

Figure 1. Extrapolation of conductance ratios to infinite dilution for KCl at 25°C

+ Ovenden, 2010 atm (27) ● Present work, 1925 atm
 — Theoretical limiting slope - - - Hand-drawn slopes

straight line through the data points. This generally leads to slopes too low and an extrapolant too high because the deviations from the limiting slope are negative at the higher concentrations (9). With this in mind, the extrapolation through the concentration-dependent data can be carried out more confidently (Figure 1).

Figure 1 shows that a single experimental point appropriately placed can yield an accurate infinite dilution value when used in conjunction with the theoretical limiting slope. This practice assumes that measurements can be made with enough confidence to rely upon a single data point at each temperature for a given salt system. In this regard, we carried out many hundreds of individual measurements prior to our point-slope program. The uncertainty in the single point is no greater than that introduced in extrapolating from a typically scattered set; thus, the procedure is justified by the saving of time.

Previous workers have variously treated the concentration dependence of κ_p/κ_1 . Körber found that for KCl solutions κ_p/κ_1 decreased monotonically in the range 10^{-4} – $3N$ —i.e., the concentration dependence was in the wrong direction (26). Ellis (7) reported that in the range 10^{-3} – $10^{-1}N$ for KCl and HCl the effect of concentration was negligible. One practice

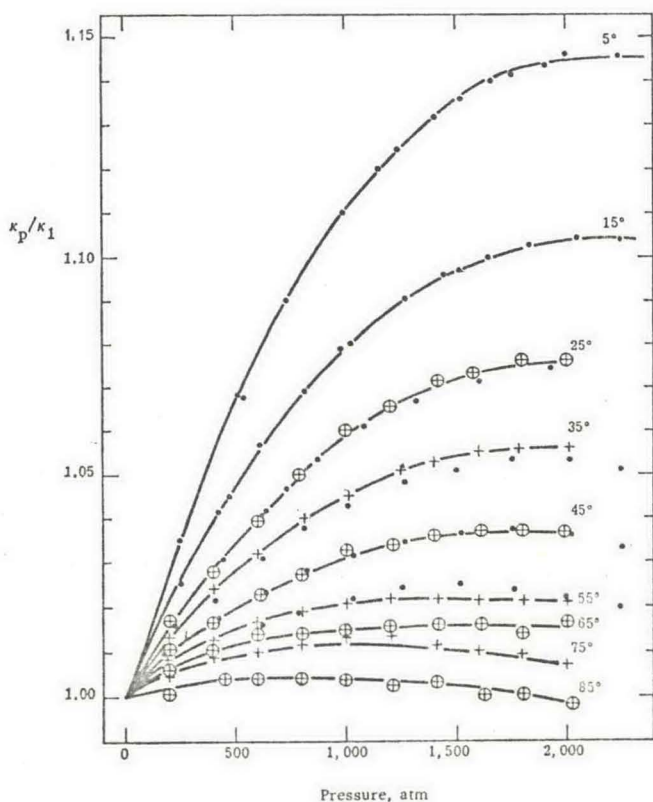


Figure 2. Conductance of KCl solutions at infinite dilution as function of pressure

⊕, + Ovenden (27) ● Present work

is to disregard the relatively small concentration dependence and to take results at one concentration, say 10 mM (22). This procedure introduces a systematic pressure- and temperature-dependent error at infinite dilution (0.35% at 25°C and 2000 atm for NaCl) (9).

The most careful work to date is that of Ovenden (27). Figure 2 compares our infinite dilution data with those of Ovenden for KCl. Agreement is excellent—typically 0.1% and never worse than 0.2%—contrasted with previous disagreements in the literature, even at high concentrations as discussed by Ellis (7), Hamann (10), and Horne et al. (22).

ACKNOWLEDGMENT

The authors extend their appreciation to Helmut Lingertat, who assisted in carrying out the experimental work.

