Thermodynamic Data for Decomposition Reactions studied by Differential Scanning Calorimetry: a Cautionary Note

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A RECENT COMMUNICATION[1] has prompted us to draw attention to the difficulties associated with the use of thermoanalytical techniques in deriving certain thermodynamic data. Olafsson and Byran[1] in their study of amino-acid complexes employ an approach based on Kissinger's method,[2] which was devised to study the kinetics of reactions of the type $A(s) \rightarrow B(s) + C(g)$ by following the variation in the position of peak maxima as a function of heating rate in differential thermal analysis (DTA). The use of differential scanning calorimetry† in place of DTA disposes of one of the deficiencies, previously noted,[3] of Kissinger's method—that the maximum reaction rates do not, in general, occur at the peak maxima in DTA. But more fundamental objections still remain. The equation cited by Olafsson and Byran[1] is based on the assumption that the rate of decomposition of solids may be represented by:

$$d\alpha/dt = k(1-\alpha)^n \exp(-E/\boldsymbol{R}T) \qquad (1)$$

where k is a rate constant, α is the fraction decomposed in a time t, n is the order of reaction, which has an activation energy E. Recently,[4,5] we have demonstrated the general untenability of equation (1) in solid-state decompositions. In the first place it is misleading, if not meaningless, to use the concept of reaction order. The alternative and legitimate kinetic formulations are well-known,[6,7] and are of quite a different form from that which normally applies for reactions in the liquid phase [where (1) is valid and may be used[3] in kinetic studies employing DTA]. In certain circumstances (*e.g.* during deceleration of reaction when

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† A better term is differential enthalpic analysis (DEA).

$\alpha \rightarrow 1$) an equation of the form $d\alpha/dt = k(1 - \alpha)$, ostensibly of "first order" may, however, be justifiably employed. But, in all instances, the activation energy that appears in equation (1) is imprecisely defined and it is not known to which of the many (or combinations of many) processes such as nucleation, interface recession, consecutive decompositions, *etc.*, it refers. Moreover, it does not seem prudent to imply, as do Olafsson and Byran,[1] that the activation energies for the thermal decomposition of copper complexes of amino-acids may be quantitatively related to thermodynamic data for these solids. It is salutary to recall that in many much simpler systems[9,10] for which enthalpy and activation energy data have been collected separately, there appears to be no obvious correlation between the two.

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