Thermochimica Acta, 23 (1978) 201–212

KINETIC PARAMETERS FROM THE NON-ISOTHERMAL DECOMPOSITION OF A MULTI-COMPONENT SOLID

RICHARD R. BAKER

Group Research & Development Centre, British-American Tobacco Co. Ltd., Regent's Park Road, Southampton SO9 1PE (England)

(Received 2 June 1977)

ABSTRACT

The literature on the application of isothermal homogeneous gas or liquid phase kinetic equations to the non-isothermal decomposition of solids is briefly reviewed. It is concluded that the deriving of kinetic parameters for solid-state decomposition reactions in terms of Arrhenius pre-exponential factor, activation energy and reaction order is empirically useful, but the theoretical significance that these parameters have for gas and liquid phase reactions cannot be extended to the solid phase. A method is presented whereby these kinetic parameters can be derived when a multi-component solid decomposes non-isothermally into several products. The formations of hydrogen, methane, and ethane from the thermal decomposition of tobacco are best described by a mechanism in which each product is formed from a different solid component. The high correlation coefficients obtained show that the homogeneous kinetic and Arrhenius equations are very good empirical descriptions of the reactions.

INTRODUCTION

During the last twenty years, thermal techniques have been used to study the kinetics of solid-state decomposition reactions under non-isothermal conditions[1]. Many methods have been proposed for the exact evaluation of the kinetic parameters and these have been reviewed extensively, e.g. in refs.[2–10]. Refinements of these methods are being continually proposed, e.g., refs.[11–16]. All the existing methods are concerned with the overall decomposition of one solid in isolation, or the production of a specific product (or occasionally a small number of products) from the solid. However, in some systems of practical importance, the reactant is a mixture of several independent solid components, each of which can decompose into several products. Tobacco is such a mixture, and the observed product formation rate/temperature profiles of the evolved gases from the non-isothermal decomposition of tobacco often consist of several peaks, each peak in a specific temperature region[17–20]. In a given temperature region, the products can arise from one of several alternative possible mechanisms, for example:

(a) each of the observed products is formed from a different solid component;

(b) all the products are formed competitively from the same component.

The kinetic parameters for the formation of a given product in a given temperature region are dependent on the mechanism of production. A general computer program has been written which calculates the kinetic parameters for the competitive formation of any number of products from one solid component (mechanism b); if the number of products is set equal to one, that product is formed according to mechanism (a).

However, considerable controversy has recently arisen in the literature concerning the application of homogeneous-type kinetic equations to solid-state reactions under non-isothermal conditions. Since this forms the basis of the method described later in this paper, the literature is briefly reviewed in the following section.

BACKGROUND LITERATURE

In many of the kinetic treatments of non-isothermal solid-state reactions, it has been assumed that isothermal homogeneous gas or liquid phase kinetic equations can be applied, so that at any time the rate of reaction is given by:

$$-\frac{dc}{dt} = kc^n = A\,e^{-E/RT}\,c^n \tag{1}$$

where the symbols are defined in the Nomenclature section.

A characteristic feature of solid-state reactions is the destruction of the structure of the reactant solid phases. This differs sharply from reactions in the gas or liquid phase, in which the fluid reacting phase exists continuously throughout the reaction, with a continuous variation in the concentrations of the components Consequently, the concept of reaction order, as it is understood in the fluid phases (representing the number of molecules which collide prior to reaction), has only limited applicability to solids[21, 22]. The reaction order is defined in terms of reactant concentrations (eqn (1)). For the definition to have any meaning, these concentrations must have constant values throughout the reacting material. This is not the case for solid-phase reactions. However, in practice, some function of the sample weight is used instead of c, in differential thermogravimetric analysis. In the analysis of the present study, a function of the gas phase concentration of products to be released over the remainder of the pyrolysis is used instead of c. Consequently, alternatives believed to represent the solid reactant concentration are always used in practice.

Unfortunately, even the empirical use of eqn (1) does not necessarily give consistent results for all solid-state reactions, and alternative forms of the equation have been proposed (e.g., refs.[23-29]). In general, the isothermal rate of a solid-state reaction can be written:

$$-\frac{dc}{dt} = k \cdot f(c) \tag{2}$$

and, in practice, it is often found[30-33] that $f(c)$ can be replaced by c^n.

