429.
171 E. A. Dorko, R. S. Hughes and C. R. Downs, *Anal. Chem.*, 42 (1970) 253.
172 D. Maclean and R. L. Tranter, *J. Phys. Sci. Instrum.*, 4E (1971) 455.
173 J. B. Gayle and C. T. Egger, *Anal. Chem.*, 44 (1972) 421.
174 G. E. James and H. L. Pardue, *Anal. Chem.*, 40 (1968) 796.
175 M. A. Hughes and R. Hart, in H. G. Wiedemann (editor), *Thermal Analysis*, Vol. 1, Birkhäuser, Basel, 1972, p. 243.
176 J. Huggins in S. L. Friess, E. S. Lewis and A. Weisberger (editors), *Use of Computers* in *Investigation of Rates and Mechanisms of Reactions*, Interscience, New York, 1961.
177 F. L. McCrackin, unpublished results, see J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 70A (1966) 487.
178 S. Wold, *Kemi. Tidskr.*, 12 (1970) 16.
179 P. D. Gwinup, *Dissertation*, Oklahoma State Univ., Stillwater, 1967.
180 G. Beech, *J. Chem. Soc. (A)*, (1969) 1903.
181 J. M. Schempf, F. E. Freeberg, D. I. Royer and F. M. Augeloris, *Anal. Chem.*, 38 (1966) 521.
182 J. R. Soulen, *Anal. Chem.*, 34 (1962) 137.
183 J. Šesták, V. Šatava and V. Řihák, *Silikaty*, 11 (1967) 315.
184 J. Šesták, A. Brown, V. Řihák and G. Berggren, in R. F. Schwenker and P. D. Garn (editors), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1035.
185 F. Škvára and J. Šesták, unpublished results.
186 D. W. Johnson and P. K. Gallagher, *J. Phys. Chem.*, 75 (1971) 1179.
187 J. W. Frazer, *Chem. Instrum.*, 2 (1970) 271.
188 J. M. McCormick and M. G. Salvadori, *Numerical Methods in FORTRAN*, Prentice-Hall, Inc., Englewood Cliffs, New Jersey.
189 D. Amstutz, in H. G. Wiedemann (editor), *Thermal Analysis*, Vol. 1, Birkhäuser, Basel, 1972, p. 415.
190 J. Vachuška and M. Vobořil, unpublished results.
191 F. Škvára, *Silikaty*, 17 (1973) 109.
192 P. J. Reddy and P. S. Murti, *Indian J. Technol.*, 9 (1971) 161.
193 D. Fraser and R. F. Pilgrim, *Can. Metal. Quart.*, 7 (1969) 167.
194 G. Berggren, *Scandinavian Conf. on Thermal Analysis*, Nordforsk, Helsinki, February, 1972.
195 F. Cornic, *J. Polym. Sci.*, C25 (1968) 131.
196 S. R. Urzendowski and A. H. Guenther, *J. Thermal Anal.*, 3 (1971) 379.
197 V. S. Sharma and D. L. Lenssing, *Talanta*, 18 (1971) 1137.
198 H. M. Heuvel and K. C. J. Lindt, *Anal. Chem.*, 42 (1970) 1044.
199 C. R. Smith and F. R. Sale, *J. Phys. E.*, 4 (1971) 366.
200 W. W. Wendlandt, *Thermochim. Acta*, 5 (1973) 225.
201 P. S. Nolan and H. E. Lemay, *Thermochim. Acta*, 6 (1973) 179.