

# INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON PHYSICOCHEMICAL MEASUREMENTS  
AND STANDARDS\*

## RECOMMENDED REFERENCE MATERIALS FOR REALIZATION OF PHYSICOCHEMICAL PROPERTIES

(Recommendations 1976)

EDITOR: K. N. MARSH

### SECTION: ELECTROLYTIC CONDUCTIVITY

COLLATORS: E. JUHÁSZ & K. N. MARSH

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INTRODUCTION

Electrolytic conductivity  $\kappa$ , formerly called specific conductance, is defined by the equation

$$\kappa = j/E \quad (1)$$

where  $j$  is the electric current density and  $E$  is the electric field strength (Ref. 1). The SI unit for electrolytic conductivity is the Siemens per metre ( $S\ m^{-1}$ ).

As it is difficult and expensive to construct cells that have accurately known dimensions, it is usual to measure the electrolytic conductance of an electrolyte by use of a rigid cell for which the cell constant  $k_{cell}$  has been determined by means of a reference solution of known electrolytic conductivity. The relationship used for calibration of the cell is

$$k_{cell} = \kappa/G \quad (2)$$

where  $G$  is the conductance of the cell containing the reference solution and  $\kappa$  is the electrolytic conductivity of the reference solution. The SI unit for the cell constant is the reciprocal metre ( $m^{-1}$ ). At present the only values of conductivity known sufficiently accurately to be used for reference purposes are those of aqueous solutions of potassium chloride. Potassium chloride of high purity is available and the solutions prepared from it on a mass basis as suggested by Jones and Bradshaw (Ref. 2) are reproducible and stable.

The recommendations given here were taken from reference 2 and recalculated by use of the conversion: international ohm = 1.00049 ohm. The values were then corrected for the effect of the difference between IPTS-48 and IPTS-68 (Ref. 3) by use of the temperature dependence of the conductivity of potassium chloride solutions given by Bremner and Thompson (Ref. 4). A recent absolute determination of the conductivity of one of the reference solutions at 273.15, 291.15, and 298.15 K by Saulnier and Barthel (Refs. 5,6) has confirmed, to just within the experimental uncertainties, the values of Jones and Bradshaw. Values of the electrolytic conductivity of potassium chloride solutions at other concentrations can be obtained from empirical equations expressing the dependence of conductivity on concentration within  $\pm 0.02$  per cent with reference to the various reference solutions (Refs. 7-11).

In measuring the resistances of the reference solutions, an alternating current bridge should preferably be used and any electrode effects should be eliminated by making measurements at various frequencies in properly designed conductance cells using an adequate thermostatt as described by Robinson and Stokes (Ref. 12).

There is a lack of reference materials for conductance measurements in the ranges above and below that covered by potassium chloride solutions, and also for molten salts. For molten salts the present practice is to use aqueous potassium chloride solutions to determine the cell constant at 298.15 K and then correct for the effects of thermal expansion (Ref. 13).

The following provisos apply to the information on reference materials; (a) the recommended materials have not been checked independently by the IUPAC, (b) the quality of the material may change with time, (c) the quoted sources of supply may not be the exclusive sources because no attempt has been made to seek out all possible alternative sources, and (d) the IUPAC does not guarantee any material that has been recommended.

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1.

Physical Property: Electrolytic Conductivity,  $\kappa$

Units:  $\text{S m}^{-1}$

Recommended reference material: Potassium chloride (KCl)

Range of variables: 0 to 25°C,  $7 \times 10^{-2}$  to  $11 \text{ S m}^{-1}$

Physical state within the range: aqueous solution

Class: Calibration and Test Material; Certified Reference Material

Contributor: T. Plebanski

*Intended usage:* Calibration of conductivity cells.

*Sources of supply and/or method of preparation:* Potassium chloride of purity not less than 99.99 mass per cent is dissolved in water that has been distilled or passed through an ion-exchange resin to reach a conductivity of at least  $1.2 \times 10^{-4} \text{ S m}^{-1}$  at 298.15 K. The preparation of the solutions and corrections for the conductivity of distilled water is described by Jones and Bradshaw (Ref. 1). The conductivity of the solution is given by  $\kappa(\text{soln}) = \kappa(\text{ref.}) + \kappa(\text{H}_2\text{O})$ . Potassium chloride certified for the present purpose is available from supplier (A). Analytical grade potassium chloride recrystallized twice from conductivity water and dried at 770 K for 24 hours is usually suitable as a reference material.

*Pertinent physicochemical data:* The values given for the three reference solutions defined below (often termed 1.0, 0.1, and 0.01 demal solutions), at the three temperatures are the corrected values of Jones and Bradshaw (Ref. 1). A recent absolute determination of the conductance of solution C (defined below) by Saulnier and Barthel (Ref. 2) agrees with the Jones and Bradshaw values to within 0.01 per cent at 273.15 K and 0.07 per cent at 298.15 K (Ref. 3).

