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Electrical Conductance Cell Assembly for Use with Aqueous Solutions up to 800°C and 4000 Bars*

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An electrical conductance cell assembly, designed for use with aqueous solutions at extremes of temperature and pressure, is described. Its utility was demonstrated by measurements of the conductance of 0.010 molal KCl solution at 800°C and at pressures up to 4000 bars.

INTRODUCTION

AQUEOUS solutions at high temperatures, especially under supercritical conditions, have received considerable renewed interest in the past several years. A general review of investigations in this field has been published elsewhere.¹ The interest originates in part from geochemical problems,² from the efforts to synthesize crystals hydrothermally,³ and from the long range consideration of homogeneous nuclear reactors.⁴ Information about the formation and mobility of ions in such solutions is still very limited. Determination of electrolytic conductance can furnish such information.

Electrical conductance data on a large number of aqueous solutions were obtained by A. A. Noyes and co-workers,⁵ using cells capable of operating at temperatures up to 306°C and at pressures up to about 100 bars. Some investigators have determined solubilities and conductances of solutes in nonaqueous solvent such as sulfur dioxide and methanol at moderately high temperatures.^{6,7} Fogo, Copeland, and Benson⁸ constructed an all platinum cell and made very accurate conductance measurements of NaCl in water at pressures up to 300 bars and at temperatures between 378 and 393°C, i.e., slightly above 374°C, the critical temperature of water. More recently, Corwin, Bayless, and Owen⁹ have determined the conductance

of NaCl in H₂O at 390°C and at densities up to 0.50 g/cm³.

At temperatures several hundred degrees above the critical temperature, in order to reach solvent densities approaching those of the liquid state at low temperature, the conductance cell must be operated at pressures up to several thousand bars. Such a cell has to be made from a material of very high tensile strength at high temperatures. Walls and insulation must resist the corrosive action of supercritical solutions. One type of cell to meet these requirements has been used and was described previously.¹⁰ Based on the experience with this earlier cell, an improved conductance cell has been designed and used for preliminary measurements. It is described below.

DESIGN

The main problem in constructing a high temperature, high pressure conductance cell is to find an electrode insulation which withstands the combined action of temperature, pressure, and corrosion. In this cell, as well as in the previous model, one electrode is the wall of the cylindrical cell and the other one is a small platinum cylinder at the end of a platinum rod. This rod is insulated by a tube of sintered, pure and nonporous aluminum oxide.¹¹ The insulated electrode rod leads out of the cell proper through a thick-walled, metal tube into a cold closure where plastic can be used for insulation and packing. Thus, there are no concentrated mechanical forces acting on the brittle insulation material in the high temperature region. The construction of the cell and details are shown in Fig. 1.

The main body (1), machined from a forged billet of a nickel-based alloy, Udimet 700 (0.1% C, 15% Cr, 19% Co, 5% Mo, 3.5% Ti, 4.5% Al, 1% Fe, 0.03% B, and remainder Ni),¹² has a cylindrical hole honed to a mirror-like finish to receive the similarly machined lining tube of 75% platinum-25% iridium alloy¹³ with a 0.040-in. wall. Flanges on the ends of the tube were machine spun over the internal shoulder within the hole to retain the lining in position. Two screwed caps (2) of Udimet alloy force the tungsten

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¹ E. U. Franck, *Angewandte Chemie* **73**, 309-322 (1961).

² G. W. Morey, *Econ. Geol.* **52**, 225 (1957); P. Niggli, *Das Magma und Seine Produkte* (Akademische Verlagsgesellschaft, Leipzig, 1937).

³ R. A. Laudise and J. W. Nielsen, "Hydrothermal Crystal Growth." To be published as a chapter in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York).

⁴ H. F. McDuffie, *Fluid Fuel Reactors*, edited by J. A. Lane, H. G. MacPherson, and F. Maslan (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), Chap. 3, pp. 85-127.

⁵ A. A. Noyes, *The Electrical Conductivity of Aqueous Solutions*, Publication No. 63 (Carnegie Institution of Washington, Washington, D. C., 1907).

⁶ I. B. Hannay and I. Hogarth, *Proc. Roy. Soc. (London)* **29**, 324 (1879); **30**, 178 (1880); I. B. Hannay, *ibid* **30**, 478, 484 (1880).

⁷ A. Hagenbach, *Z. Physik* **1**, 481 (1900); *Ann. Physik* **5**, 276 (1901); **8**, 568 (1902); reviewed by H. S. Booth and R. M. Bidwell, *Chem. Rev.* **44**, 477 (1949).

