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3.9 Electrochemistry

3.9.1 Standard solutions for calibrating conductivity vessels

The primary standards for conductivity for KCl solutions were established by Jones and Bradshaw (1933) using the demal unit for concentration and the international ohm. In 1948 the international ohm was replaced by the absolute ohm as the unit of resistance. Recently, the standards have been redetermined at NIST (formerly NBS) in the USA using a cell with well-defined geometry (Wu, Pratt and Koch, 1989). It is proposed that the demal (D) unit be replaced eventually by molality and the measurements will be extended over the range 0–60 °C. There is good agreement between the redetermined values and corrected Jones and Bradshaw values.

Conductivity of potassium chloride solutions at 25 °C

g KCl per kg solution in vacuo	κ/(S cm^{-1})
7.474 58 (0.1 D)	0.012 854
0.745 819 (0.01 D)	0.001 408 6
7.455 10 (0.1 m)	0.012 821 7
0.745 510 (0.01 m)	0.001 407 9

Units: m/mol kg^{-1} H_2O; D/mol kg^{-1} solution.

The following equation, which gives the molar conductivity of aqueous potassium chloride solution at 25 °C in the range 0.01 mol dm^{-3} < c < 0.10

mol dm^{-3}, is also useful for cell calibration (Chiu and Fuoss, 1968):

$$\frac{\Lambda}{S\ cm^{-1}} = 149.79 - 94.84c^{1/2} + 58.65c \log c + 220.9c - 228.9c^{3/2}$$

A.K. Covington

« Previous Section

Next Subsection »

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