The work of MacCallum and Tanner[34], and independently that of Draper[35] and Comel et al.[36] have initiated extensive discussion concerning the applicability of extending the isothermal mathematical treatment to non-isothermal conditions. Their contention is that under non-isothermal conditions, the reactant concentration is a function of both temperature and time:

$$c = f(T, t) \tag{3}$$

Consequently, partial differentiation of eqn (3) gives:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \left(\frac{\partial c}{\partial t}\right)_T + \left(\frac{\partial c}{\partial T}\right)_t \frac{\mathrm{d}T}{\mathrm{d}t} \tag{4}$$

Thus, the reaction rate under non-isothermal conditions, $\mathrm{d}c/\mathrm{d}t$, is not equal to the isothermal rate, $(\partial c/\partial t)_T$, as it is assumed in all mathematical treatments. Many authors using varied arguments, have subsequently pointed out that the term $(\partial c/\partial_T)_t$ has no logical sense and does not exist in reality[37-42], resulting in $\mathrm{d}c/\mathrm{d}t = (\partial c/\partial t)_T$, as is generally assumed. MacCallum[43] has tried to defend the validity of eqn (4) by using an analogy to a varying-volume decomposition, but this analogy has been shown to be ambiguous[41].

Simmons and Wendlandt[44] have shown mathematically, and Šesták and Kratochvíl[45] by thermodynamic arguments, that there is no fundamental error involved in extending isothermal kinetic equations to non-isothermal conditions. In confirmation of this, it is found that in some studies where a given reaction has been examined under both isothermal and non-isothermal conditions, no significant differences are found[46-51]. However, in other studies[9, 52], it is found that the Arrhenius parameters calculated from data obtained under isothermal conditions differ from those obtained under non-isothermal conditions. The parameters A and E have also been observed to change with heating rate[53-62] and are generally found to be related:

$$\ln A = u + wE \tag{5}$$

where u and w are constants. Various derivations of eqn (5) have been published[52, 63-66], and the significance of the equation has been discussed at length elsewhere[67-70].

Many methods have been proposed for the exact evaluation of the non-isothermal equations obtained, e.g., refs.[2-16]. Many of these methods are based on approximations which can lead to error. Consequently, even with the same experimental data, different evaluation methods may result in different values for the kinetic parameters n, A and E, e.g., refs.[9, 71-73]. It would appear that the overwhelming consensus of opinion is that these discrepancies are due to mathematical approximations, not to the validity of the basis of the mathematical methods.

As a final comment on the validity of non-isothermal measurements, it has been pointed out[35] that non-isothermal determination of the kinetic parameters of reactions of solids are in fact the only valid measurements. The very nature of an isothermal determination dictates that the cold sample has to be pre-heated to the required temperature prior to the isothermal measurements being made. If the reaction rate is fast, considerable quantities of the solid can have reacted before isothermal conditions are established, i.e., a large proportion of the solid will have reacted under non-isothermal conditions. Furthermore, Ozawa[74] has pointed out that non-isothermal measurements have an additional advantage over isothermal measurements in that, for a reaction system in which multiple reactions proceed concurrently, the nature of the reaction may be revealed by variation of the heating rate.

The Arrhenius equation arises in gas- and liquid-phase reactions because of an equilibrium between activated and non-activated molecules according to the Boltzmann distribution, followed by formation of an activated complex from activated molecules, and subsequent formation of product molecules. Solid-state decomposition reactions do not proceed by such a mechanism, and it has been claimed that the Arrhenius equation is not justified theoretically for such reactions[21, 35, 62, 68]. Modified or alternative forms to the Arrhenius equation have been proposed [35, 52, 75, 76], especially to solid-phase reactions proceeding non-isothermally. With the exception of the modification given in refs. 75 and 76 (and 84)[*], they have been described as having questionable validity[77].

It is true that no general transition state theory of reaction rates has as yet been fully developed for solid-phase reactions[78]. However, the development of such theories for some specific solid decomposition reactions has been partially successful in correctly predicting the Arrhenius pre-exponential factors[79-82]. Thus, there is some theoretical justification for assuming that the Arrhenius equation applies to reactions involving reactant solid. The large number of such reactions that have rates which vary with temperature according to the Arrhenius equation, e.g., refs.[6, 7, 46-62], suggests that the equation is often a very successful empirical model for the temperature-dependence of solid-state decomposition reactions[83], even though strictly speaking it is used outside its range of theoretical validity[68]. Thus, the deriving of kinetic parameters for such reactions in terms of A, E and n is a completely formal approach for empirical convenience, and the significance they have for gas- or liquid-phase reactions cannot be extended to the solid phase[62, 70].

CALCULATION OF ARRHENIUS PARAMETERS

Typically, product formation rate/temperature profiles of several evolved gases are obtained from the non-isothermal decomposition of a multi-component solid (e.g., Fig. 1 for the formation of gases from tobacco decomposition). In a given temperature region, these products can arise from one of several alternative possible mechanisms:

(a) Each of the observed products is formed from a different solid component.

