

Sharp J H, Brindley G W & Narahari Achar B N. Numerical data for some commonly used solid state reaction equations. *J. Amer. Ceram. Soc.* 49:379-82, 1966. [Materials Research Laboratory, Pennsylvania State University, University Park, PA]

A convenient method to allow comparison of experimental kinetic data with calculated data from commonly used equations involves the use of reduced time plots. Tables are provided to facilitate these comparisons, which lead to better understanding of the reaction mechanism. [The SC7® indicates that this paper has been cited in over 260 publications, making it this journal's most-cited paper.]

## Reduced Time Plots for Kinetic Analysis

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In 1963 I left England to join the late Professor George W. Brindley as a postdoctoral research associate, and in 1964 we added a graduate assistant, B.N. Narahari Achar, from Bangalore, India, to the team. Financial support had been granted by the US Air Force to study the kinetics and mechanism of dehydroxylation of minerals that might be found on the moon. Brindley always referred to it as his lunacy program, but still insisted that the quality of the research was of a high standard.

We soon realised that kinetic equations based on the concept of order of reaction, which are so useful when investigating reactions in the gas phase or in solution, are not strictly applicable to heterogeneous systems in which the area of the reaction interface is of greater significance than the concentration of the reactant. Instead, alternative models must be considered, based upon the rate-determining step being dependent upon nucle-

ation, growth of nuclei, diffusion of material to or from the reaction interface, or even the supply of heat to this interface during an endothermic reaction.

Other workers had shown that the use of reduced time plots (in which the fraction reacted,  $\alpha$ , is plotted, for example, against  $t/t_{0.5}$ , where  $t_{0.5}$  is the time taken to reach a fraction reacted of 0.5) allowed the determination of whether a set of experimental data follows the same kinetic mechanism. We showed that by calculating reduced time curves of  $\alpha$  versus  $t/t_{0.5}$  for commonly used solid-state reaction equations, it is easy to compare the experimental reduced time plot with these calculated plots and hence to determine the kinetic mechanisms.

The paper has been cited frequently for three reasons. First, it provided a set of kinetic equations applicable to solid-state reactions at a time when books on chemical kinetics were totally dominated by the approach based on the concept of order of reaction. Second, use of the numerical tables avoided lengthy calculations at a time when ready access to computers was much less common than it is today. Third, the reduced time method provided a great advance over the tedious trial-and-error procedure for the determination of the kinetic equation that best fits the experimental data.

Later, in Sheffield, we developed an alternative approach, sometimes known as the log-log method.<sup>1</sup> A disadvantage of reduced time plots is that a curve is compared with another curve. Although the log-log method and subsequent refinements<sup>2</sup> avoid this, they are complementary to, and have by no means replaced, the reduced time method. We always envisaged that parameters based on values of  $\alpha$  other than 0.5 would sometimes be preferable, and one recent example<sup>3</sup> has used  $t/t_{0.9}$ . In the same paper, the method is extended to embrace constant-rate thermal analysis. It is gratifying that even in an age when rapid computational facilities are readily available, the method and tables given in the paper are still finding widespread application.

1. Hancock J D & Sharp J H. Method of comparing solid-state kinetic data and its application to the decomposition of kaolinite, brucite and  $\text{BaCO}_3$ . *J. Amer. Ceram. Soc.* 55:74-7, 1972. (Cited 70 times.)
2. Jones L F & Dollimore D. Comparison of experimental kinetic data with master data using a linear plot method. *Thermochim. Acta* 13:240-5, 1975. (Cited 10 times.)
3. Reading M. The kinetics of heterogeneous solid state decomposition reactions: a new way forward? *Thermochim. Acta* 135:37-37, 1988.