THE DISTINGUISHABILITY OF SELECTED KINETIC MODELS FOR ISOTHERMAL SOLID-STATE REACTIONS

MICHAEL EWART BROWN

Chemistry Department, Rhodes University, Grahamstown, 6140 (South Africa)

AND ANDREW KNOX GALWEY

Chemistry Department, Queen's University, Belfast BT9 5AG (U.K.)

(Received 6 March 1978)

ABSTRACT

Data generated from selected model expressions for solid-state kinetics have been analysed in terms of expressions of closely-related form to test distinguishability of the models on which the expressions are based. Random errors have then been introduced into these data and the data have been re-analyzed in terms of the original and closely-related expressions. As is to be expected, introduction of errors decreases distinguishability further and estimates have been made of the accuracy of measurement of the extent of reaction, α, required, the most suitable ranges of α to use, from plots of residuals, and the acceptable levels of various statistical parameters, for reliable distinction between alternative models.

INTRODUCTION

Most studies of the kinetics and mechanisms of thermal decomposition of solids incorporate consideration of the geometry of advance of the reactant–product interface. This usually requires a quantitative, detailed and critical comparison of fractional reaction (α)–time measurements, for the isothermal rate process of interest, with theoretical kinetic expressions derived from various assumed models for product phase nucleation and growth. Derivations of the most commonly used expressions, summarized in Table 1, are given in reviews by Jacobs and Tompkins[1], Young[2], Hulbert[3] and Delmon[4]. Geometric deductions based on kinetic measurements are frequently confirmed and extended by microscopic observations of partially decomposed reactant.

After determining which of the available rate expressions provides the most acceptable fit to the experimental data, the temperature variation of the appropriate rate coefficient, k, is used to calculate an activation energy, E, a parameter which has frequently been identified (by analogy with the accepted interpretation for homogeneous reactions) with the energy barrier to reaction. Attempts have often been made to associate the value of E with a specific chemical transformation at the reaction interface.

TABLE 1

BROAD CLASSIFICATION OF SOLID-STATE RATE EXPRESSIONS, $f(\alpha) = kt$

	$f(\alpha)$
1. Acceleratory α–time curves	
P1 power law	$\alpha^{1/n}$
E1 exponential law	$\ln \alpha$
2. Sigmoid α–time curves	
A2 Avrami–Erofeev	$[- \ln (1 - \alpha)]^{1/2}$
A3 Avrami–Erofeev	$[- \ln (1 - \alpha)]^{1/3}$
A4 Avrami–Erofeev	$[- \ln (1 - \alpha)]^{1/4}$
B1 Prout–Tompkins	$\ln [\alpha/(1 - \alpha)]$
3. Deceleratory α–time curves	
3.1 Based on geometrical models	
R2 contracting area	$1 - (1 - \alpha)^{1/2}$
R3 contracting volume	$1 - (1 - \alpha)^{1/3}$
3.2 Based on diffusion mechanisms	
D1 one-dimensional diffusion	α^2
D2 two-dimensional diffusion	$(1 - \alpha) \ln (1 - \alpha) + \alpha$
D3 three-dimensional diffusion	$[1 - (1 - \alpha)^{1/3}]^2$
D4 Ginstling–Brounshtein	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$
3.3 Based on "order of reaction"	
F1 first order	$- \ln (1 - \alpha)$
F2 second order	$1/(1 - \alpha)$
F3 third order	$[1/(1 - \alpha)]^2$

The rate coefficients, k, although all with dimensions [time]$^{-1}$, are of course different in e
The times, t, are assumed to have been corrected for any induction period, t_0.

It is the intention of the present communication to focus attention (
the comparison of experimental data with the more commonly used rate
so that the reliability of geometric and other mechanistic deductions, whi
an integral part of most kinetic analyses, can be assessed realistically
always desirable that interpretation of rate data should be supported by
and other relevant observations, it is none the less appropriate to consi(
tively the factors controlling the limits within which it is possible to distingui
of observations to alternative kinetic expressions. Somewhat surpi
problem has not been discussed in the literature and the present critic;
intended to identify some of the considerations which can increase the
analysis of rate data.

Rate expressions

The kinetic expressions which have found the most widespread ap
in studies of the isothermal decompositions of solids are summarized
labelled according to the system given by Sharp et al.[5] Tables of numeric
several of these equations have been published[4-7]. The expressions in

grouped according to the shape of the α–time curves as acceleratory, sigmoid or deceleratory. The deceleratory group is further subdivided according to the controlling factor assumed in the derivation, as geometric, diffusion or reaction order. Ng[8] has shown that the expressions of Table 1, as well as several others less frequently encountered, can be represented by the general relation

$$d\alpha/dt = k\alpha^{1-p}(1 - \alpha)^{1-q}$$

with $0 < p < 1$ and $0 < q < 1$. Sesták and Berggren[9] have proposed an alternative general equation

$$d\alpha/dt = k\alpha^n(1 - \alpha)^m(- \ln(1 - \alpha))^r$$

The concept of reaction order (expressions F1, F2 and F3 of Table 1) must be applied with care to rate processes involving solids. Acceptable solid-state interpretations of obedience to equation F1 have been given[1], though the use of this relation to obtain kinetic information from non-isothermal measurements has not always been satisfactorily confirmed or justified. Some decompositions proceeding in vitreous reactant phases have been shown[10, 11] to obey equations F2 or F3.

Methods of testing kinetic obedience

Probably the most widely used approaches to the identification of the rate equation which provides the most satisfactory fit to the experimental measurements (in the form of a series of (α_i, t_i) values for the isothermal rate process) are the following ((i) and (ii) have been used most frequently). (i) The linearity of plots[12] of calculated values of $f(\alpha_i)$ against time for each kinetic expression, $f(\alpha) = kt$. The coincidence of experimental points with curves calculated from the theoretical equation for: (ii) α-reduced time[5], (iii) $(d\alpha/dt)$-time[4], (iv) $(d\alpha/dt)$-reduced time[13], and (v) calculated master values of α-reduced time[14]. Where there is an initial deviation, perhaps due to a preliminary reaction, or doubt about the warm-up period, the reduced time method ((ii) above) may be modified by the use of two defined reference points in the comparison of families of curves[15].