(b) All the products are formed from the same solid component, with a common rate-determining step.

---

[*] These references merely take into consideration the known temperature-dependence of the pre-exponential factor.

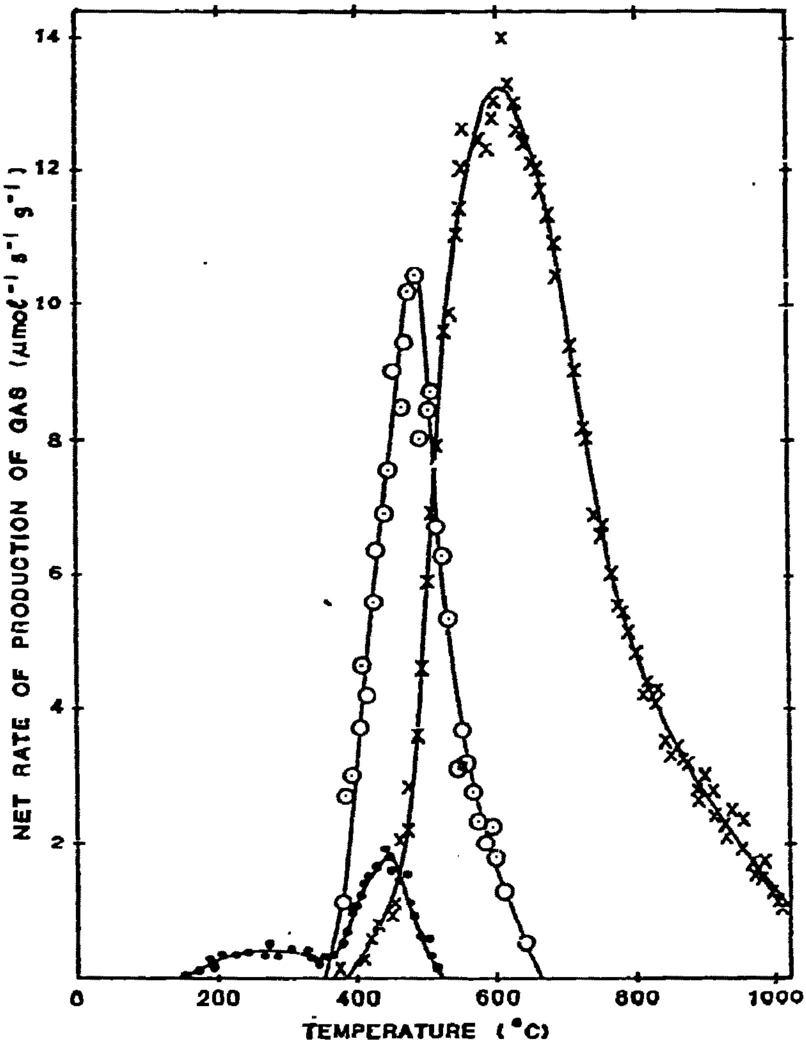

Fig. 1. Formation rate profiles of some evolved gases from tobacco decomposition. Tobacco heated in argon at 1.3 K s^{-1}; input flow of argon into pyrolysis furnace = 8.33 cm^3 s^{-1}. x, Hydrogen; O, methane; ●, ethane × 2.

(c) All the products are formed from the same solid component, with different rate-determining steps. There are two possibilities for this latter type of mechanism:

(i) independent reactions, where one fraction (a_1) of the component decomposes with Arrhenius parameters A_1 and E_1, a second fraction (a_2) decomposes independently with Arrhenius parameters A_2 and E_2, etc.

(ii) competitive reactions, in which each decomposition has a rate proportional to a function of the concentration of the remaining material in the solid.

Mechanisms (a) and (c(i)) are indistinguishable kinetically, and so mechanism (c(i)) is not considered further in the present paper. In order to determine which of these alternative mechanisms is occurring for a given set of data, the kinetic parameters for each gas in each mechanism are calculated, and the mechanism which gives the most consistent parameters for all the gases is taken as being the best mechanism.

This is done with the aid of a computer program, as follows. A mechanism is assumed for the formation of the gases, i.e., it is assumed that a certain number of products (y) are formed competitively from the same solid component. Over the temperature region in which the gases are formed (T_1 to T_v), a list of temperatures T_m is input into the program, together with the corresponding reaction rates R_{im} (μmol s^{-1} g^{-1}) and amount of product formed in the temperature region up to that temperature, F_{im} (μmol g^{-1}) for each product i ($i = 1, 2 \ldots y$; $m = 1, 2 \ldots v$). Values of R_{im} can be read off the profiles (e.g., Fig. 1) at specific temperature intervals; values of F_{im} can be obtained by calculating the area under the formation rate/*time* profile up to temperature T_m. If the formation profile consists of multiple peaks (e.g., the ethane profile in Fig. 1), which result from the formation of the gas from several components, the temperature region of interest must be deconvoluted from the profile by hand.

