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Note

Proportionality between the extent of reaction and enthalpy

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The determination of kinetic parameters from thermal analysis studies (differential thermal analysis and differential scanning calorimetry) involves numerous assumptions. Seldom are these stated explicitly and hardly ever are they investigated. In this paper we are concerned with the assumption of a direct proportionality between the extent of reaction and the enthalpy change. It lies at the heart of obtaining the triplet of information: rate, temperature and extent of reaction, which is the starting point for kinetic investigations. Such an assumption must be made because the thermal analysis curve does not provide independent information about the relationship between extent of reaction and the enthalpy change. However, it is necessarily true only for certain ideal thermodynamic processes.

The systems studied by thermal analysis seldom lend themselves to alternative methods of investigation. A recent investigation of the kinetics of the solid-state reaction between tungsten and potassium dichromate provided the opportunity for making a comparison between the use of thermal analysis and spectrophotometry for the determination of extent of reaction. The stoichiometry of the reaction can be represented by the equation [1] $W + 2K_2Cr_2O_7 = WO_3 + 2K_2CrO_4 + Cr_2O_3$. The use of spectrophotometry to determine the extent of reaction has been based on the determination of the chromate ion [2]. The analysis is made complicated by the equilibrium established between dichromate and chromate ions in solution $Cr_2O_7^{2-} + H_2O = 2CrO_4^{2+} + 2H^+$. By working with alkaline solutions we have ensured that the equilibrium is displaced to the chromate ion. Thus for the stoichiometric reaction the amount of chromate ion determined will fall from four moles to two moles as the reaction proceeds to completion.

The experiments were carried out using a mixture containing 50% tungsten and 50% potassium dichromate (by weight). This mixture contains a two-fold excess of tungsten. It was prepared by sieve-mixing the weighed components. The tungsten (Murex) had a particle size of 1.0 μm measured by the Fisher sub-sieve sizer. Potassium dichromate was ball-milled to a particle size of 6 μm.

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Samples of the mixture were sealed in glass tubes under vacuum and heated in an oven for varying periods (45 min to 90 h) and temperatures (630–660 K). For analysis by spectrophotometry, 1 mg samples were extracted with 0.05 mol dm^{-3} aqueous KOH and made up to 100 cm^3. The absorbance was measured at a wavelength of 373 nm using a Perkin–Elmer scanning spectrophotometer (model 402). The concentration of chromate ion was calculated from the Beer–Lambert relationship. The absorption coefficient $\epsilon = (4.81 \pm 0.01) \times 10^3$ dm^3 mol^{-1} cm^{-1} was measured in subsidiary experiments and is in agreement with the values reported in ref. 2. The fractional extent of reaction was calculated from the relationship $\alpha = 2 - [CrO_4^{2-}]/[Cr_2O_7^{2-}]$ where $[Cr_2O_7^{2-}]$ is the concentration of the dichromate ion corresponding to the initial mixture.

The determination of the extent of reaction by thermal analysis was based on a comparison between the enthalpy change measured for the partially reacted residues and that for the initial sample. The measurements were made using two thermal analysers both manufactured by Stanton Redcroft (now PL Thermal Sciences), DTA model 674 and DTA–TG model STA 781. The samples were heated at 10 K min^{-1} in platinum crucibles to a temperature of about 900 K. An atmosphere of argon was maintained in the apparatus to prevent aerial oxidation of the tungsten. The presence of unreacted potassium dichromate in the residues from the oven was indicated by the fusion endotherm at about 670 K, followed by an exotherm from the subsequent reaction with tungsten. The enthalpy change was calculated for the *isothermal* reaction at the same temperature used in the oven experiments. The net area of the peaks was corrected for the contribution of the heat capacity of the reaction system. The enthalpy change was measured for the initial mixture and corrected to the same temperature. The fractional extent of the reaction in the oven was calculated as $\alpha = (\Delta H_i - \Delta H_r)/\Delta H_i$ where ΔH_r is the enthalpy change measured for the partially reacted residue and ΔH_i is the enthalpy change for the initial mixture (corresponding to complete reaction). The exotherm obtained for the partially reacted samples was broad, often delayed until fusion of the potassium dichromate was complete, and extending to 850 K. This may be compared with the unreacted samples where the exotherm immediately followed the onset of fusion.

The results obtained by spectrophotometry and thermal analysis are compared in Fig. 1. There is a correspondence between the analytical results obtained by the two techniques which lends support to the use of thermal analysis to measure extents of reaction. The results are persuasive but the spectrophotometric measurements are not independent of a knowledge of the stoichiometry of the reaction between tungsten and potassium dichromate. Because the reaction is gas-less and there is no mass transfer from the system, the heat capacity corrections are not large (1–2% of the enthalpy changes) but in principle must be incorporated. In systems which

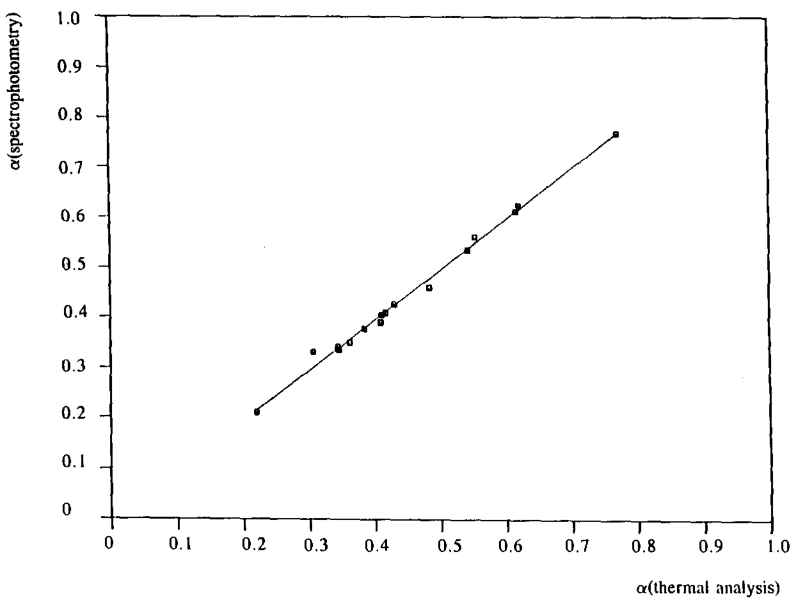

Fig. 1. Comparison between the fractional extent of reaction determined by spectrophotometry and by thermal analysis.

are gassy the effective change in heat capacity may be large but because the thermodynamic system is no longer closed, the interpretation of the curves becomes less certain.

REFERENCES

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