There is considerable variation in the literature concerning the range of α which is accepted by different workers as sufficient evidence of obedience to a particular rate expression ($f(\alpha) = kt$) using method (i) above. Carter[12] regards it as important that conformity should be maintained until very close to $\alpha = 1.0$, whereas other workers have found evidence of changes in mechanism, and, therefore, in kinetic characteristics, earlier in the reaction.

The decision as to which of the available kinetic expressions provides the most acceptable fit to a given set of isothermal (α_i, t_i) measurements requires consideration of: (i) the α–time ranges within which the expressions themselves are most readily distinguished, and (ii) the experimental accuracy with which magnitudes of α must be determined to enable such distinctions to be made with certainty. A comprehensive treatment of all aspects of these problems is clearly beyond the scope of a single article and we have selected, as being of greatest general interest, the following

approach. Calculated α–time values for expressions in Table 1 (the generating equation) were analyzed by rate equations of similar form (the analyzing equation). These trial analyses were examined for linearity according to method (i) above, over selected ranges of the dependent variable, α. The influence of various levels of random error introduced into α was also considered. The results of these comparisons are presented below, following a discussion of the criteria which can be used to represent deviations of data from exact obedience to the analyzing expression.

Criteria for expressing deviation of data points from a theoretical line

Various standard statistical criteria may be used to provide a measurement of the aggregate deviation of a set of measured points from the calculated (least-squares) line through them. Parameters most usually quoted are the correlation coefficient, r; the standard error of the slope of the regression line, s_b; and the standard error of the estimate of y from x, s_{yx} (also known as the standard error of the regression). Davis and Pryor[17] have pointed out the inadequacies of r and the advantages of using s_b, in that it incorporates the desirable qualities of s_{yx} and is also dependent upon the range of the independent variable, x, used in the analysis.

The use of a single parameter to express the deviation of data from a line does not, however, reveal the existence of systematic variations of experimental or generated points from the analyzing expression. The magnitudes and directions of such deviations are, however, of great practical importance in identifying the kinetic expression which gives the best fit to the observations. The appropriate information is given in plots of residuals[16] (i.e., the differences between what is actually observed and what is predicted by the regression equation) against either variable (i.e., dependent or independent), and this approach is used in the comparisons below. By the use of calculated data for analysis (representing an exact obedience to a given expression and incorporating a controlled level of inaccuracy) it is possible to determine the level of accuracy which must be achieved in experimental work to make a positive identification of obedience to a particular expression in preference to the others considered.

Relatively few experimental studies have reported statistical parameters applicable to the kinetic analyses. Examination of residuals has been used by Leiga[18] to distinguish between conformity to the power and to the exponential laws during the acceleratory period of silver oxalate decomposition, and by Johnson and Gallagher[19] in the kinetic analysis of the decomposition of freeze-dried iron(III) sulphate. Green[20] has considered, in general terms, the testing of hypotheses in kinetic analyses. For two proposed models the ratio $F = (s_{xy})_2^2/(s_{xy})_1^2$ is used as the criterion in the standard F-test. Hypothesis 2 (i.e., the fit of data by model 2) is rejected in favour of model 1 if F is larger than the appropriate critical value, at the chosen level of significance, obtained from F tables. Wagner et al.[21] have dealt with the optimization of kinetic parameters once a particular model has been assumed.

Experimental errors

The sources, nature and magnitudes of random and systematic errors in experi-

mentally determined values of α, t and T for solid-phase decomposition reactions have not been the subject of detailed discussion in the literature. The magnitudes and properties of such inaccuracies are, however, important factors in the reliability of conclusions obtained in kinetic analyses.

Random errors in time measurement are probably sufficiently small to be neglected in most reaction rate studies. An important systematic error arises from the induction period or the time required to heat the reactant to the temperature of the reaction vessel, and this can be difficult to measure realistically. However, in plots of $f(\alpha)$ against time the delay appears as a change of intercept on the time axis and does not influence the shape of the curve or the magnitude of k. Induction periods are, however, an important problem in reduced-time methods of analysis.

Benson[22] has given a general discussion of the precision of analysis, the reaction interval to be included and the temperature control required to achieve stated limits of accuracy of measurements of rate coefficients, k, and of activation energies, E. He concludes that T must be known to $\pm 0.03\%$ (or ± 0.2 K at 600 K) to limit the error in k to $\pm 1\%$. He notes that control better than ± 1 K is difficult above 600 K, with consequent errors of $\pm 5\%$ in k and about $\pm 10\%$ in E. In studies of solid-state reactions it must also be remembered that the problems of temperature control extend beyond the achievement of satisfactory control of the reactant environment, in that self-heating (or self-cooling) may occur, particularly in rapidly decomposing samples of large mass. Temperature inhomogeneities are increased further by changing thermal conductivity characteristics during chemical change and gas evolution.

Thus, providing adequate temperature control can be achieved, errors in α will be of greatest significance in obscuring the fit of this parameter to theoretical kinetic expressions. Systematic errors in α may arise (inter alia) from the following sources. (i) Inaccuracy in determination of the value of the measured parameter (e.g., reactant mass, gas pressure, etc.) corresponding to completion of the reaction under investigation and to which all other values are related in α. (ii) A leak or other source of release of gas into the system. (iii) Adsorption of gaseous product onto a solid product or the reaction vessel walls, etc. (iv) An initial reaction or desorption of adsorbed gases on heating the reactant before the onset of the process being investigated. Independent measurement of these contributions to the overall observations can sometimes be incorporated in the kinetic analysis.

