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Note

NUMERICAL DATA FOR THE COMMONLY USED SOLID-STATE REACTION EQUATIONS

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A table of ln g(α) for α ranging from 0.001 to 0.999 at increments of 0.001 for the common forms of g(α) for nine commonly used solid-state reaction equations has been evaluated. The use of the table for the evaluation of reaction mechanisms and the determination of kinetic parameters from a single non-isothermal run has been explained.

Deduction of the mechanism of a thermal decomposition reaction by use of non-isothermal kinetic methods has been discussed by Sestak and Berggren [1] and Satava [2]. The procedure used by Satava is based on the assumption that the non-isothermal reaction proceeds in an infinite time interval isothermally, where the rate may be expressed as

$$\mathrm{d}\alpha/\mathrm{d}t = Z \exp(-E/RT)\mathrm{f}(\alpha) \tag{1}$$

where f(α) depends on the mechanism of the process, α, and E, R, T and Z are the fraction decomposed, energy of activation, gas constant, absolute temperature and frequency factor, respectively. With a constant temperature increase, $\mathrm{d}T/\mathrm{d}t = \phi$, integration of eqn. (1) leads [3,4] to

$$\int_0^{\alpha} \mathrm{d}\alpha/\mathrm{f}(\alpha) = \mathrm{g}(\alpha) = ZE/R\phi\,\mathrm{p}(x) \tag{2}$$

where p(x) is defined [3–6] as

$$\mathrm{p}(x) = \exp - x/x - \int_{+x}^{\alpha} \exp - u/u\,\mathrm{d}u = \exp - x/x + E_i(-x) \tag{3}$$

where $u = E/RT$, $x = E/RT_\alpha$ and T_α is the temperature at which the fraction α of the starting material has reacted.

From the logarithmic form of eqn. (2)

$$\ln \mathrm{g}(\alpha) - \ln \mathrm{p}(x) = \ln ZE/R\phi \tag{4}$$

it can be seen that the right-hand side is independent of temperature, while the left-hand side is temperature dependent. To a first approximation, the function ln p(x) is a linear function of $1/T_\alpha$ if x is sufficiently large and, therefore, ln g(α) must also be a linear function of $1/T_\alpha$. For the correct

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mechanism, ln g(α) vs. $1/T$ should be a straight line [2]. For other incorrect mechanisms this will not be true. Although the sensitivity of this procedure for the determination of mechanisms is not very high, it yields very useful information.

In non-isothermal kinetic studies E is evaluated from the slope tan β of the straight-line approximation of the plot of ln g(α) vs. $1/T$ by using one of the following equations [7]

$$E = \frac{-449 + \tan\beta/2.303}{217} 10^3 \text{ (cal/mol)} \tag{5}$$

$$E = \frac{1.987}{2}\left(-\tan\beta + \left(\tan^2\beta + 8\tan\beta\bar{T}\right)^{1/2} \text{ (cal/mol)}\right. \tag{6}$$

The latter is considered to be a more appropriate approximation because it takes into consideration the position of the line in the temperature scale ($\bar{T}_{av}$). The intercept of the plot gives ln Z from which Z is calculated.

The method given above for the handy evaluation of the reaction mechanism and the determination of associated kinetic parameters from a single non-isothermal run is believed to be well founded and, because of its simplicity, has become a basic method in regular kinetic investigations.

Many of the equations that are used for studying the kinetics of solid-state reactions (Table 1) are of the form g(α) = kt where g(α) depends on the mechanism controlling the reaction [2]. In order to elucidate the mechanism and the associated kinetic parameters from a single non-isothermal run by the method described above, it is necessary to have a table of ln g(α) at

TABLE 1

Kinetic equations

Function	Equation	Rate-controlling process
D_1	$\alpha^2 = kt$	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha = kt$	Two-dimensional diffusion,cylindrical symmetry
D_3	$[1-(1-\alpha)^{1/3}]^2 = kt$	Three-dimensional diffusion,spherical symmetry; Jander equation
D_4	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3} = kt$	Three-dimensional diffusion, spherical symmetry; Ginstling–Brounshtein equation
F_1	$-\ln(1-\alpha) = kt$	Random nucleation, one nucleus on each particle
A_2	$[-\ln(1-\alpha)]^{1/2} = kt$	Random nucleation; Avrami equation I
A_3	$[-\ln(1-\alpha)]^{1/3} = kt$	Random nucleation; Avrami equation II
R_2	$1-(1-\alpha)^{1/2} = kt$	Phase boundary reaction, cylindrical symmetry
R_3	$1-(1-\alpha)^{1/3} = kt$	Phase boundary reaction, spherical symmetry

intervals of α for the common forms of $g(\alpha)$. The table given by Giess [8] for $g(\alpha)$ is limited to the data for diffusion-controlled reactions. Sharp et al. [9] have given numerical tables of $g(\alpha)$ for nine equations corresponding to reactions which are diffusion controlled, reaction-rate controlled, obey first-order kinetics, or follow the Avrami–Erofeev equation. Their table of $g(\alpha)$ is for increments of $\alpha = 0.01$. However, tables of $\ln g(\alpha)$ at smaller increments of α (0.001) for the common forms of $g(\alpha)$ and the commonly used solid-state reaction equations will be more useful for the analysis of data.

Values of $\ln g(\alpha)$ for the nine commonly used reaction equations have been evaluated using functional values of α that were obtained with the computer program FORTRAN IV*. The values of $\ln g(\alpha)$ given in the tables could be used directly for the quick analytical computation of data for the evaluation of kinetic parameters as described earlier. Whereas the tables of Giess [8] and Sharp et al. [9] give values of $g(\alpha)$, the present data give values of $\ln g(\alpha)$ which could be directly used for analysis and therefore, in this respect, are a definite improvement on the earlier ones. Moreover, this table will be of immense use in laboratories where computing facilities are not available.

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* A table of these values had been deposited with, and can be obtained from Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/302/Thermochim. Acta, 83 (1984) 387.