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KINETIC ANALYSES OF CONSECUTIVE SOLID-STATE DECOMPOSITIONS ILLUSTRATED WITH IRON(II) SULFATE

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ABSTRACT

Use of consecutive reaction analysis for the derivation of kinetic parameters is demonstrated for the solid state decompositions which often include fractional orders of reaction. The differential equations describing the relative amounts of reactants and products during an isothermal decomposition are solved numerically by machine. Unlike previously used methods for solid-state decompositions there is no need to assume that the rate constant of the first step is much greater than that of the second. Also, the technique allows the interpretation of experimental data throughout the entire range of the reaction. The treatment was applied to the two-step decomposition of iron(II) sulfate in a dry nitrogen atmosphere. The results show the data to fit consecutive half-order reactions.

INTRODUCTION

The use of kinetic equations to describe consecutive reactions in solution and gas-phase studies are relatively common. The derivation and in some cases the solution of the pertinent differential equations for integral orders of reaction are presented in several texts[1-5]. Solutions of the differential equations for the cases of the fractional orders which are common to solid-state decompositions have not been reported.

In a previous study by these authors[6] it was reported that iron(II) sulfate thermally decomposed in nitrogen according to the following two-step consecutive reaction:

$$2FeSO_4 \rightarrow Fe_2O_2SO_4 + SO_2$$

$$Fe_2O_2SO_4 \rightarrow Fe_2O_3 + SO_3$$

Since these two reactions appeared well resolved in time, particularly for the freeze-dried samples, the data were treated as though the first reaction was complete at the outset of the second reaction. This approximation to the treatment of consecutive reactions has also been used by Bond and Jacobs[7] for the decomposition of sodium nitrate.

Studies in other systems which may have consecutive decomposition reactions have prompted these authors to analyze more closely the use of consecutive reactions with fractional orders. Consider the reactions

$$A \xrightarrow{k_1} B + \text{gas}$$

$$B \xrightarrow{k_2} C + \text{gas}$$

where A, B, and C are solid reactants or products and their fractional concentrations are A, B and C. Thus, the rate equations are

$$\frac{dA}{dt} = -k_1 A^n \qquad (1)$$

$$\frac{dB}{dt} = k_1 A^n - k_2 B^m \qquad (2)$$

$$\frac{dC}{dt} = k_2 B^m \qquad (3)$$

where n and m are the orders of the first and second reactions respectively. A, B, and C are defined as fractional concentrations

$$A + B + C = 1. \qquad (4)$$

Considered here are the cases where n and m can have the values of 0, $\frac{1}{2}$, $\frac{2}{3}$, and 1 corresponding to the linear law, contracting area, contracting volume, and first-order models, respectively.

Equation (1) can be integrated directly to obtain the amount of A. Boundary conditions for the integration are $A = 1$ at t_0 where t_0 is starting time. The analytical solution to Eqn. (2) is obviously simple for some combinations of n and m. However, for other combinations, particularly where m is non-integral, the analytical solution is not simple. For this study numerical solutions were thus chosen.

Using Eqn. (4) and knowing the amounts of A and B, one can find the amount of C and it is unnecessary to evaluate Eqn. (3) directly.

EXPERIMENTAL

The sample preparation and data acquisition techniques for freeze-dried iron(II) sulfate samples decomposed in nitrogen are described in a previous work[6]. The raw weight versus time data were converted to fraction reacted, α, using the appropriate starting and final weights, w_0, and w_f. In this case, w_0 represents the weight as if the sample were $FeSO_4$ and w_f represents the weight of the sample as Fe_2O_3.

The machine computation technique used selected values of k_1, k_2, t_0, n, and m, and solved Eqns. (1) and (2) to determine the relative amounts of A and B at each of the experimental time points. Solution of Eqn. (2) was based on Runge–Kutta techniques for the first two points and then on Milne's predictor corrector method for subsequent points (data points were taken at equal time intervals). Given a value of

A and B at each time point, the fraction of C was found by difference. Then the value of α predicted at each time by these choices of k_1, k_2, t_0, n, and m is given by

$$\alpha = B\left(\frac{w_0 - w_i}{w_0 - w_f}\right) + C$$

where w_i is the intermediate weight for the sample as if it were all B or in this case $Fe_2O_2SO_4$. The standard deviation was calculated between these predicted α points and the actual experimental α points, and was used as a degree of fit parameter.

An iterative scheme was employed to vary k_1, k_2, and t_0 such as to minimize the standard deviation at a fixed set of n and m. The iteration was allowed to proceed until a minimum in the standard deviation was found. This minimum was defined as a set of k_1, k_2, and t_0 such that a 1% change of any parameter in either direction would cause a rise in the standard deviation. This procedure was then completed for each of the 16 combinations of m and n which represent the data for each isothermal experiment.