The present study is restricted to investigation of the influence of random errors, computer generated and evenly distributed up to a selected maximum percentage of each α value. (Although not included in the present account, a number of other error distributions can be envisaged and could be incorporated in a similar analysis. These include error within a constant range (representing, for example, the inaccuracy with which a mass measurement may be made in a thermogravimetric study) or dependent upon a squared term (as could arise from pressure measurements using a McLeod gauge).) The present study reports comparison of generated values of α (containing various selected maximum levels of percentage error in α) with appropriate

134

analyzing expressions. Since it is known that each set of data is being compared with a "wrong" analyzing equation, the statistical parameters so obtained are just above the upper limit for distinguishing between model expressions at the given error level. Thus these conclusions can be used to provide a statistical basis for the estimation of the error levels in experimental results which can be accepted as demonstrating an acceptable fit to the analyzing equation. Comparisons of the type described will determine whether a decision on the fit of data to the model can be made. An even more quantitative approach could include the use of standard statistical F-tests as described by Green[20].

Generation of α–time data

For the purpose of calculation, values of the rate coefficient were arbitrarily chosen to give $\alpha = 0.98$ at $t = 100$. α–time curves drawn on this basis for the sigmoid and deceleratory groups of equations in Table 1 are given in Fig. 1(a) and (b),
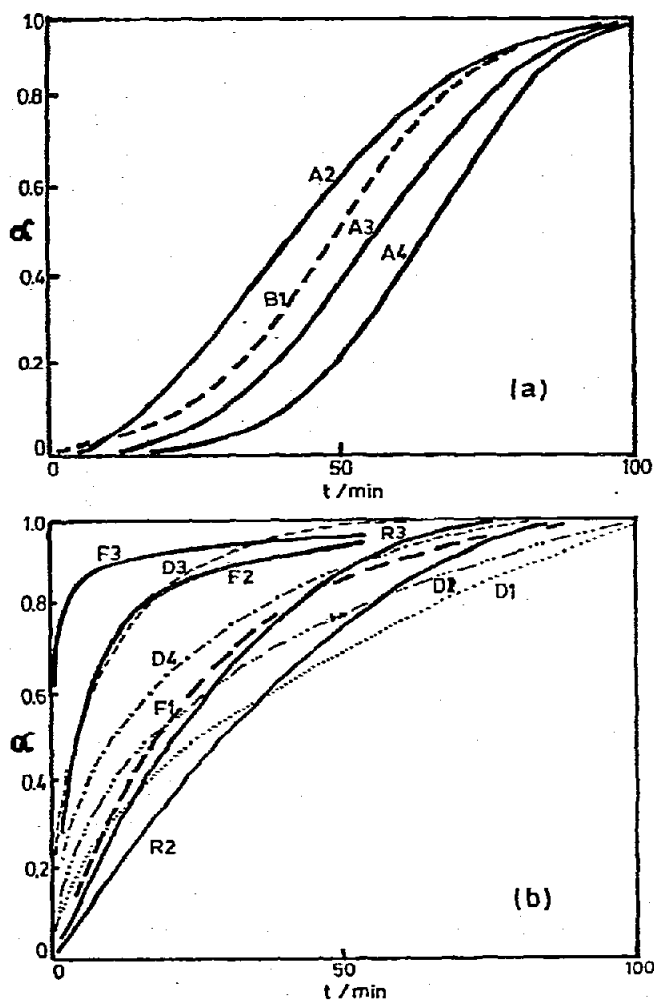
Fig. 1. α–time curves for selected kinetic models (see Table 1): (a) sigmoid group; (b) deceleratory group.

respectively. Due to the influence of the exponent, n, values of rate coefficients, k', obtained by least-square fit of the analyzing equation to the generated α–time data are closer to the value calculated for the analyzing model than the original value of k in the generating equation. Accordingly, before comparing the standard errors of the two slopes (k and k'), calculated values of s_b have been converted to percentages of the slopes, b, i.e. $\%s_b = 100\,s_b/b$.

RESULTS AND DISCUSSION

From the many possible combinations of kinetic expressions for which statistical investigations of distinguishability could be made, the following were selected for consideration here as being of the greatest practical interest.

(a) The sigmoid group (A2, A3, A4 and B1). When errors are introduced and re-analysis includes consideration of the generating expression, there are sixteen possible combinations.

TABLE 2

DEVIATION TYPES OVER α RANGE 0.05–0.95

(Represented by letters, see text: positive deviations to the right; low α values at tops of letters)

Generating/analyzing expressions	Deviation type	Generating/analyzing expressions	Deviation type
Sigmoid group		*Deceleratory group (contd.)*	
A2/A3	D	R3/F1	b
A2/A4	D	R3/R2	d
A2/B1	D		
		Deceleratory regions of sigmoid group	
A3/A2	ɑ	A2/F1	ɑ
A3/A4	D	A2/R2	b
A3/B1	ƹ	A2/R3	$
A4/A2	ɑ	A3/F1	ɑ
A4/A3	ɑ	A3/R2	b
A4/B1	ƹ	A3/R3	$
B1/A2	ɑ	A4/F1	ɑ
B1/A3	$	A4/R2	$
B1/A4	$	A4/R3	ɑ
Deceleratory group		B1/F1	D
F1/R2	d	B1/R2	b
F1/R3	d	B1/R3	b
R2/F1	D		
R2/R3	b		

TABLE 3

CLASSIFICATION OF GENERATING/ANALYZING EXPRESSION COMBINATIONS ACCORDING TO DEVIATION TYPE

(see also Table 2)

D	α	S	?	B	D
Sigmoid group					
A2/A3	A3/A2	B1/A3	A3/B1		
A2/A4	A4/A2	B1/A4	A4/B1		
A2/B1	A4/A3				
A3/A4	B1/A2				
Deceleratory group					
R2/F1				R2/R3	F1/R2
				R3/F1	F1/R3
					R3/R2
Deceleratory regions of sigmoid group					
B1/F1	A2/F1	A2/R3		A2/R2	
	A3/F1	A3/R3		A3/R2	
	A4/F1	A4/R2		B1/R2	
	A4/R3			B1/R3	

(b) The deceleratory group (F1, R2 and R3). These give a further nine combinations.