The total amounts of products formed from the solid component over the temperature region up to each temperature T_m (F_m, μmol g^{-1}) are calculated:

$$F_m = \sum_{i=1}^{i=y} F_{im}\, b_i \tag{6}$$

The total amount of products formed from the solid component over the whole temperature region (F, μmol g^{-1}) is given by:

$$F = \sum_{i=1}^{i=y} F_{iv}\, b_i \tag{7}$$

For each product i, and a given value of the reaction order n, values of the rate constant k_{im} (s^{-1} μmol^{1-n} g^{n-1} for an nth order reaction) are calculated at each temperature T_m:

$$k_{im} = \frac{R_{im}}{(F - F_m)^n} \tag{8}$$

ln k_{im} is linearly regressed* against $1/T_m$, and the Arrhenius parameters A_i and E_i are calculated from the values of the intercept and gradient, respectively:

$$A_i = \exp\,(\text{intercept}) \tag{9}$$

$$E_i = -\,1.987\,(\text{gradient}) \tag{10}$$

For each product i, values of A_i, E_i, and the correlation coefficient of the regression (r_i) are calculated for values of the reaction order n from 0 to 3.0 in steps of 0.25, and for $n = 0.666$.

---

* The limiting values of k_{im} corresponding to $R_{im} = 0$ and $F = F_m$ are omitted from the regression.

TABLE 1

KINETIC PARAMETERS FOR FORMATION OF METHANE ONLY FROM ONE TOBACCO COMPONENT[a]

Reaction order (n)	*Correlation coefficient* (r)	A[b]	E[c]
0	0.180	6.84	1.44
0.25	0.581	13.2	4.45
0.50	0.849	25.6	7.46
0.67	0.934	39.7	9.47
0.75	0.957	49.4	10.5
1.00	0.989	95.3	13.5
1.25	0.993	184	16.5
1.50	0.989	356	19.5
1.75	0.981	688	22.5
2.00	0.973	1.33×10^3	25.5
2.25	0.966	2.57×10^3	28.5
2.50	0.959	4.96×10^3	31.5
2.75	0.953	9.58×10^3	34.5
3.00	0.948	1.85×10^4	37.6

[a] Calculated from the profile in Fig. 1. Number of data values used in the regression (c) = 10.

[b] Arrhenius pre-exponential factor, s^{-1} μmol^{1-n} g^{n-1} for an nth order reaction.

[c] Activation energy (kcal mol^{-1}).

TABLE 2

BEST KINETIC PARAMETERS FOR FORMATION OF HYDROGEN, METHANE, AND ETHANE IN ITS HIGH-TEMPERATURE REGION[a], EACH PRODUCT FORMED EXCLUSIVELY FROM A DIFFERENT TOBACCO COMPONENT

Product	n[b]	A[b]	E[b]	r[b]	F[b]
Hydrogen	1.50	50.7	22.9	0.942	2,700
Methane	1.25	184	16.5	0.993	1,140
Ethane	1.00	2.50×10^6	26.0	0.993	68.1

[a] The high-temperature formation region for ethane is from 300 to 534°C. Hydrogen and methane are formed over the temperature ranges 400 to 1140°C, and 250 to 700°C, respectively. Number of data values used in the regressions (c) = 16 for hydrogen, 10 for methane, and 11 for ethane.

[b] Defined in Nomenclature Section.

RESULTS AND DISCUSSION

The data in Fig. 1 are tested against the alternative types of mechanism outlined in the above Section (in the present treatment, it is assumed that all the stoichiometric constants, b_i, are equal to unity). The kinetic parameters obtained for the formation of methane from tobacco, in a mechanism where methane only is formed from one component in the tobacco (mechanism(a)), are given in Table 1. The calculated Arrhenius A factor and activation energy increase with increasing values of the

TABLE 3

KINETIC PARAMETERS FOR FORMATION OF (a) HYDROGEN AND METHANE, AND (b) HYDROGEN, METHANE AND HIGH-TEMPERATURE ETHANE, COMPETITIVELY FROM THE SAME TOBACCO COMPONENT