Conductivity  $\kappa$  at various temperatures

Solution $T_{68}/K$	A $\kappa/S\ m^{-1}$	B $10\ \kappa/S\ m^{-1}$	C $10^2\ \kappa/S\ m^{-1}$
273.15	6.514	7.134	7.733
291.15	9.781	11.163	12.201
298.15	11.131	12.852	14.083

solution A: 71.1352 gram potassium chloride in 1 kilogram of aqueous solution

solution B: 7.41913 gram potassium chloride in 1 kilogram of aqueous solution

solution C: 0.745263 gram potassium chloride in 1 kilogram of aqueous solution

All values given above refer to true mass "in vacuo". When weighing in air the following densities at 293.15 K may be used: KCl (solid),  $1.98 \times 10^3\ \text{kg m}^{-3}$ ; Solution A,  $1.0444 \times 10^3\ \text{kg m}^{-3}$ ; Solution B,  $1.0030 \times 10^3\ \text{kg m}^{-3}$ ; Solution C,  $0.9987 \times 10^3\ \text{kg m}^{-3}$ .

The uncertainty in the values of conductivity of the solutions above is  $\pm 0.1\%$  at the 99% confidence level.

An alternative technique for calibrating conductance cells is to use a potassium chloride solution of known concentration together with an equation representing the molar conductance over the appropriate concentration range. The recommended equations which cover the various concentration and temperature ranges are given in terms of the molar conductance  $\Lambda$  where  $\Lambda = \kappa/c$ .

(1) In the concentration range between  $c = 10^{-4}$  to  $0.04\ \text{mol dm}^{-3}$  at 298.15 K the Justice equation (Ref. 4),

$$\Lambda / \text{mS m}^2 \text{ mol}^{-1} = 14.984 - 9.484c^{1/2} + 5.861c \log c + 22.89c - 26.42c^{3/2} \quad (1).$$

(2) In the concentration range between  $c = 0.01$  to  $0.10\ \text{mol dm}^{-3}$  at 298.15 K the Chiu-Fuoss equation (Ref. 5),

$$\Lambda / \text{mS m}^2 \text{ mol}^{-1} = 14.988 - 9.485c^{1/2} + 2.547c \ln c + 22.0c - 22.9c^{3/2} \quad (2).$$

(3) In the concentration range between  $0.05$  and  $1.0\ \text{mol dm}^{-3}$  at 298.15 K the Rostock equation (Ref. 6),

$$\Lambda / \text{mS m}^2 \text{ mol}^{-1} = 14.995 - 9.925c^{1/2} + 13.575c - 12.075c^{3/2} + 5.787c^2 - 1.172c^{5/2} \quad (3).$$

(4) In the concentration range  $10^{-4}$  to  $0.05\ \text{mol dm}^{-3}$  at 291.15, 283.15, and 273.15 K the Barthel *et al.* equations (Ref. 7),

291.15 K

$$\Lambda / \text{mS m}^2 \text{ mol}^{-1} = 12.945 - 8.035c + 3.286c \log c + 15.43c - 14.30c^{3/2} \quad (4).$$

283.15 K

$$\Lambda / \text{mS m}^2 \text{ mol}^{-1} = 10.7314 - 6.495c + 2.706c \log c + 1.254c - 11.03c^{3/2} \quad (5).$$

273.15 K

$$\Lambda / \text{mS m}^2 \text{ mol}^{-1} = 8.1659 - 4.778c + 2.059c \log c + 9.38c - 2.93c^{3/2} \quad (6).$$

These equations reproduce the conductivity of the appropriate reference solutions to within 0.015 per cent. The experimental results on which the above equations are based have been obtained using cells whose constants have been determined using the Jones and Bradshaw reference solutions and a molar mass of potassium chloride of  $74.555 \text{ g mol}^{-1}$ . It should be noted that if authors use the Jones and Bradshaw values when expressed in International ohms on the 1948 temperature scale then their results will be approximately on those scales irrespective of the measuring devices used. The above equations have been corrected to absolute ohms and the 1968 International Practical Temperature Scale.

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## CONTRIBUTORS

E. Juhasz,  
National Office of Measures,  
Orszagos Meresugyi Hivatal,  
1224 Budapest XII,  
Nemetvolgyi ut 37-39  
(HUNGARY)

T. Plebanski,  
Research and Development Centre  
for Standard Reference Materials,  
UL. Elektoralna 2,  
PL 00-139, Warsaw  
(POLAND)

K. N. MARSH,  
Department of Physical and Inorganic Chemistry,  
University of New England,  
Armidale, N.S.W. 2351  
(AUSTRALIA)

## LIST OF SUPPLIERS

- (A) Research and Development Centre for Standard  
Reference Materials,  
UL. Elektoralna 2,  
PL 00-139, Warsaw  
(POLAND)