(c) The deceleratory regions of the sigmoid group. The analysis of the deceleratory regions of the sigmoid group (A2, A3, A4 and B1) by the deceleratory models (F1, R2 and R3) gives a further twelve combinations.

The technique illustrated here through application to these selected important equations may be extended readily to other kinetic expressions, other ranges of α and other types of error in α.

Results of these analyses are presented, in the most compact format that is compatible with clarity, in Tables 2–8. These refer to comparisons in two α ranges ($0.05 < \alpha < 0.95$ and $0.20 < \alpha < 0.80$), other possibilities obviously exist. The influence of inaccuracy of data is reported for three (pseudo) random error levels (1,5 and 10% maximum of α) to indicate trends and permit interpolation (again, many other possibilities exist). Statistical parameters obtained by re-application of the generating equation after inclusion of random errors in α values are subscripted zero. The tables report only the parameters which refer to that alternative expression which is most accurately obeyed. The ratios of parameters for both analyzing and generating expressions give a direct indication (ratio <1) of which is statistically the more acceptable. Where there is little to choose between two alternative analyzing expressions, or there is a change in the closest analyzing expression as the error is increased, values for both expressions have been tabulated.

TABLE 4

SIGMOID GROUP

α Range: 0.05–0.95

Basic expression	Closest analyzing expression	Statistical parameter	Random error level (max % of α)				Deviation type
			0	1	5	10	
A2	—	$(\%s_b)_0$	0	0.0939	0.515	1.19	
		r_0	1	1	0.9998	0.9988	
		$(s_{yx})_0$	0	0.00162	0.00913	0.0220	
	A3	$\%s_b$	2.17	2.11	1.82	1.47	
		r	0.9960	0.9963	0.9972	0.9982	D
		s_{yx}	0.0262	0.0255	0.0226	0.0187	
		$s_b/(s_b)_0$	∞	22.5	3.53	1.24	
		$s_{yx}/(s_{yx})_0$	∞	15.7	2.48	0.85	
A3	—	$(\%s_b)_0$	0	0.0784	0.429	0.988	
		r_0	1	1	0.9998	0.9992	
		$(s_{yx})_0$	0	0.95×10^{-3}	0.0053	0.0126	
	A4	$\%s_b$	1.14	1.08	0.850	0.683	
		r	0.9989	0.9990	0.9994	0.9996	D
		s_{yx}	0.0108	0.0102	0.0082	0.0068	
		$s_b/(s_b)_0$	∞	13.8	1.98	0.69	
		$s_{yx}/(s_{yx})_0$	∞	10.7	1.55	0.54	
A4	—	$(\%s_b)_0$	0	0.0708	0.387	0.888	
		r_0	1	1	0.9999	0.9993	
		$(s_{yx})_0$	0	0.67×10^{-3}	0.0037	0.0088	
	A3	$\%s_b$	1.14	1.20	1.51	2.01	
		r	0.9989	0.9988	0.9981	0.9966	D
		s_{yx}	0.0138	0.0146	0.0186	0.0256	
		$s_b/(s_b)_0$	∞	16.9	3.90	2.26	
		$s_{yx}/(s_{yx})_0$	∞	21.8	5.02	2.91	
B1	—	$(\%s_b)_0$	0	0.113	0.619	1.44	
		r_0	1	1	0.9997	0.9982	
		$(s_{yx})_0$	0	0.0071	0.0401	0.0967	
	A4	$\%s_b$	1.28	1.23	1.00	0.790	
		r	0.9986	0.9987	0.9991	0.9995	S
		s_{yx}	0.0121	0.0116	0.0097	0.0078	
		$s_b/(s_b)_0$	∞	10.9	1.62	0.55	
		$s_{yx}/(s_{yx})_0$	∞	1.63	0.24	0.08	

TABLE 5

SIGMOID GROUP

α Range: 0.20–0.80

Basic expression	Closest analyzing expression	Statistical parameter	Random error level (max % of α)				Deviation type
			0	1	5	10	
A2	—	$(\%s_b)_0$	0	0.0280	0.143	0.293	
		r_0	1	1	1	1	
		$(s_{yx})_0$	0	0.21×10^{-3}	0.0011	0.0023	
	A3	$\%s_b$	1.38	1.35	1.25	1.13	
		r	0.9990	0.9990	0.9991	0.9993	D
		s_{yx}	0.0072	0.0071	0.0067	0.0061	
		$s_b/(s_b)_0$	∞	48.2	8.74	3.86	
		$s_{yx}/(s_{yx})_0$	∞	33.8	6.09	2.65	
A3	—	$(\%s_b)_0$	0	0.0250	0.128	0.262	
		r_0	1	1	1	1	
		$(s_{yx})_0$	0	0.13×10^{-3}	0.68×10^{-3}	0.0014	
	B1	$\%s_b$	0.470	0.460	0.446	0.494	
		r	0.9999	0.9999	0.9999	0.9999	$\updownarrow$
		s_{yx}	0.0120	0.0118	0.0115	0.0130	
		$s_b/(s_b)_0$	∞	18.4	3.48	1.89	
		$s_{yx}/(s_{yx})_0$	∞	90.8	16.9	9.29	
A4	—	$(\%s_b)_0$	0	0.0235	0.120	0.246	
		r_0	1	1	1	1	
		$(s_{yx})_0$	0	0.96×10^{-4}	0.50×10^{-3}	0.0010	
	B1	s_b	0.566	0.597	0.729	0.906	
		r	0.9998	0.9998	0.9997	0.9995	$\updownarrow$
		s_{yx}	0.0144	0.0153	0.0189	0.0238	
		$s_b/(s_b)_0$	∞	25.4	6.08	3.68	
		$s_{yx}/(s_{yx})_0$	∞	159	37.8	23.8	
B1	—	$(\%s_b)_0$	0	0.0344	0.176	0.360	
		r_0	1	1	1	0.9999	
		$(s_{yx})_0$	0	0.88×10^{-3}	0.0045	0.0095	
	A3	$\%s_b$	0.470	0.479	0.523	0.603	
		r	0.9999	0.9999	0.9998	0.9998	$	
		s_{yx}	0.0025	0.0025	0.0028	0.0033	
		$s_b/(s_b)_0$	∞	13.9	2.97	1.68	
		$s_{yx}/(s_{yx})_0$	∞	2.84	0.62	0.35	
	A4	$\%s_b$	0.566	0.545	0.461	0.359	
		r	0.9998	0.9998	0.9999	0.9999	$	
		s_{yx}	0.0023	0.0022	0.0019	0.0015	
		$s_b/(s_b)_0$	∞	15.8	2.62	1.00	
		$s_{yx}/(s_{yx})_0$	∞	2.50	0.42	0.16	