⁸ J. K. Fogo, C. S. Copeland, and S. W. Benson, *Rev. Sci. Instr.* **22**, 765 (1951); *J. Chem. Phys.* **22**, 212 (1954).

⁹ J. F. Corwin, R. G. Bayless, and G. E. Owen, *J. Phys. Chem.* **64**, 641 (1960).

¹⁰ E. U. Franck, *Z. physik Chem., Neue Folge* **8**, 92-105 (1956).

¹¹ Degussa of Frankfurt (Main), Germany.

¹² Utica Drop Forge and Tool Division of Kelsey-Hayes Company, Utica, New York.

¹³ J. Bishop & Company, Malvern, Pennsylvania.

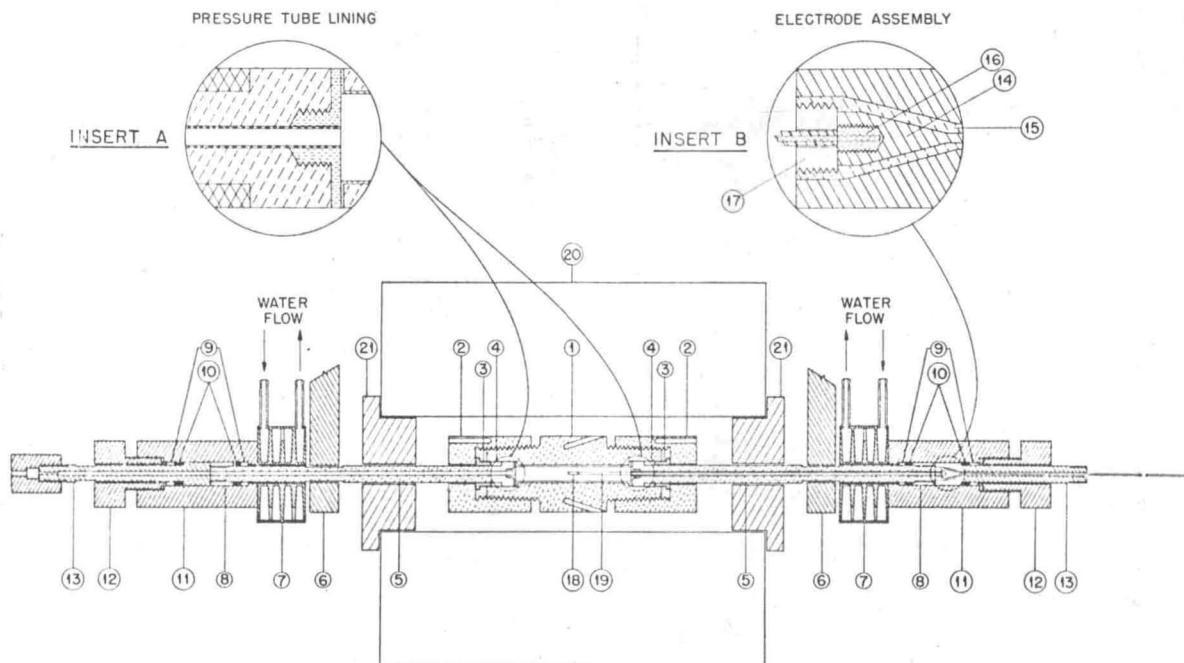


FIG. 1. Conductance cell assembly.

carbide retaining rings (3) against the copper packing rings (4) which seal and hold the enlarged ends of the pressure tubes (5) against the internal shoulder. This forms a Bridgman closure serviceable at high temperatures.

The pressure tubes of Udimet alloy have outer and inner diameters of 0.400 and 0.090 in. and enlarged ends of 0.600 in. diam. The flat surfaces of the enlarged ends have 0.060-in. thick face-plates of platinum-iridium alloy fastened to the tubes as shown in insert A, Fig. 1. The pressure tubes are lined with inserted platinum-iridium alloy tubes with 0.010-in. walls which are gold soldered to the face-plates. The volume contained in the chamber between the face-plates is approximately 3.7 cm³.

