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Note

Comments on Šesták and Berggren's algorithmization of solid state kinetics

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Šestak and Berggren[1] have examined eighteen of the models used to describe isothermal kinetics and suggested that an equation containing three exponential terms would provide an improved analytical form. This takes into account most of the several possible influences operating to determine the overall kinetics of the process.

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

It must be recognized that in this form the exponents must be treated first in a very pragmatic way, as purely mathematical terms. From the relative magnitudes of the exponents (derived from experimental data) some conclusions might be obtainable. If a reaction is accurately describable by a more limited expression, for example using two of the terms, the third exponent will go to zero. Hence for any reaction, if any exponents approach zero closely, mechanisms requiring that term may be dropped from consideration. Very little more can be learned from the equation.

With the present methods of data acquisition and treatment, it is possible to obtain "best values" of n, m, and p, with considerable initial effort in developing the program. Once the program is developed, however, the evaluations of the exponents for another reaction, or for the same reaction under different conditions (atmosphere or pressure, for example), are not difficult. Interpretation still is. The computed values will reflect the influence of concurrent processes and hence have some indistinct meaning because several models invoke two of the exponential terms.

The temptation to find the best values of the exponents for one reaction, then another and another, is undoubtedly strong, but this would overlook the real capability of the computer and data acquisition equipment. The evaluation of the three exponents and k in principle could be determined from four values of $d\alpha/dt$ or five consecutive values of α (with equal Δt's) and additional values simply improve the precision. Accumulation of several hundred data points during a single run is not difficult. Computation of the several constants for the whole set of data should be performed as a matter of course. If *all* the data fit the equation well, the values are ready for interpretation. In the more probable case, the values will not fit well throughout the course of the reaction, so the next step in computation can be taken.

The typical computer can be programmed to perform the computations over a continuously changing set of data. One may take, arbitrarily, a set of twenty consecutive measurements and compute the *best values* of the constants, then move along the data set in increments of one or more (depending upon the budget) adding in the next group of values and dropping the earliest. The multiple computations of k, m, n and p would disclose trends in values which may in turn be relatable to a changing mechanism.

The computations involve linearization of the equation by taking logarithms of the terms. A precaution must be taken. In this form the value of p is highly sensitive to apparent error in α, particularly as α approaches unity, so excursion beyond justifiable limits may be seen in small data segments and in late stages of the decomposition. Repeated processing of the data with limits derived from the initial computation should enable good estimation of p. Its fluctuation in the initial computation may become a useful measure of (a) the quality of the data or (b) the validity of the description. Other terms may be needed.

For non-isothermal experiments, the Arrhenius equation can be used, if desired, in the initial computations or the values of $k(T)$ used in separate computations to evaluate the apparent activation energy. The number of data points being computed should be adjusted so that the temperature change over the set is small; the smaller the better, within the range of practicality.

It is fairly safe to predict that most solid decompositions will show variations in the exponents due to changes in the physical process. Young[2] has shown that as many as five discernible regions may be found in a plot of α versus t (isothermal).

A changing process should become evident from changing values of the three exponents, but the *overall* rate constant may change in an unpredictable manner. If the immediate goal is evaluation of the apparent activation energy, some smoothing may be necessary. If the need to refine the interpretation of the data is great enough, the single rate constant describing the overall process might then be replaced by separate rate constants, k_m, k_n and k_p, in a new set of computations to ascertain the relative contributions and estimate an activation energy for each process.

A relatively large number of data points obtained under carefully controlled conditions (and checked for reproducibility) could be used with confidence in deducing the nature of decomposition processes at various stages of the whole decomposition. The technology is available. The ability to delineate the several processes will be a tremendous aid in understanding the nature of particular decompositions; it will no longer be necessary to consider a large number of unique reactions as part of a class of reactions.

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2 D. A. Young, *Decomposition of Solids*, Pergamon Press, Oxford, 1966.