Note

A NEW DIFFERENTIAL METHOD FOR DETERMINING ORDERS AND RATES OF REACTIONS AND ITS APPLICATION TO SOLID STATE REACTIONS. PART I. SOME SIMPLE DECOMPOSITIONS

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The kinetics of decomposition of solids has attracted a great deal of attention [1,2]. Various mathematical models have been proposed and of these, those describing phase boundary controlled or random nucleation processes involve a priori the concept of an order [3,4] (or index [5]) of reaction. These rate equations are collected in Table 1. The method outlined here allows the order of such reactions to be determined directly from the experimental results.

THEORY

Consider a reaction proceeding according to the relationship

$$-\frac{dA}{dt} = kA^n \tag{1}$$

Then, for $n \neq 1$

$$\frac{1}{A^{n-1}} - \frac{1}{A_0^{n-1}} = (n-1)kt \tag{2}$$

from which

$$A^{n-1} = \left[(n-1)kt + \frac{1}{A_0^{n-1}} \right]^{-1} \tag{3}$$

TABLE 1

Selected mechanisms for which the concept of an order of reaction is valid

Mechanism *	Differential form	Integral form	Order, n
Phase boundary controlled R_2	$k(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$	0.5
Phase boundary controlled R_3	$k(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$	0.666
First order F_1	$k(1-\alpha)$	$\ln(1-\alpha)$	1.0

* Notation of Sharp et al. [3].

and

$$A^n = A\left[(n-1)kt + \frac{1}{A_0^{n-1}}\right]^{-1} \tag{4}$$

From eqns. (1) and (4)

$$-\frac{dA/dt}{A} = X = k\left[(n-1)kt + \frac{1}{A_0^{n-1}}\right]^{-1} \tag{5}$$

and

$$\frac{1}{X} = -\frac{A}{dA/dt} = (n-1)t + \frac{1}{kA_0^{n-1}} \tag{6}$$

Then, if $1/X$ is plotted against t, a straight line of slope $(n-1)$ is obtained, whose intercept on the $1/X$ axis is $(kA_0^{n-1})^{-1}$. Since $(n-1)$ is already established from the slope, and A_0 is known, k can also be determined. Although eqn. (2) does not hold when $n = 1$, the results of eqns. (5) and (6) still apply, since for $n = 1$ we have

$$A = A_0 e^{-kt} \tag{7}$$

$$-\frac{dA}{dt} = kA_0 e^{-kt} \tag{8}$$

$$-\frac{dA/dt}{A} = X = k \tag{9}$$

which is the result obtained by setting $(n-1) = 0$ in eqn. (5).

METHOD

Consider three values of A, $(A = A_{n-1}, A_n, A_{n+1})$ at times $t(t = t_{n-1}, t_n, t_{n+1})$. In order to determine X at time t_n, we take the finite differences

$$\Delta_{n-1,n} = \Delta_1 = A_{n-1} - A_n$$
$$\Delta_{n,n+1} = \Delta_2 = A_n - A_{n+1}$$

Then $X_{t=t_n}$ is defined as $(1/A_n)[(\Delta_1 + \Delta_2)/(t_{n+1} - t_{n-1})]$.

The method has been tested [6] for simulated rate data for reactions of orders 0, 1, 2, 3, allowing for errors in observation and for irregularity in the time intervals, and also for a variety of homogeneous and heterogeneous reactions, with orders ranging from 0 to 2 and over extent of the reaction ranging from 20 to 100%. In all cases there is good agreement with the literature values of both n and k. Note that, in this method there is no need to make any prior assumption about the value of n, as there is in the method of integration. It is therefore particularly suitable for the study of solid state reactions, since the large variety of possible mechanisms, as tabulated for instance in ref. 4, often makes it difficult to make a legitimate prior assump-

TABLE 2

Rate constants calculated by differential and integral methods

Reaction	Ref.	n*	h* (s^{-1})	c*	n**	h** (s^{-1})	T (K)	Sample size (mg)
Dehydroxylation of talc	7	0	5.18×10^{-3}	$\pm 3.1 \times 10^{-4}$ ***	1	5.58×10^{-3}	1159	27.6
Decomposition of CaCO$_3$ in vacuo	9	0.63	1.24×10^{-3}	0.995	$\frac{2}{3}$	1.34×10^{-3}	933	
Decomposition of CaCO$_3$ in oxygen	10	0.48	4.35×10^{-4}	0.993	$\frac{1}{2}$	4.51×10^{-4}	981	32.13
Dehydration of Cu(sal)$_2 \cdot$ 4 H$_2$O	13	0.62	4.33×10^{-4}	0.996	$\frac{2}{3}$	$\sim 4.98 \times 10^{-4}$	343	~85
Dehydration of Cu(sal)$_2 \cdot$ 4 H$_2$O	13	0.62	5.10×10^{-4}	0.989	$\frac{2}{3}$	$\sim 5.82 \times 10^{-4}$	353	~85
Dehydration of Cu(sal)$_2 \cdot$ 4 H$_2$O	13	0.64	6.94×10^{-4}	0.989	$\frac{2}{3}$	$\sim 8.05 \times 10^{-4}$	363	~85

* Order, rate constant and correlation coefficient determined from plots of X^{-1} vs. t.