TABLE 6

DECELERATORY GROUP

α Range: 0.05–0.95

Basic expression	Closest analyzing expression	Statistical parameter	Random error level (max % of α)				Deviation type
			0	1	5	10	
F1	—	$(\%s_b)_0$	0	0.138	0.761	1.77	
		r_0	1	1	0.9995	0.9973	
		$(s_{yx})_0$	0	0.0046	0.0270	0.0680	
	R3	$\%s_b$	3.43	3.35	3.03	2.55	
		r	0.9902	0.9906	0.9923	0.9945	D
		s_{yx}	0.0249	0.0245	0.0229	0.0201	
		$s_b/(s_b)_0$	∞	24.3	3.98	1.44	
		$s_{yx}/(s_{yx})_0$	∞	5.33	0.85	0.30	
R2	—	$(\%s_b)_0$	0	0.0474	0.255	0.571	
		r_0	1	1	0.9999	0.9997	
		$(s_{yx})_0$	0	0.44×10^{-3}	0.0024	0.0055	
	R3	$\%s_b$	1.57	1.64	1.95	2.43	
		r	0.9979	0.9977	0.9968	0.9950	D
		s_{yx}	0.0115	0.0121	0.0148	0.0192	
		$s_b/(s_b)_0$	∞	34.6	7.65	4.26	
		$s_{yx}/(s_{yx})_0$	∞	27.5	6.17	3.49	
R3	—	$(\%s_b)_0$	0	0.0727	0.395	0.898	
		r_0	1	1	0.9999	0.9993	
		$(s_{yx})_0$	0	0.54×10^{-3}	0.0030	0.0071	
	R2	$\%s_b$	1.57	1.52	1.32	1.03	
		r	0.9979	0.9980	0.9985	0.9991	D
		s_{yx}	0.0144	0.0140	0.0124	0.0100	
		$s_b/(s_b)_0$	∞	20.9	3.34	1.15	
		$s_{yx}/(s_{yx})_0$	∞	25.9	4.13	1.41	

TABLE 7

DECELERATORY GROUP

α Range: 0.20–0.80

Basic expression	Closest Analyzing expression	Statistical parameter	Random error level (max % of α)				Deviation type
			0	1	5	10	
F1	—	$(\%s_b)_0$	0	0.0366	0.187	0.383	
		r_0	1	1	1	0.9999	
		$(s_{yx})_0$	0	0.48×10^{-3}	0.0025	0.0053	
	R3	$\%s_b$	1.96	1.94	1.84	1.72	
		r	0.9979	0.9979	0.9981	0.9984	σ
		s_{yx}	0.0063	0.0063	0.0061	0.0058	
		$s_b/(s_b)_0$	∞	53.0	9.84	4.49	
		$s_{yx}/(s_{yx})_0$	∞	13.1	2.44	1.09	
R2	—	$(\%s_b)_0$	0	0.0168	0.0858	0.176	
		r_0	1	1	1	1	
		$(s_{yx})_0$	0	0.72×10^{-4}	0.37×10^{-3}	0.78×10^{-3}	
	R3	$\%s_b$	0.961	0.984	1.08	1.20	
		r	0.9995	0.9995	0.9994	0.9992	D
		s_{yx}	0.0031	0.0032	0.0036	0.0041	
		$s_b/(s_b)_0$	∞	58.6	12.6	6.82	
		$s_{yx}/(s_{yx})_0$	∞	44.4	9.73	5.26	
R3	—	$(\%s_b)_0$	0	0.0232	0.118	0.242	
		r_0	1	1	1	1	
		$(s_{yx})_0$	0	0.76×10^{-4}	0.39×10^{-3}	0.82×10^{-3}	
	R2	$\%s_b$	0.961	0.944	0.875	0.786	
		r	0.9995	0.9995	0.9996	0.9997	σ
		s_{yx}	0.0041	0.0040	0.0038	0.0035	
		$s_b/(s_b)_0$	∞	40.7	7.42	3.25	
		$s_{yx}/(s_{yx})_0$	∞	52.6	9.74	4.27	

