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Note

A NEW TECHNIQUE OF ANALYSIS FOR THE INVESTIGATION OF KINETIC DATA USING THE DIFFERENTIAL SCANNING CALORIMETER

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ABSTRACT

This method of analysis for kinetic data of solid state chemical reactions takes advantage of the binomial series expansion to normalize various mathematical expressions related to various solid state models into a power series. This facilitates analysis by computer methods, in that deviations of the various models will be perceptible at the outset.

Let us first define the general differential form for any solid decomposition reaction. Thus

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (1)$$

Integrating the above equation gives us

$$g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = k\int^{\alpha} dt \qquad (2)$$

If we were to plot g(α) on the y-axis and time t on the x-axis, we would notice slight or major deviations from the predicted straight line. This method fits a polynomial equation to the data by means of a least-squares analysis, whereby several curve-fitting tests are applied in order to determine which mathematical model agrees with the data.

In this method the independent variable, α, the fraction reacted, is expanded in a power series and then subject to a variety of statistical tests to determine the extent of its linearity. Obviously, from the inspection of the empirical polynomial equation one can see from the magnitude of the coefficients its deviation from a straight line. In addition to a purely mathematical analysis, we can also conjecture about the physical phenomenon that the solid sample underwent. For example, if we subject the data to an Avrami—Erofeyev equation and perceive deviations from linearity at large values of

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α, we can conclude that the kinetics of the reaction are no longer obeyed when those deviations become manifest. In other words, we can conclude that either the model does not fit the data accurately, leading to the assumption that the sample reacts by a completely different mechanism, or there is a change in mechanism occurring at some interval, in which the mathematics is detecting its incipient deviation. Since the mechanics of polynomial regressions are well established, the power series type formula was chosen. All of the expansions reduce to a power series form, thus facilitating handling of the data. A tremendous savings in computer time comes about because the same functional relationship is used for all the final statistical analysis.

The first step in analyzing the integrated form of the kinetics expression is to expand it in a power series and then apply the principles that were expounded in the previous section. The binomial theorem can be used to best advantage in that in this expanded form the polynomial can be reduced to a power series.

The binomial theorem states

$$(1+\alpha)^{\beta} = \sum_{k=0}^{\infty} \binom{\beta}{k} \alpha^{k} \quad -1 < \alpha < 1 \tag{3}$$

Expanding eqn. (4) we arrive at

$$(1+\alpha)^{\beta} = 1 + \beta\alpha + \frac{\beta(\beta-1)\alpha^{2}}{2!} + \frac{\beta(\beta-1)(\beta-2)\alpha^{3}}{3!} + \tag{4}$$

Let us now apply the above results to the various solid state models. For the contracting model of the form

$$g(\alpha) = 1 - (1-\alpha)^{1/2} \tag{5}$$

we have an expansion

$$(1-\alpha)^{1/2} = 1 - \frac{\alpha}{2} - \frac{\alpha^{2}}{8} - \frac{\alpha^{3}}{16} - \frac{5}{128}\alpha^{4} + \ldots \tag{6}$$

Therefore,

$$1 - (1-\alpha)^{1/2} = \frac{\alpha}{2} + \frac{\alpha^{2}}{8} + \frac{\alpha^{3}}{16} + \frac{5}{128}\alpha^{4} + \ldots \tag{7}$$

which is of the form

$$1 - (1-\alpha)^{1/2} = a_0 + a_1\alpha + a_2\alpha^{2} + a_3\alpha^{3} + c_4\alpha^{4} + \ldots \tag{8}$$

where

$a_0 = 0$ $\quad a_1 = 0.5$ $\quad a_2 = 0.125$

$a_3 = 0.0625$ $\quad a_4 = 0.0390625$

For contracting geometry of the form

$$g(\alpha) = 1 - (1-\alpha)^{1/3} \tag{9}$$

we arrive at the final equation

$$1-(1-\alpha)^{1/3}=\frac{\alpha}{3}+\frac{\alpha^2}{9}+\frac{5}{81}\alpha^3+\frac{10}{243}\alpha^4 \qquad (10)$$

For the Ginstling—Brounshtein equation which is of the form

$$g(\alpha)=(1-\tfrac{2}{3}\alpha)-(1-\alpha)^{2/3} \qquad (11)$$

we arrive at the final equation

$$(1-\tfrac{2}{3}\alpha)-(1-\alpha)^{2/3}=\tfrac{1}{9}\alpha^2+\tfrac{8}{81}\alpha^3+\ldots \qquad (12)$$

For the first-order nucleation type mechanism, we must first expand the logarithmic form.

Thus, for the nucleation of the form

$$g(\alpha)=-\ln(1-\alpha) \qquad (13)$$

we arrive at the final form

$$-\ln(1-\alpha)=\alpha+\frac{\alpha^2}{2}+\frac{\alpha^3}{3}+\ldots \qquad (14)$$

For the two-dimensional diffusion equation which is of the form

$$g(\alpha)=(1-\alpha)\ln(1-\alpha)+\alpha \qquad (15)$$

we arrive at the final equation

$$(1-\alpha)\ln(1-\alpha)+\alpha=\tfrac{1}{2}\alpha^2+\tfrac{1}{3}\alpha^3+\tfrac{1}{12}\alpha^4 \qquad (16)$$

We run into higher-order models which do not lend themselves readily to a series expansion. In that case we could either approximate such models and then by checking the resultant coefficients we could infer as to the nature of the model or simply use other techniques for those difficult models. If there are deviations in the model, they will manifest themselves by deviations in the fraction reacted. Once again, this may be due to the inadequacy of the model or it may be due to a change in mechanism of reaction.

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