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Note

CAN A RATE CONSTANT INDEPENDENT OF SAMPLE SIZE BE OBTAINED FROM THE RATE EQUATION GENERALLY USED IN THERMAL ANALYSIS?

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I believe that the answer to this question raised by Gy. Pokol [1] can only be 'NO' in all cases where reactions are concerned involving the loss of water vapor from fine-grained solids such as clay minerals. The reason for the emphatic 'NO' arises from the dependence of the reaction not only on temperature and time, but also on the variable water vapor pressure generated by the reaction itself. Perhaps in an ideally dispersed sample the water vapor pressure might be controlled sufficiently by the temperature of the surrounding equipment, but in any actual experiments where even small samples are loosely contained in sample holders, some variation of $p(H_2O)$ must inevitably occur within the sample studied.

In extreme cases, the effects of the generated water vapor pressure can be very large and exemplify the nature of the effect. Thus, with a pressed disc of kaolinite about 3 mm thick heated isothermally at 517°, the exterior surface can be about 95% dehydroxylated when the interior is no more than 40% reacted. Discs prepared under similar pressure conditions and ranging in thickness from about 0.4–2.7 mm thickness and heated isothermally at 497° showed dramatically different rates of overall dehydroxylation [2].

These experiments, now old history, showed strikingly the effect of entrapped water vapor on the reaction rates. These inherent problems are greatly reduced by using small samples of loosely packed material but can it ever be asserted that in kinetic experiments which involve the removal of water from surfaces and from the ambient atmosphere wholly eliminate the effect of the water vapor released by the reaction?

Experiments under isothermal conditions with small and loosely dispersed samples under conditions of controlled water vapor pressure offer a better solution to these inherently difficult questions [3, 4], but they take much longer to carry out.

References

1 Gy. Pokol, J. Thermal Anal., 23 (1982) 235.

2 G. W. Brindley and M. Nakahira, Clay Minerals Bull., 3 (1957) 114.

3 G. W. Brindley, J. H. Sharp, J. H. Patterson and B. N. N. Achar, Amer. Mineral., 52 (1967) 201.

4 G. W. Brindley, B. N. N. Achar and J. H. Sharp, Amer. Mineral., 52 (1967) 1697.