TABLE 8

DECELERATORY REGION OF SIGMOID GROUP

Basic expression	Closest analyzing expression	Statistical parameter	Random error level (max % of α)				Deviation type
			0	1	5	10	
A2	R3	$\%s_b$	0.549	0.495	0.584	1.61	
(0.43 < α < 0.97)		r	0.9997	0.9998	0.9997	0.9977	S
		s_{yx}	0.0041	0.0038	0.0047	0.0141	
	R2	$\%s_b$	1.78	1.70	1.34	0.666	
		r	0.9972	0.9974	0.9984	0.9996	b
		s_{yx}	0.0170	0.0164	0.0134	0.0070	
A3	R3	$\%s_b$	0.699	0.771	1.29	2.64	
(0.55 < α < 0.97)		r	0.9997	0.9996	0.9988	0.9951	S
		s_{yx}	0.0046	0.0051	0.0091	0.0204	
	R2	$\%s_b$	1.31	1.21	0.776	0.289	
		r	0.9988	0.9990	0.9996	0.9999	b
		s_{yx}	0.0108	0.0101	0.0067	0.0027	
A4	R3	$\%s_b$	1.01	1.11	1.71	3.16	
(0.58 < α < 0.97)		r	0.9993	0.9992	0.9981	0.9936	D
		s_{yx}	0.0064	0.0071	0.0117	0.0237	
	R2	$\%s_b$	1.01	0.920	0.507	0.664	
		r	0.9993	0.9995	0.9998	0.9997	S
		s_{yx}	0.0081	0.0074	0.0043	0.0060	
B1	R3	$\%s_b$	1.49	1.42	1.13	0.706	
(0.52 < α < 0.97)		r	0.9984	0.9986	0.9991	0.9997	b
		s_{yx}	0.0098	0.0095	0.0077	0.0050	

The following general conclusions emerge from these results.

(i) There is little to choose between $\%s_b$ and s_{xy} as indicators of the excellence-of-fit. (The parameters s_b and s_{xy}, applied over the same α and x range, would give equivalent results).

(ii) The introduction of small (up to 1 %) random errors in α results in marked increases in the magnitudes of $\%s_b$ and of s_{xy}, but this rate of increase becomes less pronounced as the maximum error levels rise further.

(iii) The correlation coefficient, r, is a most insensitive indicator of the applicability of a rate expression. Values are reported here only because correlation coefficients are so commonly reported and the high values obtained here, using an "incorrect" expression, emphasize the caution that is necessary in interpreting r-values found.

More specific conclusions are discussed in the context of individual groups of expressions below.

Plots of the residuals, $f'(\alpha) - f(\alpha)$, against α for the various generating and most acceptable analyzing expressions are given in Figs. 2–4. Curve shapes of plots for sigmoid (Fig. 2) and deceleratory (Fig. 3) expressions for the larger ($0.05 < \alpha < 0.95$) and smaller ($0.20 < \alpha < 0.80$) ranges are similar, though the magnitudes of deviation were reduced over the smaller α range. Introduction of random errors results in a random scatter of points on these plots. For convenience of reference in the text, systematic deviations of the type shown in Figs. 2–4 may be schematically represented by the letters D, ◖, $, ♭, b, d, p and q. The vertical stroke represents zero deviation, α increasing downwards, and positive deviations occurring to the right. Thus, D
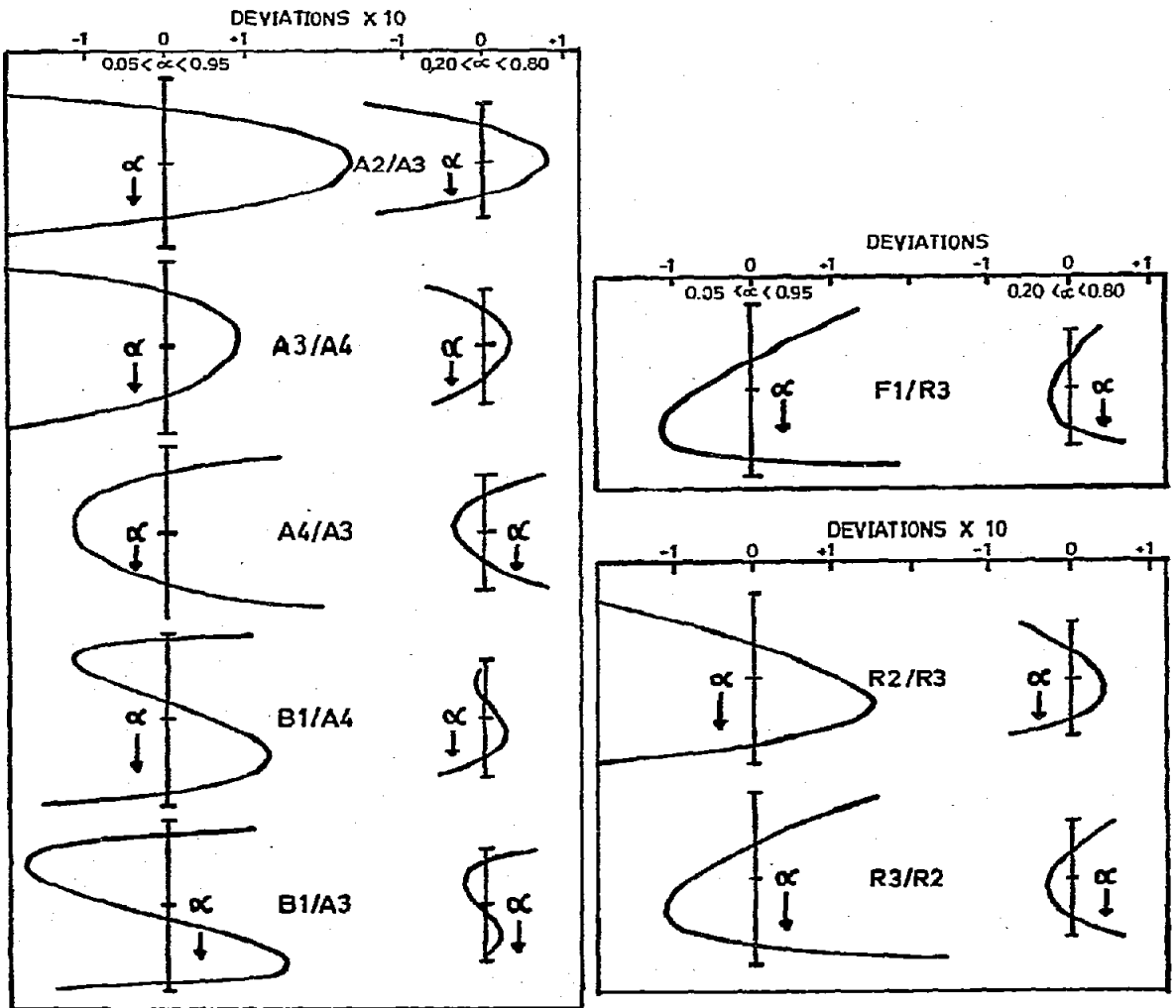
Fig. 2. Residual curves for the sigmoid group of kinetic expressions. Deviations are the differences between the values of the analyzing and generating expressions at any given value of α.