The rate constant k has been expressed here as

$$\frac{d\alpha}{dt} = k(1-\alpha)^n$$

for any one reaction. This definition of the rate constant is not consistent for the fractional orders ½ and ⅔ which were expressed previously[6] in the integrated forms known as contracting area and contracting volume equations

$$1-(1-\alpha)^{\frac{1}{2}} = k't$$

and

$$1-(1-\alpha)^{\frac{1}{3}} = k't.$$

Upon differentiation these are

$$\frac{d\alpha}{dt} = k'\frac{(1-\alpha)^n}{1-n}.$$

Thus for the fractional orders

$$k' = k(1-n)$$

and to be consistent with previous data[6] the values of k' are reported in the following data.

Arrhenius plots were made from these rate data to give an activation energy and pre-exponential terms.

RESULTS

Examples of calculated curves along with the associated experimental data points for the fraction reacted are shown in Fig. 1 for selected reaction orders. The

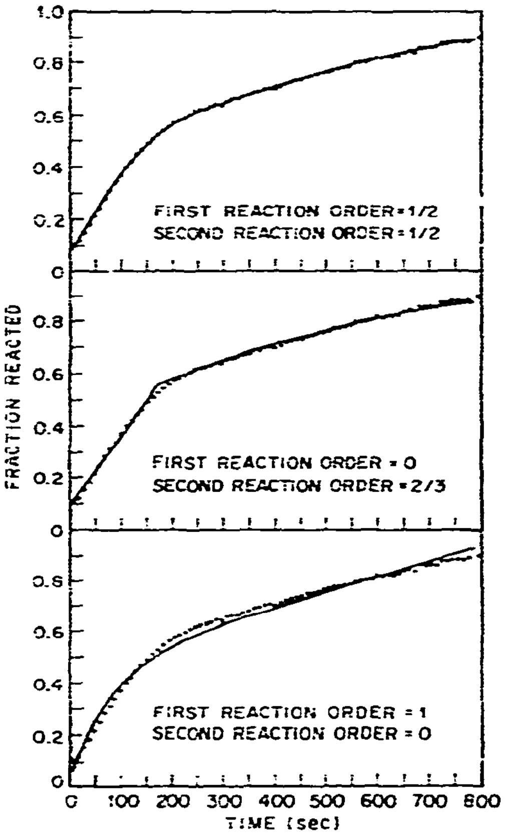

Fig. 1. Selected examples of calculated reaction curves with the experimental data for decomposition of $FeSO_4$ at 575 °C in N_2.

upper curve in Fig. 1 with reaction order $\frac{1}{2}$ followed by order $\frac{1}{2}$ represents the best fit for these data while the other two cases illustrate the nature of the curves where the selected orders do not represent the data as well. Table I gives, for these same data, the standard deviation of the curve from the data points for each of the sixteen combinations tried. This shows that the $\frac{1}{2}$ order for both the first and the second reaction gives a minimum standard deviation.

TABLE I

STANDARD DEVIATIONS BETWEEN THE CALCULATED AND EXPERIMENTAL α POINTS FOR DECOMPOSITION OF $FeSO_4$ AT 575 °C IN N_2

Order of first reaction	*Order of second reaction*			
	0	$\frac{1}{2}$	$\frac{2}{3}$	1
0	0.0104	0.0081	0.0091	0.0137
$\frac{1}{2}$	0.0104	0.0051	0.0063	0.0108
$\frac{2}{3}$	0.0127	0.0073	0.0077	0.0111
1	0.0195	0.0135	0.0128	0.0133

Figure 2 shows the calculated amounts of the starting $FeSO_4$, the intermediate $Fe_2O_2SO_4$, and the final product Fe_2O_3, for the data set used in Fig. 1 and Table I. This ideal representation shows the relative amounts which would be present for the consecutive half order reactions over the entire reaction range even though the experimental data there were fit only in the α range 0.1 to 0.9.

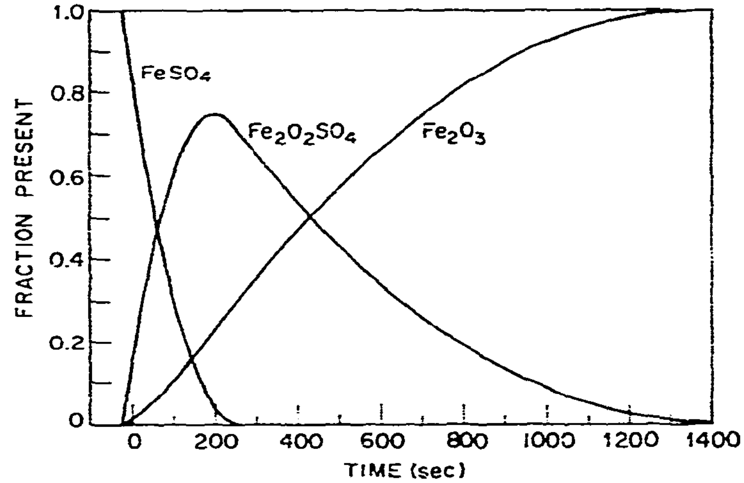

Fig. 2. Relative amounts of products and reactants for an ideal consecutive half-order decomposition of $FeSO_4$ at 575°C in N_2.

