

Note

GRAPHICAL ANALYSIS OF ISOTHERMAL TG DATA FOR MECHANISM

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This paper is a follow-up to previous publications [1,2] which involve graphical analysis of non-isothermal TG data for mechanism (or for n in n -type reactions). The graphical analysis method is now extended to isothermal TG data.

As previously indicated [3], isothermal kinetics of a solid-state reaction can be represented in a general manner by the expression

$$g(\alpha) = kt \quad (1)$$

where, $g(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$, k = rate constant, t = elapsed reaction time, and α = degree of conversion. From eqn. (1), for two different values of t for any particular isothermal TG curve

$$\frac{t_1}{t_2} = \frac{g(\alpha_1)}{g(\alpha_2)} \quad (2)$$

From eqn. (2), it is apparent that for a constant value of t_1/t_2 , values of α_1 , α_2 data sets for various theoretical solid-state mechanisms can be readily estimated. Thus, values of α_1 vs. α_2 at an arbitrary time ratio of two, can be plotted for the various mechanisms. Such plots have already been constructed for twelve different theoretical mechanisms involving non-isothermal TG data [(RH)₂/(RH)₁ = 2] [1,2] and they also apply to isothermal TG data ($t_1/t_2 = 2$). For this reason, these plots are not presented in this paper.

TESTING THE GRAPHICAL METHOD

In order to test the preceding graphical procedure for isothermal data ($t_1/t_2 = 2$), literature data was employed. Thus, Brown and Phillpotts [4] used the kinetic parameters $E = 23.9$ kcal mole⁻¹, $A = 1.8832 \times 10^{15}$ min⁻¹, and calculated the following α , t (min) values at 300 K for an R3-type contracting volume mechanism: 0.203,10; 0.377,20; 0.523,30; 0.645,40; 0.743,50; 0.822,60; 0.883,70; 0.928,80. By utilizing the graph in ref. 2, the

following values of α are obtained for an R3-type mechanism [corresponding t values (min) are given in parentheses]: 0.375 (20), 0.645 (40), 0.825 (60), 0.925 (80). The agreement is excellent and most assuredly denotes that an R3 mechanism prevails.

In addition to isothermal solid-state reactions, the preceding graphical method can be applied to determine first-order or pseudo-first-order reactions in solution. Thus, Frost and Pearson [5] have tabulated raw kinetic data for the cleavage of diacetone alcohol to acetone in the presence of a large excess of alkali at 25°C. The following graphically interpolated values of α , t (sec) were obtained, respectively: 0.40, 30; 0.455, 35; 0.50, 40; 0.545, 45; 0.58, 50; 0.65, 60; 0.71, 70; 0.755, 80; 0.795, 90; 0.83, 100; 0.86, 120. By utilizing the graph in ref. 1 for n -type reactions, the following values of α were obtained for $n = 1$ [$t_1/t_2 = 2$ and t values (sec) are in parentheses]: 0.64 (60), 0.705 (70), 0.755(80), 0.793 (90), 0.82 (100), 0.88 (120). These results are in excellent agreement with the interpolated experimental values for a pseudo-first-order reaction. This reaction has been found [5] to be pseudo-first-order, being dependent on the first power of the diacetone alcohol concentration and on the first power of the hydroxide ion concentration (the latter, however, remains constant during the reaction).

When accurate α and t values are employed, the plots depicted in refs. 1 and 2 (or similar plots at values of t_1/t_2 other than two) can provide strong support for certain solid-state mechanisms (or for unimolecular reactions in solution or gas phase) determined from isothermal TG (or DSC) data by other more classical procedures. Of course, after mechanism has been established, kinetic parameters such as E and A can be estimated.

REFERENCES

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