Mechanism	*n*	H_2 (F = 2,700 μmol g^{-1})			CH_4 (F = 1,140 μmol g^{-1})			C_2H_6 (F = 68.1 μmol g^{-1})		
		A	*E*	*r*	*A*	*E*	*r*	*A*	*E*	*r*
Component → H_2 + CH_4	0	1.46	−0.965	−0.074	6.84	1.44	0.180	—	—	—
	0.25	2.86	3.19	0.281	1.57	2.18	0.280	—	—	—
	0.50	5.59	7.34	0.633	3.61×10^{-1}	2.91	0.381	—	—	—
	0.67	8.74	10.1	0.786	1.35×10^{-1}	3.41	0.446	—	—	—
	0.75	1.09×10	11.5	0.836	8.30×10^{-2}	3.65	0.480	—	—	—
	1.00	2.13×10	15.6	0.917	1.91×10^{-2}	4.39	0.573	—	—	—
	1.25	4.17×10	19.8	0.942	4.38×10^{-3}	5.12	0.657	—	—	—
	1.50	8.15×10	23.9	0.946	1.01×10^{-3}	5.86	0.730	—	—	—
	1.75	1.59×10^{2}	28.1	0.943	2.31×10^{-4}	6.60	0.791	—	—	—
	2.00	3.11×10^{2}	32.2	0.937	5.32×10^{-5}	7.33	0.841	—	—	—
	2.25	6.08×10^{2}	36.4	0.931	1.22×10^{-5}	8.07	0.881	—	—	—
	2.50	1.19×10^{3}	40.5	0.926	2.81×10^{-6}	8.81	0.912	—	—	—
	2.75	2.32×10^{3}	44.7	0.920	6.45×10^{-7}	9.54	0.936	—	—	—
	3.00	4.53×10^{3}	48.8	0.916	1.48×10^{-7}	10.3	0.954	—	—	—
Component → H_2 + CH_4 + C_2H_6	0	1.46	−0.965	−0.074	6.84	1.44	0.180	7.17×10	7.17	0.621
	0.25	2.87	3.19	0.281	1.59	2.19	0.282	1.25×10	7.57	0.648
	0.50	5.62	7.35	0.633	3.68×10^{-1}	2.95	0.385	2.16	7.97	0.673
	0.67	8.81	10.1	0.786	1.39×10^{-1}	3.45	0.452	6.71×10^{-1}	8.23	0.690
	0.75	1.0×10	11.5	0.836	8.55×10^{-2}	3.70	0.485	3.76×10^{-1}	8.37	0.693
	1.00	2.16×10	15.7	0.916	1.98×10^{-2}	4.45	0.579	6.52×10^{-2}	8.76	0.720
	1.25	4.23×10	19.8	0.941	4.60×10^{-3}	5.21	0.663	1.13×10^{-2}	9.16	0.741
	1.50	8.29×10	24.0	0.946	1.07×10^{-3}	5.96	0.735	1.97×10^{-3}	9.56	0.761
	1.75	1.62×10^{2}	28.1	0.943	2.48×10^{-4}	6.71	0.796	3.42×10^{-4}	9.95	0.780
	2.00	3.18×10^{2}	32.3	0.938	5.74×10^{-5}	7.47	0.845	5.94×10^{-5}	10.3	0.797
	2.25	6.24×10^{2}	36.5	0.932	1.33×10^{-5}	8.22	0.884	1.03×10^{-5}	10.7	0.814
	2.50	1.22×10^{3}	40.6	0.926	3.09×10^{-6}	8.97	0.915	1.79×10^{-6}	11.1	0.829
	2.75	2.40×10^{3}	44.8	0.921	7.17×10^{-7}	9.72	0.938	3.11×10^{-7}	11.5	0.843
	3.00	4.69×10^{3}	48.9	0.916	1.66×10^{-7}	10.5	0.955	5.40×10^{-8}	11.9	0.856

reaction order n. The highest correlation coefficient is obtained for a reaction order of 1.25, although reaction orders of 1.0 and 1.5 give almost as high correlation coefficients. Thus, the best kinetic parameters for methane formation are those corresponding to a reaction order of 1.25; these parameters are summarised in Table 2 for hydrogen, methane and ethane formation in mechanism (a), where each product is formed from a different solid component. The high values of the correlation coefficients obtained, especially for methane and ethane production, indicate that the rate equation:

$$\text{rate} = (F - F_\infty)^n A\, \mathrm{e}^{-E/RT} \tag{13}$$

is a very good empirical relationship for the decomposition, and that mechanism (a) is a good model for the formation of these products from the thermal decomposition of tobacco.

An alternative model to consider for the data in Fig. 1 is mechanism (b), in which all the products are formed from one solid component with a common rate-determining step. However, if this mechanism was occurring, the product ratios would be independent of temperature, and inspection of the results in Fig. 1 shows that this is clearly not the case.