At the five experimental temperatures used (475, 500, 525, 550, 575°C) the following consectutive order pairs showed good fit to the data: $\frac{1}{2}$, $\frac{1}{2}$; $\frac{2}{3}$, 0; and $\frac{2}{3}$, $\frac{1}{2}$. The $\frac{1}{2}$, $\frac{1}{2}$ case is used for illustration since the results can then be compared directly with those published earlier[6] and since the calculated activation energies were nearly the same for any of these closely fitting cases.

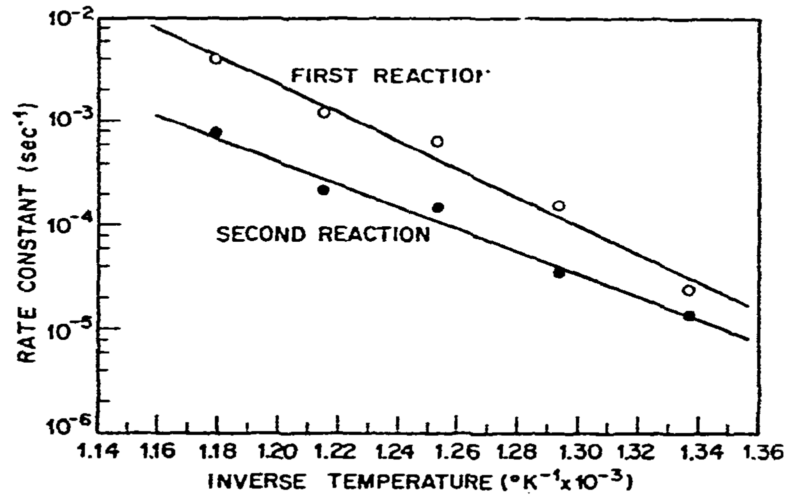

Fig. 3. Arrhenius plots for the decomposition of $FeSO_4$ in N_2 using consecutive half-order reactions.

Examples of the plots used for obtaining the activation energies and pre-exponential terms for the first and second reactions are shown in Fig. 3. The parameters derived from these plots are given in Table II.

TABLE II

ACTIVATION ENERGIES AND PRE-EXPONENTIAL TERMS FOR THE DECOMPOSITION OF $FeSO_4$ IN N_2 USING CONSECUTIVE HALF-ORDER REACTIONS

		This consecutive reaction analysis	*Previous individual reaction analysis*
First reaction	activation energy (kcal/mol)	62.2	61.1
	pre-exp. term (sec^{-1})	4.42×10^{13}	3.32×10^{13}
Second reaction	activation energy (kcal/mol)	49.9	48.1
	pre-exp. term (sec^{-1})	4.88×10^{9}	1.79×10^{9}

DISCUSSION

One of the objectives of this work was to compare the kinetic parameters derived by this consecutive reaction analysis with those derived in previous work[6] where an important simplifying assumption was made. This assumption was that the first reaction was essentially complete before the second started. In other words, the two consecutive reactions were assumed to be distinctly separated in time. This simplified treatment can only be used if the rate constant for the first reaction is much greater than that for the second. The consecutive reaction analyses presented in this work will, however, apply regardless of the relative magnitudes of the rate constants.

Both the simplified treatment and the present treatment show consectutive half-order reaction kinetics to represent these data. Also, from Table II it can be seen that both treatments give nearly the same activation energy and pre-exponential terms despite the fact that the two analyses must use different ranges of alpha. In the simplified treatment the two individual reactions were analyzed over the alpha ranges 0.05–0.90 and 0.10–0.90 respectively. The present treatment however, uses the range in alpha of 0.10–0.90 for the entire two-step decomposition. Thus while the present treatment did not analyze as much data at the very early and very late portions of the reactions it did include all of the data at the latter part of the first reaction and at the beginning of the second reaction which was omitted in the previous treatment.

CONCLUSION

The use of the concept of consecutive reactions in the analysis of solid-state decomposition kinetics has been limited to a few cases in which approximations have been used based on the assumption that the rate of the first reaction is considerably greater than that of the second. In this work the differential equations which define such reactions have been stated and the techniques for their solution have been outlined.

In the application of these techniques to the two-step decomposition of iron(II) sulfate in nitrogen it was found that the derived kinetic parameters differed little from those previously calculated using the simplifying assumptions. This suggests that in this case the previous assumptions of well-defined reactions was well founded. The technique does, however, offer the advantage of being able to treat cases where the magnitudes of the rate constants are close and also allows one to analyze data over the entire reaction range.

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