Fig. 3. Residual curves for selected deceleratory kinetic expressions. Deviations are the differences between the values of the analyzing and generating expressions at any given value of α.
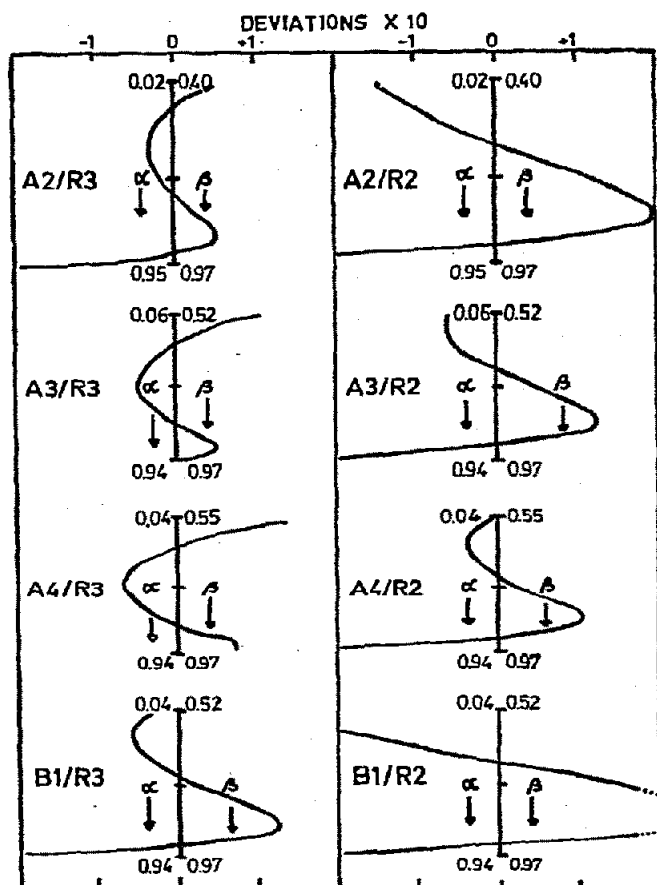
Fig. 4. Residual curves for the deceleratory regions of the sigmoid group of kinetic expressions. Deviations are the differences between the values of the analyzing and generating expressions at any given value of α.

represents a maximum positive deviation in the middle of the α range, while p and b also represent positive deviations, but the maximum occurs at low and high values of α, respectively. The distinction between these qualitative representations is necessarily somewhat arbitrary.

The trends revealed by examination of similar residual plots of the calculated deviations of experimental points from the regression line for a proposed model, against α, could be used, together with Tables 2 and 3 as indications of: (i) alternative rate equations with which the data should be compared and (ii) the α ranges over which the distinguishability is greatest.

The sigmoid group (A2, A3, A4 and B1) (Tables 4 and 5, Fig. 2)

The following conclusions are derived from the data in Tables 4 and 5 and plots of residuals (of which only examples of closest agreement are recorded in Fig. 2).

(a) *The range $0.05 < \alpha < 0.95$.* A3 and A4 are most difficult to distinguish from each other and it is especially likely that A4 may appear to fit when A3 should apply. Deviations are at a maximum in the mid-α range (i.e. type D). There are also

difficulties in distinguishing between the applicability of B1 and A4, even at 1% maximum error levels. Here $\%s_b$ emerges as the most reliable statistical parameter. Obedience to A2 could be confused with obedience to A3. The similarity, however, becomes critical only at an error level between 5–10% α, which can usually be bettered experimentally.

(b) *The range 0.20 < α < 0.80.* Here it is found that, compared with the wider α range, A3 and A4 are more difficult to distinguish from B1 than each other and s_{xy} is found to be the most useful statistical parameter for this purpose. B1 is most likely to be indistinguishable from A3 at low error levels (up to 1%) and with A4 at higher error levels (> 1%) and $\%s_b$ is the most reliable parameter. A3 is more readily distinguished from the A2 expression.

The deceleratory group (F1, R2 and R3) (Tables 6 and 7, Fig. 3).

Over both α ranges, the equations F1 and R2 are most likely to be incorrectly identified as R3, while R3 itself is most closely comparable with R2. Both R2 and R3 are relatively readily distinguishable from F1. In the absence of error, greater distinguishability is obtained over the wider α range, but as the error level is increased the reduced α interval provides the greater discrimination. Since deviations are of the type D and Q, distinguishability is greatest in the mid-α range.

The deceleratory regions of the sigmoid curves (Table 8, Fig. 4)

Kinetic analyses of sigmoid curves have often proceeded in two stages in which data for the acceleratory stage is tested for obedience to the power or exponential laws (P1 or E1) and the deceleratory stage is analyzed according to the geometric or reaction-order expressions (R2, R3 or (usually) F1). The points of inflection, α_m, at which the rate is a maximum, for the sigmoid curves are[8]: A2 (0.39); A3 (0.49); A4 (0.53) and B1 (0.50). For the purpose of the present comparisons, the deceleratory regions of these curves were rescaled with $\beta = (\alpha - \alpha_m)/(1 - \alpha_m)$, (i.e. $\beta = 0$ at $\alpha = \alpha_m$ and $\beta = 1$ when $\alpha = 1$) representing the fraction of the deceleratory decomposition complete, and the origin of the axes relocated with the point (0,0) at $(\alpha = \alpha_m, t = t_m)$. The rate coefficient in the generating expression was selected to give $\alpha = 0.98$ when $t = t_m + 100$. With B1, for which $\alpha_m = 0.50$, t_m was arbitrarily set at 100 and k'' chosen as half the value used in earlier analyses.