The final model to test against the data in Fig. 1 is mechanism (c(ii)), competitive formation of the products from one solid component. Table 3(a) shows the kinetic parameters calculated for a mechanism in which hydrogen and methane are formed competitively from the same tobacco component. The apparent Arrhenius parameters for hydrogen formation and their variation with n, are similar to those obtained for the mechanism when hydrogen only was formed from one tobacco component. However, those for methane formation are very different (cf. Tables 1 and 3 (a))—with the competitive formation mechanism, the activation energies are only 27–49% the value of those in Table 1, and the Arrhenius A factor falls with increasing reaction order. The correlation coefficient for methane formation continuously rises with increasing reaction order, and is obviously out of phase with the correlation coefficient/reaction order relationship for hydrogen formation. Clearly, the competitive decomposition mechanism is dominated by the parameters for hydrogen decomposition, and in this case a competitive decomposition is probably not the correct mechanism.

The kinetic parameters calculated for hydrogen, methane, and high-temperature ethane formed competitively from the same tobacco component are shown in Table 3(b)). The inclusion of ethane into the competitive decomposition mechanism makes little difference to the kinetic parameters for hydrogen and methane formation (cf. Tables 3(a) and 3(b)), and there is no reaction order for ethane formation for which there is a particularly high correlation coefficient, suggesting that mechanism (c(ii)) is not occurring.

Consequently, in the above examples, good correlation coefficients can be obtained for methane and ethane formation with mechanism (a) in which they are each formed exclusively from different tobacco components; the variation of correlation coefficients is inconsistent when the kinetic parameters are calculated using a mechanism in which both products are formed competitively with hydrogen from the same tobacco component. Thus, in this particular case, it may be concluded that the former mechanism is occurring. For other groups of products, the distinction is less clear, and is possible only after studying the effect of heating rate, as suggested by Flynn and Wall[5], and Ozawa[74].

ACKNOWLEDGEMENT

The computing assistance of Mrs. B. M. Watts is gratefully acknowledged.

NOMENCLATURE

A	Arrhenius pre-exponential constant (units of s^{-1} μmol^{1-n} g^{n-1} for an nth order reaction)
E	Activation energy (cal mol^{-1})
F	Total amount of products formed from a solid component over the whole temperature region ($\mu mol\ g^{-1}$)
F_m	Amount of products formed in a given temperature region from a solid component up to temperature T_m ($\mu mol\ g^{-1}$)
F_{im}	Amount of product i formed in a given temperature region from a solid component up to temperature T_m ($\mu mol\ g^{-1}$)
R	Universal gas constant, 1.987 cal mol^{-1} K^{-1}
R_m	Overall rate of decomposition of a given solid component at temperature T_m ($\mu mol\ s^{-1}\ g^{-1}$)
R_{im}	Rate of formation of product i from a given solid component at temperature T_m ($\mu mol\ s^{-1}\ g^{-1}$)
T	Temperature (K)
a	Fraction of solid component which undergoes a particular reaction
b	Stoichiometric constant
c	"Concentration" of solid component ($\mu mol\ g^{-1}$)
e	Exponential operator
f	Function
k	Rate constant (units of s^{-1} μmol^{1-n} g^{n-1} for an nth order reaction)
n	Reaction order
r	Correlation coefficient
t	Time (s)
u	Constant used in eqn (5)
v	Number of data values (for temperature, reaction rate, and amount of product formed) in a given temperature region
w	Constant used in eqn (5)
y	Number of products formed competitively from a given solid component

Subscripts

i	Product number ($i = 1, 2 \ldots y$)

m Data number (for temperature, reaction rate, and amount of product formed) in a given temperature region ($m = 1, 2 \ldots \nu$)

