An inconsistency in the second dissociation constant data of sulphuric acid at elevated temperatures and pressures

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Recently, Franck, Hartmann and Hensel[1] published information on the second dissociation constant (K_2) of sulphuric acid as a function of temperature and pressure. They made conductance measurements at temperatures from 45° to 190°C and at pressures from one to 8000 bars. Unfortunately, if one extrapolates these results over a very short temperature interval, *i.e.* to 25°C, 1 bar, the value obtained for K_2 is 0·017 mol. 1⁻¹. This value is in considerable disagreement, about 50 per cent, with values derived by a large number of other workers.

In a paper by Covington, Dobson and Wynne-Jones[2] it was shown by the analysis of new e.m.f. data and comparison with at least five other workers, that the value should be around 0·011 mol. kg⁻¹ at 25°C. Also, it was shown that total variation in values derived from the different sources were within 5 per cent of this value.

The present observation therefore suggests that the results of Franck *et al.* are in considerable error, at least in the 1 bar range, *i.e.* 6·84, 0·821, 0·161, 0·086 mol. 1.⁻¹ $\times$ 10³ for K_2 at 45°, 100°, 160° and 190°C, respectively. The accompanying graph (Fig.) of an almost linear plot of pK_2 against $1/T°10^3$ K shows the discrepancy clearly.

The source of this discrepancy is not apparent. Slight differences in pressure units and concentration scales would not account for the differences. It could be that there is a discontinuity between 25° and 45°C. This, however, is most unlikely, as maxima and minima are generally noted at very much higher temperatures.[3] The bisulphate ion dissociation constant is known to exhibit maxima and minima at 120°, 220° and 250°C.

The reported experimental data of Franck *et al.* is of high internal consistency and if the values are to be used it would be perhaps better to apply a 'correction' term based on a K_2 of 0·011 mol. 1.⁻¹ at 25°C. The values of K_2 then at 45°, 100°, 160° and 190°C at 1 bar would be about 4·57, 0·588, 0·118, and 0·062 mol. 1.⁻¹ $\times$ 10³ respectively.

It is to be noted, of course, that the discrepancy may be operable at the more elevated and other pressures.
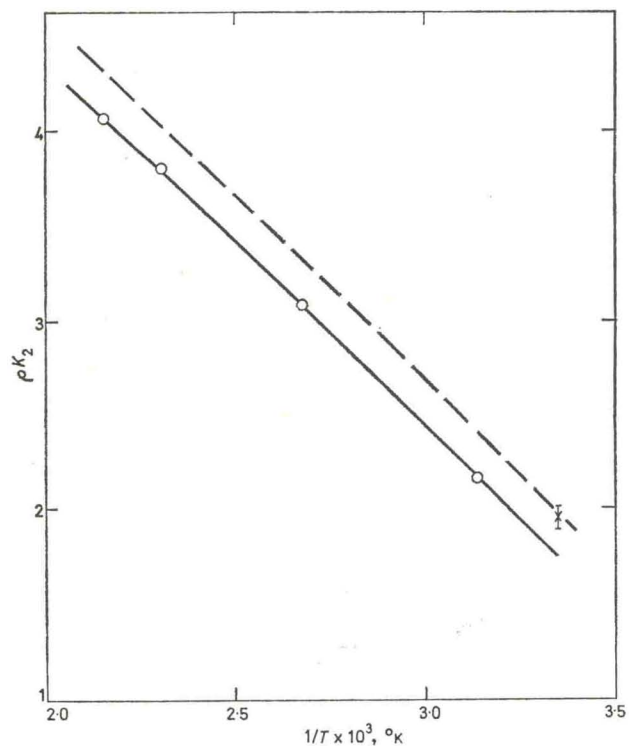
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Fig. *The temperature dependence of the second dissociation constant of sulphuric acid at 1 bar*
The variation of pK_2 *with temperature*
○ *Franck, Hartmann and Hensel*
⊤⊥ *Range of value at 25°C from Covington, Dobson & Lord Wynne-Jones, and other workers in reference 2.*

References

[1] Franck, E. U., Hartmann, D. & Hensel, F., *Disc. Faraday Soc.*, 1965, **39**, 200

[2] Covington, A. K., Dobson, J. V. & Lord Wynne-Jones, *Trans. Faraday Soc.*, 1965, **61**, 2057; a bibliography is also contained in this paper.

[3] Makisimova, I. N., *Russ. J. phys. Chem.*, 1967, **41**, 27