

THE STABILITY CONSTANT OF THE TRIS-1,10-PHENANTHROLINE FERROUS ION*

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Dwyer and Nyholm (1946) first determined the stability constant of the intensely red coloured tris-1,10-phenanthroline ferrous ion (ferroin). No evidence had been reported for other species involving ferrous ion and phenanthroline. Assuming no interaction between ferric ion and phenanthroline they attributed the change in redox potential of the ferrous-ferric couple caused by the addition of phenanthroline to be due to the formation of the tris complex ferrous ion. The $\log K_s$ for the overall stability constant was found to be 17.7. Subsequently Dwyer and McKenzie (1947) determined the constant for the tris-2,2'-dipyridyl ferrous ion by a similar method and obtained a $\log K_s$ of 16.4 ± 0.5 . At the same time McKenzie (1947) demonstrated that citrate ion interfered markedly in the determination of iron by dipyridyl, but not in the determination of phenanthroline. This work showed that the phenanthroline complex was more stable than the redox results indicated.

Baxendale and George (1950) showed by kinetic and equilibrium measurements that $\log K_s$ for the dipyridyl complex was 17.1 in reasonable agreement with the redox determination. However, spectrophotometric and kinetic studies of ferroin by Lee, Kolthoff, and Leussing (1948*a*, 1948*b*) gave a $\log K_s$ of 21.3. Brandt, Dwyer, and Gyarfás (1954) presumed that the discrepancy of the ferroin constant based on redox measurements is due to an uncorrected interaction between ferric ion and phenanthroline. This is believed by Smith (1949, personal communication) to be in the form of a yellow-brown complex.

In the present work a redetermination of $\log K_s$ for ferroin has been made using the redox method. Care was taken to avoid a large excess of chelate since this shifts the redox potential to the very poorly poised region, with resultant difficulty in obtaining an accurate stable potential. The pH was kept in the region of 1.5, since the work of Harvey and Manning (1952) indicated that at this pH the equilibrium interaction of ferric ion and phenanthroline is negligible. Furthermore, spectrophotometric measurements at 396 and 512 m μ were made using a procedure similar to that of Harvey, Smart, and Amis (1955). These showed that there was no appreciable interaction of ferric ion and phenanthroline under the experimental conditions. The general procedure and conditions of ionic strength were similar to those of Dwyer and McKenzie (1947).

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Results and Discussion

In Table 1 are shown the pH of the reaction mixture; ΔE , the shift in redox potential; (phen H)⁺, the molar concentration of free phenanthroline ion; and the log K_s of the overall stability constant of ferroin at 25 °C.

TABLE 1
DETAILS OF REACTION MIXTURE

pH	ΔE (V)	Concentration (phen H) ⁺ (mole/l)	Log K_s
1.44	0.110	0.00205	21.2
1.45	0.0835	0.00109	21.6
1.37	0.135	0.00352	21.1

The mean log K_s value of 21.3 is in agreement with that of Lee, Kolthoff, and Leussing (1948a, 1948b). Thus under appropriate experimental conditions the redox method gives results for log K_s in accordance with the other methods and is in satisfactory agreement with the observed reactions of iron and phenanthroline.

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References

- BAXENDALE, J. H., and GEORGE, P. (1950).—*Trans. Faraday Soc.* **46**: 55.
 BRANDT, W. W., DWYER, F. P., and GYARFAS, E. C. (1954).—*Chem. Rev.* **54**: 259.
 DWYER, F. P., and MCKENZIE, H. A. (1947).—*J. Proc. Roy. Soc. N.S.W.* **81**: 97.
 DWYER, F. P., and NYHOLM, R. S. (1946).—*J. Proc. Roy. Soc. N.S.W.* **80**: 28.
 HARVEY, A. E., JR., and MANNING, D. L. (1952).—*J. Amer. Chem. Soc.* **74**: 4744.
 HARVEY, A. E., JR., SMART, J. A., and AMIS, E. S. (1955).—*Analyt. Chem.* **27**: 26.
 LEE, T. S., KOLTHOFF, I. M., and LEUSSING, B. L. (1948a).—*J. Amer. Chem. Soc.* **70**: 2348;
 LEE, T. S., KOLTHOFF, I. M., and LEUSSING, B. L. (1948b).—*J. Amer. Chem. Soc.* **70**: 3596.
 MCKENZIE, H. A. (1947).—*J. Proc. Roy. Soc. N.S.W.* **81**: 147.