REFERENCES

1 E. P. Manche and B. Carroll, in B. Carroll (Ed.) *Physical Methods in Macromolecular Chemistry*, Vol. 2, Marcel Dekker, New York, 1972, p. 239.
2 W. W. Wendlandt, *Thermal Methods of Analysis*, Wiley-Interscience, 2nd ed., 1974, pp. 45–56.
3 C. J. Keattch and D. Dollimore, *An Introduction to Thermogravimetry*, Heyden & Son Ltd., London, 2nd ed., 1975, pp. 41–46.
4 L. Reich and S. S. Stivala, *Elements of Polymer Degradation*, McGraw-Hill, New York, 1971, Ch. 2.
5 J. H. Flynn and L. A. Wall, *J. Res. Natn. Bur. Stand.*, 70A (1966) 487.
6 H. Jüngten and K. H. van Heek, *Fortschr. Chem. Forsch.*, 13 (1970) 601.
7 J. Šesták, V. Šatava and W. W. Wendlandt, *Thermochim. Acta*, 7 (1973) 447–504.
8 C. D. Doyle, in P. E. Slade and L. T. Jenkins (Eds.), *Techniques and Methods of Polymer Evaluation*, Vol. 1, Marcel Dekker, New York, 1966, Ch. 4.
9 J. R. MacCallum and J. Tanner, *Eur. Polym. J.*, 6 (1970) 907, 1033.
10 B. Carroll and E. P. Manche, *Thermochim. Acta*, 3 (1972) 449.
11 E. Segal and M. Vlad, *Thermochim. Acta*, 16 (1976) 115.
12 T. Ozawa, *J. Therm. Anal.*, 9 (1976) 369.
13 M. Selvaratnam and P. D. Garn, *J. Am. Ceram. Soc.*, 59 (1976) 376.
14 J. Vachuška and M. Vobořil, *Thermochim. Acta*, 2 (1971) 379.
15 J. M. Criado and J. Morales, *Thermochim. Acta*, 16 (1976) 382.
16 J. Šesták and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.
17 R. R. Baker, *Beitr. Tabakforsch.*, 8 (1975) 16.
18 R. R. Baker, *Thermochim. Acta*, 17 (1976) 29.
19 H. R. Burton, *Beitr. Tabakforsch.*, 8 (1975) 78.
20 H. R. Burton and G. Childs, Jr., *Beitr. Tabakforsch.*, 8 (1975) 174.
21 W. Gomes, *Nature*, 192 (1961) 865.
22 L. G. Harrison, in C. H. Bamford and C. F. H. Tipper (Eds.) *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam, 1969, Vol. 2, Ch. 5.
23 P. W. M. Jacobs and F. C. Tompkins, in W. E. Garner (Ed.) *Chemistry of the Solid State*, Butterworths, London, 1955, p. 184.
24 D. A. Young, *Decomposition of Solids*, Pergamon Press, London, 1966.
25 J. M. Thomas and T. A. Clarke, *J. Chem. Soc. (A)*, (1968) 457.
26 J. M. Thomas and T. A. Clarke, *Nature*, 219 (1968) 1149.
27 J. M. Thomas and G. D. Renshaw, *Chem. Commun.*, 1968, 1247.
28 T. A. Clarke, E. L. Evans, K. G. Robbins, and J. M. Thomas, *Chem. Commun.*, 1969, 266.
29 Wee-Lam Ng, *Aust. J. Chem.*, 28 (1975) 1169.
30 J. Zsakó, *J. Phys. Chem.*, 72 (1968) 2406.
31 P. S. Nolan and H. E. Lemay, Jr., *Thermochim. Acta*, 6 (1973) 179.
32 M. D. Judd and A. C. Norris, *J. Therm. Anal.*, 5 (1973) 179.
33 D. M. Speros and H. R. Werner, in R. S. Porter and J. F. Johnson (Eds.), *Analytical Calorimetry*, Plenum Press, New York, 1974, Vol. 3, p. 511.
34 J. R. MacCallum and J. Tanner, *Nature*, 225 (1970) 1127.
35 A. L. Draper, in H. G. McAdie (Ed.), *Proceedings of the Third Toronto Symposium on Thermal Analysis*, C.I.C., Canada, 1970, p. 63.
36 C. Comel, A. Fèvre and M. Murant, *C. R. Acad. Sci. (Paris), Ser. C*, 281 (1975) 845.
37 R. A. W. Hill, *Nature*, 227 (1970) 703.
38 R. M. Felder and E. P. Stahel, *Nature*, 228 (1970) 1085.
39 J. M. Gilles and H. Tompa, *Nature*, 229 (1971) 57.
40 P. Holba and J. Šesták, *Z. Phys. Chem., Neue Folge*, 80 (1972) 1.
41 G. Gyulai and E. J. Greenhow, *Thermochim. Acta.*, 5 (1973) 481.
42 V. M. Gorbatchev and V. A. Logvinenko, *J. Therm. Anal.*, 4 (1972) 475.
43 J. R. MacCallum, *Nature*, 232 (1971) 41.

44 E. L. Simmons and W. W. Wendlandt, *Thermochim. Acta*, 3 (1972) 498.

45 J. Šesták and J. Kratochvil, *J. Therm. Anal.*, 5 (1973) 193.

46 J. Simon, *J. Therm. Anal.*, 5 (1973) 271.

47 R. Audebert and C. Aubineau, *J. Chim. Phys.*, 67 (1970) 617.

48 P. K. Gallagher and D. W. Johnson, Jr., *Thermochim. Acta*, 6 (1973) 67.

49 S. R. Dharwadkar and M. D. Kharkhanavala, in R. F. Schwenker and P. D. Garn (Eds.), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1049.

