Letters

The nickel(II)–bromide system in dimethyl sulphoxide

In a paper by Griffiths and Phillips[1] stoichiometric stability constants 'K' were calculated and the values then used to derive thermodynamic properties of the solutions under study.

For the reaction (1) this is incorrect because the equi-

$$[NiBr_2(dmso)_4] + Br^- \rightleftharpoons [NiBr_3(dmso)]^- + 3dmso \quad (1)$$

librium constant must take into account the bromide-ion concentration and, since dimethyl sulphoxide (dmso) is also the solvent, expression (2) is applicable.

$$K = [NiBr_3(dmso)]^-/[NiBr_2(dmso)_4][Br^-] \quad (2)$$

From their Table 1 we have deduced that the concentration of Ni^{2+} was about 0.02683 mol dm^{-3}. Since the amount of Br^- complexed with Ni^{2+} and dmso is limited to between 2 × 0.02683 and 3 × 0.02683 (*i.e.* 0.054–0.081) mol dm^{-3} it seemed reasonable to assume that the bromide concentrations calculated from their Table 2 at 403 K are probably constant over the whole temperature range for each of the different Br:Ni experiments.

We have recalculated the equilibrium constants and the results are given in Fig. 1. However, we have only used data at the Br:Ni ratios 41.1, 60.4 and 82.4 at the temperatures given in their Fig. 1. Although there is some scatter at the higher temperatures the data can now be represented by a single straight line, giving ΔH = 47.9 kJ mol^{-1}. We therefore suggest there is no need to call up any special theories to account for the variation of ΔH with Br:Ni ratio which makes their Fig. 7 redundant.

George S. Perry*
Robert F. Watson
Atomic Weapons Establishment
Building A75
Aldermaston
Reading RG7 4PR, UK

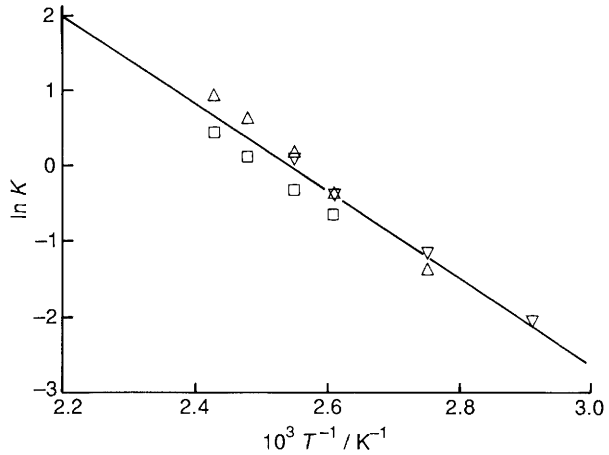

Fig. 1 Variation of equilibrium constant with temperature and Br:Ni ratio (■, 41.1:1; △, 60.4:1; ▽, 82.4:1)

References

1 T. R. Griffiths and N. J. Phillips, *J. Chem. Soc., Dalton Trans.*, 1989, 325.

Received 10*th December* 1990; *Paper* 0/05560C