Note

SOME COMMENTS ON VOLD'S THEORY OF DTA CURVE DESCRIPTION

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The rich literature concerning the description of DTA curves [1 − 10] is generally consistent with the fact that

$$\Delta H = k \cdot S \tag{1}$$

where ΔH = heat exchanged during the reaction observed, S = area of the DTA peak, and k = constant. This consistency of the results of the theoretical considerations must give rise to certain doubts, such as:

(1) The similar forms of Eq. (1) are obtained indepently of the structure of the apparatus, the type of the holder used and the method of temperature measurement, although it is obvious that the structure of the crucible [11], the so-called DDK, will affect the result, as will the ring thermocouple, and the result will also be different depending on whether a metal block is used, etc.

(2) There is no clear viewpoint as to the form of the function dependence k. It is not clear if k is a function merely of the apparatus properties or also of the sample properties, e.g. its specific heat or thermal conductivity. A list of some of the factors, e.g. the kind of gas used, the system geometry, which usually ends with "etc.", is clear evidence for this.

(3) It is not clear what should be considered as the reference areas S. The previous doubts [1, 10, 12 − 17] did not lead to an explicit explanation [18, 19].

Among the numerous models of DTA curve description, Vold's theory [3] can be found rather frequently in manuals discussing the method of thermal differential analysis [20 − 23]. According to this theory the equation of the peak area (1) is obtained by integrating the equation

$$\frac{d(\Delta T)}{dt} + A[\Delta T - (\Delta T)_x] = \frac{\Delta H}{C} \frac{dx}{dt} \tag{2}$$

where ΔT = the difference between the temperatures of the standard and tested substances, ΔH = amount of heat exchanged with the environment during the reaction, dx/dt = reaction rate, c = specific heat, t = time, and $(\Delta T)_x$ = constant.

The form dx/dt has been limited in no way. To check this conception it has been assumed that

$$dx/dt = a = \text{constant} \tag{3}$$

Taking into account this additional assumption the solution of Eq. (1) has the form

$$\Delta T = \frac{\left[A(\Delta T)_x + \frac{\Delta H}{c} a \right]}{a} - \frac{K}{A} \exp(-At) \tag{4}$$

where K = integration constant. Thus

$$\frac{d(\Delta T)}{dt} = K \exp(-AT) \tag{5}$$

i.e.

$$\frac{d(\Delta T)}{dt} \neq 0 \tag{6}$$

for each t value. Because function (4) is continuous and integrable, it cannot describe the DTA peak curve as in Fig. 1 [24]. The equation presented above shows the existence of error in the theory discussed.

The process recorded by the DTA peak is the sum of both the reaction itself, which is connected with the heat emmission and absorption, and the process of temperature compensation between the sample and the environment. Excessive simplification of the description of this phenomenon must lead to an inconsistency.
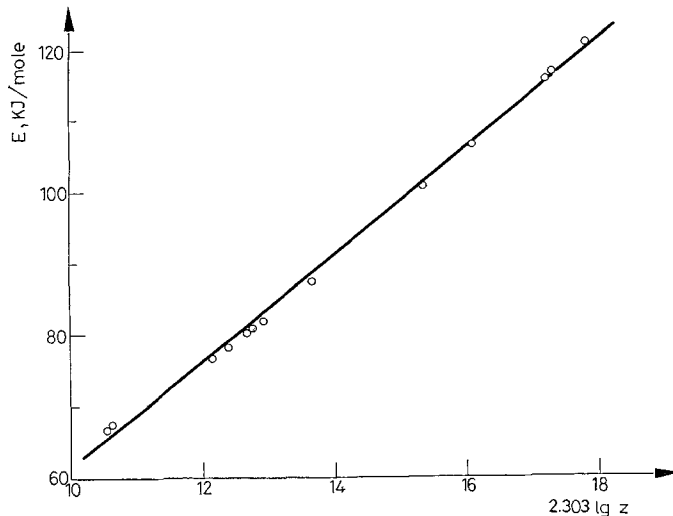

Fig. 1

In the light of the previously performed elaborations of the problems of heat exchange [25], simple and elegant solutions should not be expected even in comparatively uncomplicated cases. Perhaps the only acceptable answer is a numerical solution of specific heat-exchange test problems, [26] which can ensure a full use of the information contained in the DTA curve.

References

1. S. L. SPEIL, H. BERKELHAMER, J. A. PASK and B. DAVIS, U. S. Dep. Interior Bur. Mines, Techn. Pap., 664 (1945).
2. E. C. SEWELL, A theoretical Treatment of Quantitative DTA, Research Note Bulding Research Station, Watford, 1960.
3. M. J. VOLD, Anal. Chem., 63 (1941) 2915.
4. J. J. KERR and J. L. KULP, Am. Mineralogist, 33 (1948) 387.
5. S. L. BOERSMA, J. Am. Ceram. Soc., 38 (1955) 281.
6. W. LUGSCHEIDER, Ber. Bunsen physik. chem., 71 (1967) 228.
7. J. J. KESSIS, C. R. Acad. Sci., Paris, 270C (1970) 1201.
8. G. L. BERG and V. P. EGUNOW, J. Thermal Anal., 1 (1970) 3.
9. N. SMAJIČ, Thermal Analysis, Proc. 4 ICTA, Budapest 1974, vol. 1. 271.
10. R. C. Mackenzie (ed.) Differential Thermal Analysis, Academic Press, London, New York 1970, vol. 1. p. 31—62.
11. H. E. SCHWIETE and G. ZIEGLER, Ber. Deut. Keram. Ges., 35 (1958) 193.
12. G. ADAM and F. H. MULLER, Z. Polymere, 192 (1963) 29 - 34.
13. F. H. NORTON, J. Am. Ceram. Soc., 22 (1939) 54.
14. L. A. DEAN, Soil Sci., 63 (1947) 95.
15. M. WITTELS, Am. Mineralogist, 36 (1951) 615.
16. S. KRAIS, Silikaty, 7 (1963) 52.
17. J. ŠESTAK and G. BERGGREN, Chem. Listy, 80 (1970) 695.
18. R. C. MACKENZIE and P. F. S. RICHTIE, Thermal Analysis, Proc. 3 ICTA, Davos 1972, vol. 1. p. 37.
19. H. G. MC ADIE, Thermal Analysis, Proc. 4 ICTA, Budapest 1974, vol. 1., p. 251—255.
20. D. SCHULTZE, Differentialthermoanalyse, VEB Deutscher Verlag der Wissenschaften, Berlin 1971.
21. W. J. SMOTHER and Y. CHIANG, Handbook of Differential Thermal Analysis, Chemical Publishing Co. In., New York 1966.
22. A. P. ROLLET and R. BOUAZIS, L'analyse thermique, Gauthier-Villars, Paris 1972.
23. C. J. KEATTCH and D. DOLIMORE, An Introduction to Thermogravimetry, Heyden and Son, London, New York, Rheine 1975.
24. G. A. KORN and T. M. KORN, Mathematical Handbook, McGraw-Hill Book Co., New York, San Francisco, Toronto, Sydney 1968.
25. H. S. CARSLAW and J. C. JAEGER, Conduction of Heat in Solid, Clarendon Press, Oxford 1935.
26. G. C. PILOYAN, K. A. SEMENDYAYEV and I. B. KUDINOV, Thermal Analysis, Proc. 4 ICTA, Budapest 1974, vol. 1, p. 57.