50 T. Palanisamy, J. Gopalakrishnam, B. Viswanathan, V. Srinivasan and M. V. C. Sastri, *Thermochim. Acta.*, 2 (1971) 265.

51 A. Gheorghiu, D. Fătu and E. Segal, *Rev. Roum. Chim.*, 21 (1976) 367.

52 R. B. Prime, in R. S. Porter and J. F. Johnson (Eds.), *Analytical Calorimetry*, Vol. 2, Plenum Press, New York, 1970, p. 201.

53 I. A. Schneider, C. Vasile, D. Furnicu and A. Onu, *Makromol. Chem.*, 117 (1968) 41.

54 I. A. Schneider, C. Vasile, D. Furnicu and A. Onu, *Makromol. Chem.*, 125 (1969) 201.

55 R. N. Rogers and L. C. Smith, *Anal. Chem.*, 39 (1967) 1024.

56 M. M. Pavyluchenko, R. A. Prodan and S. A. Slyshkina, *Dokl. Akad. Nauk SSSR*, 181 (1968) 1174.

57 D. T. Y. Chen, *J. Therm. Anal.*, 7 (1975) 61.

58 J. Zsakó, F. Kékedy and Cs. Várhelyi, in H. G. Wiedemann (Ed.), *Proceedings of the Third International Conference on Thermal Analysis*, Vol. 2, Birkhaüser Verlag, Basel and Stuttgart, Switzerland, 1972, p. 487.

59 J. Zsakó, E. Kékedy and Cs. Várhelyi, *J. Therm. Anal.*, 1 (1969) 339.

60 J. Zsakó and H. E. Arz, *J. Therm. Anal.*, 6 (1974) 651.

61 J. Zsakó and Cs. Várhelyi, *J. Therm. Anal.*, 7 (1975) 33.

62 J. Zsakó, *J. Therm. Anal.*, 5 (1973) 239.

63 P. D. Garn, *J. Therm. Anal.*, 7 (1975) 475.

64 A. V. Nikolaev, V. A. Logvinenko, V. M. Gorbatchev and L. I. Myachina, in I. Buzás (Ed.), *Proceedings of the Fourth International Conference on Thermal Analysis*, Vol. 1, Heyden & Son Ltd., London, 1974, p. 47.

65 A. V. Nikolaev, V. A. Loginenko and V. M. Gorbatchev, *J. Therm. Anal.*, 6 (1974) 473.

66 V. M. Gorbatchev, *J. Therm. Anal.*, 8 (1975) 585.

67 T. Zmijewski and J. Pysiak in I. Buzás (Ed.), *Proceedings of the Fourth International Conference on Thermal Analysis*, Vol. 1, Heyden & Son Ltd., London, 1974, p. 205.

68 P. D. Garn, in I. Buzás (Ed.), *Proceedings of the Fourth International Conference on Thermal Analysis*, Vol. 1, Heyden & Son Ltd., London, 1974, p. 25.

69 P. D. Garn, *J. Therm. Anal.*, 10 (1976) 99.

70 J. Zsakó, *J. Therm. Anal.*, 9 (1976) 101.

71 G. G. Cameron and J. D. Fortune, *Eur. Polym. J.*, 4 (1968) 333.

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

73 D. T. Y. Chen and P. H. Fong, *J. Therm. Anal.*, 8 (1975) 295, 305.

74 T. Ozawa, *J. Therm. Anal.*, 9 (1976) 217.

75 T. R. Ingraham and P. Marier, *Can. J. Chem. Eng.*, 42 (1964) 161.

76 C. G. R. Nair and P. M. Madhusudanan, *Curr. Sci.*, 44 (1975) 212.

77 G. Gyulai and E. J. Greenhow, *Talanta*, 21 (1974) 131.

78 J. Šesták, V. Šatava and W. W. Wendlandt, *Thermochim. Acta*, 7 (1973) 403–446.

79 M. Polanyi and E. Wigner, *Z. Phys. Chem.*, A139 (1928) 439.

80 R. D. Shannon, *Trans. Faraday Soc.*, 60 (1964) 1902.

81 I. Proks, *Chem. Zvesti*, 20 (1966) 697.

82 H. F. Cordes, *J. Phys. Chem.*, 72 (1968) 2185.

83 J. H. Flynn and B. Dickens, *Thermochim. Acta*, 15 (1976) 1.

84 H. R. Petty, E. T. Arakawa and J. K. Baird, *J. Therm. Anal.*, 11 (1977) 417.