From comparison of the data it is found that F1 is the least accurate representation of the deceleratory periods of the sigmoid expressions (A2, A3, A4 and B1). R3 gives the most acceptable fit, particularly to B1, but also to the deceleratory periods of A2, A3 and A4 at low error levels. The similarity between R3 and B1 increases as the error level is increased, but with A2, A3 and A4, R2 emerges as the more satisfactory representation as the error level rises. The change from R3 to R2 as the closest analyzing expression occurs, as the error level rises, in the sequence A4, A3 and finally A2.

Use of rate coefficients in activation energy determinations

The rate coefficients, k, for each of the generating expressions were doubled and

the effect on the apparent rate coefficient, k', obtained by a least-squares analysis using a closely related analyzing expression, was determined. In all such comparisons, the apparent rate coefficients, k', were within 1% of twice their original values. This provides strong support for a conclusion reported by (inter alia) Johnson and Gallagher[19] and Yankwich and Zavitsanos[23] that the calculated magnitude of the activation energy for a reaction is not sensitive to the particular rate equation used in the kinetic analysis.

CONCLUSIONS

The theoretical analyses and kinetic comparisons given above provide quantitative information concerning the magnitudes of the differences in those α–time kinetic expressions which have found most general use in studies of rates of solid-state decompositions. These results can be applied in the testing of experimental data, by indicating the equations between which distinctions are most difficult, the α ranges within which differences are greatest, and the levels of accuracy of data required, to enable reliable distinctions to be made. It is concluded from a critical consideration of these model calculations that a single statistical parameter is not usually capable of providing the evidence upon which a particular kinetic obedience can be positively demonstrated. The shapes of plots of residuals give more systematic information and such comparisons of experimental results with theoretical relations through Figs. 2–4 and Tables 2 and 3 may be used to decide which alternative kinetic equations should be tested and the ranges of α within which the distinguishability is greatest.

The present communication has been concerned with those kinetic equations which have found greatest application in studies of the decompositions of solids, considered in two α ranges and at three levels of error, of one type, in α. Clearly the approach is capable of extension in a variety of directions; to additional equations, ranges of α and experimental inaccuracies. A comprehensive examination of all systems of interest is not practicable.

It may also be necessary to consider other influences such as the distribution of crystal sizes in the reactant, changes in mechanism during the course of reaction, etc. Finally, it should be emphasized that it is also necessary to support the mechanistic interpretation of a kinetic observation (however accurate) with other relevant measurements. Microscopic examination is particularly valuable in this respect. Kinetic characteristics may change during a rate process of interest (e.g. cessation of nucleation on complete reaction of surfaces of particles, sintering of product, strain-induced disintegration or reactant crystals, etc.), and obedience to a particular rate equation may be consistent with more than a single nucleation and growth model.

REFERENCES

1 P. W. M. Jacobs and F. C. Tompkins, in W. E. Garner (Ed.), *Chemistry of the Solid State*, Butterworth, London, 1955, Chap. 7.
2 D. A. Young, *Decomposition of Solids*, Pergamon, London, 1966.
3 S. F. Hulbert, *J. Br. Ceram. Soc.*, 6 (1969) 11.
4 B. Delmon, *Introduction à la Cinetique Hétérogène*, Technip, Paris, 1969.
5 J. H. Sharp, G. W. Brindley and B. N. Narahari Achar, *J. Am. Ceram. Soc.*, 49 (1966) 379.
6 E. A. Geiss, *J. Am. Ceram. Soc.*, 46 (1963) 374.
7 T. R. Ingraham, *Thermal Analysis, Proc. 1st Symp. Toronto*, 1965, p. 81.
8 Wee-Lam Ng, *Aust. J. Chem.*, 28 (1975) 1169.
9 J. Sesták and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.
10 A. K. Galwey, *J. Chem. Soc. A*, (1966) 87.
11 R. J. Acheson and A. K. Galwey, *J. Chem. Soc. A*, (1967) 1167; (1968) 942.
12 R. E. Carter, *J. Chem. Phys.*, 34 (1961) 2010; 35 (1961) 1137.
13 M. Selvaratnam and P. D. Garn, *J. Am. Ceram. Soc.*, 59 (1976) 376.
14 L. F. Jones, D. Dollimore and T. Nicklin, *Thermochim. Acta*, 13 (1975) 240.
15 M. E. Brown, D. Dollimore and A. K. Galwey, *J. Chem. Soc., Faraday Trans. I*, 70 (1974) 1316.
16 N. R. Draper and H. Smith, *Applied Regression Analysis*, Wiley, New York, 1966.
17 W. H. Davis and W. A. Pryor, *J. Chem. Educ.*, 53 (1976) 285.
18 A. G. Leiga, *J. Phys. Chem.*, 70 (1966) 3262.
19 D. W. Johnson and P. K. Gallagher, *J. Phys. Chem.*, 75 (1971) 1179.
20 J. R. Green, *Trans. Faraday Soc.*, 65 (1969) 3288.
21 M. Wagner, G. Czerlinski and M. Pring, *Comput. Biol. Med.*, 5 (1975) 105.
22 S. W. Benson, *The Foundations of Chemical Kinetics*, McGraw-Hill, New York, 1960, p. 86.
23 P. E. Yankwich and P. D. Zavitsanos, *Pure Appl. Chem.*, 8 (1964) 287.