** Order used and rate constant determined in original study or rate constant calculated from original data by integral method.
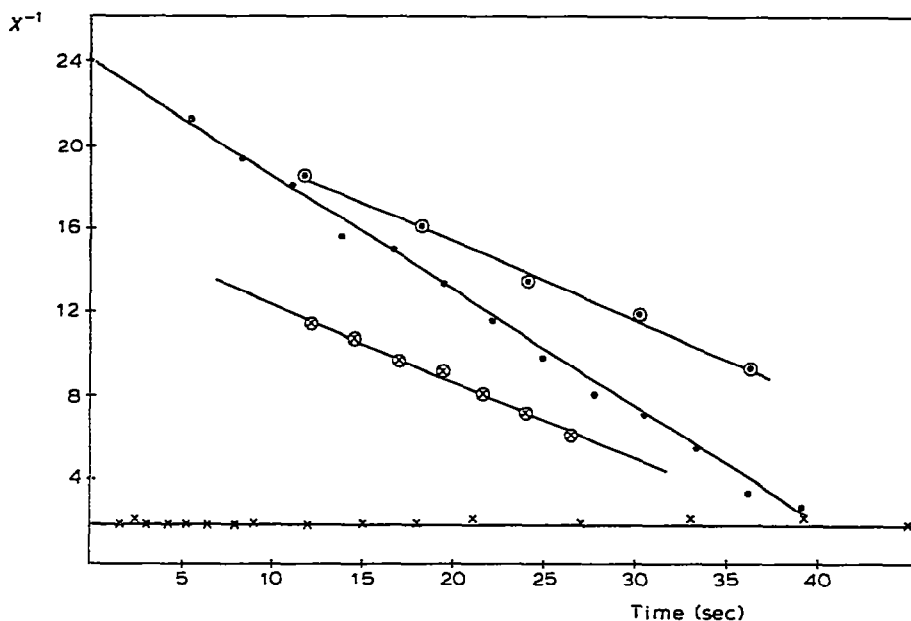
*** Standard deviation of 16 individual estimates of h.

Fig. 1. Plots of X^{-1} vs. time. ⊙, Dehydration of $Cu(Sal)_2 \cdot 4 H_2O$ in vacuo; •, decomposition of $CaCO_3$ under oxygen; ⊖, decompositoin of $CaCO_3$ in vacuo; ×, dehydroxylation of talc. Vertical axis (X^{-1}): ×, •, ⊙, × 10^{-2}; ⊖, 5 × 10^{-1}. Horizontal axis (time, sec): •, ⊙, × 10^{-2}; ×, × 10^{-1}; ⊖, × 5 × 10^{-1}.

tion about n. We now consider the application of this method to a number of simple decompositions.

(i) Dehydroxylation of talc

A thorough study of this reaction was carried out by Ward [7]. Using a complicated non-linear least squares approach he found the process to be first order. Our analysis of his published results (1159 K, 27.6 mg sample) is presented in Table 2 and Fig. 1. We find $n = 1$, $0.1 < \alpha < 0.95$, with a first order rate constant of 5.1 × 10^{-3} s^{-1}.

The interpretation of this process as first order seems valid; however, we would align ourselves with Hancock and Sharp [4] and Brindley et al. [8] in drawing attention to the difficulty of delineation between a first order process (F_1) and one controlled by diffusion in two dimensions (D_2). This difficulty is enhanced if there is a zero time error. In this case the extremely good fit obtained across a broad range of values of α by both Ward [7] and our methods leads us to conclude that the process is probable genuinely first order.

(ii) Decomposition of calcium carbonate

The thermal decomposition of calcium carbonate has been extensively studied [9—13]. The process is generally agreed to be phase boundary controlled; the effect of sweep gas sample size and other variables has been well

investigated. Thermal flux has a marked effect on the reaction. In vacuo, Criado and Morales [9] found the process to be two-thirds order; our analysis of their data is presented in Table 2 and Fig. 1. In contrast, under various sweep gases, Gallagher and Johnson [10] found the process to be one-half order; our analysis of their data is also presented. In both cases our method gives close agreement with the earlier results, suggesting that there may be a marked effect on reaction site of sample geometry or sweep gas. This is in agreement with the conclusions of Gallagher and co-workers [12].

(iii) Dehydration of copper salicylate tetrahydrate

This reaction was studied by Bassi et al. [13], who found it to be well described by a two-thirds order process. Our analysis of their data is presented in Table 2 and Fig. 1. Again we are able to determine unequivocally the order of the reaction. In this case we have further analysed our rate constants by an Arrhenius plot; we find the activation energy to be 24.34 kJ $mole^{-1}$, in close agreement with the resported value of 24.28 kJ $mole^{-1}$.

The application of this method to a number of solid state decompositions has been shown to give results in excellent agreement with those in the literature. The unequivocal determination of the order of a reaction is possible and, provided there is no serious zero time error, rate constants may also be obtained with considerable accuracy. The method provides a direct alternative to the unusually suggested Van Hoff [14] method for determination of reaction order, with the enormous advantage of being directly applicable to the experimentally observed results (weight, pressure or other measurements), and not estimated rates.

At present we are investigating the use of similar methods for the diagnosis of more complex kintics, particularly consecutive reactions. This will be reported shortly.

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