LITERATURE CITED

- (1) Brummer, S. B., *J. Chem. Phys.*, **42**, 1636 (1965).
- (2) Brummer, S. B., Gancy, A. B., "Investigation of Ion Mobility in Aqueous Solutions," Final Report, Contract No. 14-01-0001-966, covering period June 18, 1966–September 30, 1969. Prepared for Department of the Interior, Office of Saline Water, Washington, D.C. 20240.
- (3) Brummer, S. B., Hills, G. J., *Trans. Faraday Soc.*, **57**, 1816 (1961).
- (4) Brummer, S. B., Hills, G. J., *ibid.*, **57**, 1823 (1961).
- (5) Buchanan, J., PhD thesis, University of Sydney, Sydney, Australia, 1953.
- (6) Buchanan, J., Hamann, S. D., *Trans. Faraday Soc.*, **49**, 1425 (1953).
- (7) Ellis, A. J., *J. Chem. Soc.*, 1959, p 3689.
- (8) Gancy, A. B., Brummer, S. B., *J. Electrochem. Soc.*, **115**, 804 (1968).
- (9) Gancy, A. B., Brummer, S. B., *J. Phys. Chem.*, **73**, 2429 (1969).
- (10) Hamann, S. D., "Physico-Chemical Effects of Pressure," Butterworths, London, England, 1957, Chap. 7, p 118.
- (11) Hamann, S. D., Strauss, W., *Trans. Faraday Soc.*, **51**, 1684 (1955).
- (12) Hamann, S. D., Strauss, W., *Discuss. Faraday Soc.*, **22**, 70 (1956).
- (13) Harned, H. S., Owen, B. B., "Physical Chemistry of Electrolyte Solutions," 3rd ed., Reinhold, New York, N.Y., 1957 p 179.
- (14) Horne, R. A., *Nature*, **200**, 418 (1963).
- (15) Horne, R. A., Bannon, W. J., Sullivan, E., Frysinger, G. R., *J. Electrochem. Soc.*, **110**, 1282 (1963).
- (16) Horne, R. A., Birkett, J. D., *Electrochim. Acta*, **12**, 1153–60 (1967).
- (17) Horne, R. A., Courant, R. A., *J. Chem. Soc.*, 1964, p 3548.
- (18) Horne, R. A., Courant, R. A., *J. Geophys. Res.*, **69**, 1971 (1964).
- (19) Horne, R. A., Courant, R. A., *J. Phys. Chem.*, **68**, 1258 (1964).
- (20) Horne, R. A., Courant, R. A., *J. Geophys. Res.*, **69**, 1152 (1964).
- (21) Horne, R. A., Frysinger, G. R., *ibid.*, **68**, 1967 (1963).
- (22) Horne, R. A., Myers, B. R., Frysinger, G. R., *J. Chem. Phys.*, **39**, 2666 (1963).
- (23) Howard, B., PhD thesis, University of London, London, England, 1963.
- (24) Jamieson, J. C., *J. Chem. Phys.*, **21**, 1385 (1953).
- (25) Jobling, A., Lawrence, A. C. S., *Proc. Roy. Soc. (London)*, **206A**, 257 (1951).
- (26) Körber, F., *Z. Phys. Chem.*, **67**, 212 (1909).
- (27) Ovenden, P. J., PhD thesis, University of Southampton, Southampton, England, 1965.
- (28) Stearn, A. E., Eyring, H., *J. Chem. Phys.*, **5**, 113 (1937).
- (29) Strauss, W., PhD thesis, University of Sydney, Sydney, Australia, 1955.
- (30) Weir, C. E., *J. Res. Nat. Bur. Stand.* **53**, 245 (1954).
- (31) Zisman, W. A., *Phys. Rev.*, **39**, 151 (1932).

RECEIVED for review July 6, 1970. Accepted June 15, 1971. This work was supported by the Office of Saline Water under Contracts OSW-14-01-00001-425 and OSW-14-01-001-966.