Two tightly fitting stainless steel clamps (6) support the assembly. Copper cooling jackets (7) keep the ends at room temperature. The rings (8) (9) form Bridgman closures using a Neoprene packing ring (10). The threaded ring (8) which is slotted for removal, and the pressure ring (9) are made from Udimet. Closure seals and plugs (11) (12) are constructed from 410 stainless steel. The plugs hold the upper and lower closing pistons (13) in position. These pistons are made of 17-4-PH stainless steel.¹⁴ The packing around these pistons is also of Neoprene. The lower piston is connected to a stainless steel capillary tubing by a conical seal through which the solutions can be pressed into the cell. The upper piston (see insert B, Fig. 1) has a stainless steel conductor (14) which is insulated by linen reinforced Bakelite (15), cemented into position with an epoxy resin. This closure was satisfactory to 4000 bars. The threaded

platinum tip (16), which is screwed into the stainless steel cone (14) is silver soldered to the platinum electrode lead. A Teflon plug (17) completes the insulation. At the top of the upper closure piston, the conductor is connected to a shielded cable which leads to the inductance bridge.

The inner surface of the Pt-Ir liner within the cell is platinized and serves as one electrode. The second electrode is the Pt-Ir cylinder (18) which is 0.31 in. in length and has a 0.062 in. o.d. The insulation tube of pure, non-porous, sintered Al₂O₃ (19) (o.d.=0.062 in., i.d.=0.012 in.) is tapered at the lower end and protrudes into the Pt-Ir cylinder so that small variances in thermal expansion between electrode rod and insulating tube cannot affect the cell constant. The cell constant as determined with a 0.010 molal KCl solution at 25°C was approximately 0.3 cm⁻¹; the exact value will depend upon the specific dimensions and characteristics of each electrode assembly. Removal of the central electrode is accomplished by opening the upper plug and removing the upper closure piston together with electrode and insulating tube.

The cell is suspended within a resistance furnace indicated in Fig. 1. The furnace (20) can be lowered to expose the cell or to immerse it in a constant temperature bath. Split, ceramic plugs (21) close the ends of the furnace. Heating currents are controlled by three Variacs connected to different windings of the furnace. The temperature is controlled by a Chromel-Alumel thermocouple in the annular space between cell and furnace. Calibrated Pt: Pt-10% Rh thermocouples distributed over the cell and the caps permit the determination of the cell temperature and any temperature gradients along the cell. The thermocouple

¹⁴ Armco Steel Corporation, Middletown, Ohio.

voltages are measured with a Leeds and Northrup K-3 potentiometer. The gradients can be made negligible by adjusting the heating currents to the three furnace windings. Around 400°C, the temperature could be controlled to within 1°C, and around 700°C to within 2°C.

The pressures are measured by a series of calibrated bourdon gauges¹⁵ and an additional set of strain gauges.¹⁶ Both sets of pressure gauges are recalibrated by a dead weight piston gauge.¹⁷ It is thus estimated that pressure measurements between 100 and 4000 bars can be made which are accurate to well within 1%.

Conductance cell and pressure gauges are connected to a system of 316 stainless steel capillary tubes (0.020 in. i. d.) and midget stainless steel valves.¹⁸ The pressure is controlled by hand operated, single piston, pressure generators.¹⁸ The conductance cell assembly and furnace, positioned vertically, are surrounded by a 15-in.-diam, cylindrical safety shield, constructed from steel plating of 0.37 in. thickness, which is hinged at each side and opens at the front. The furnace is suspended by means of pulleys and a counter weight which allows it to be positioned easily. A relay switch on the coolant water tap automatically cuts off the electrical power to the furnace if the water stops flowing.

OPERATION

The conductance was measured with an inductance bridge¹⁹ giving data with a precision of $\pm 0.1\%$. The frequency was varied by using an af signal generator and waveform analyzer.²⁰ The cell constant was determined with a 0.010 molal KCl solution at room temperature at various pressures. Measurements, with frequent changes of conductance water, were made over the whole temperature and pressure range to insure that the "background" conductance under all conditions was low when compared with the conductance of the subsequent solutions.

¹⁵ Heise Bourdon Tube Company, Newtown, Connecticut.

¹⁶ Baldwin-Lima-Hamilton Company, Waltham, Massachusetts.

¹⁷ W. C. 'T Hart & ZN, Rotterdam, Netherlands.

¹⁸ High Pressure Equipment Company, Erie, Pennsylvania.

¹⁹ Wayne-Kerr Corporation, Philadelphia, Pennsylvania, universal bridge type B-221.

²⁰ Wayne-Kerr Corporation, audio oscillator type S-121 and waveform analyzer type A-321.

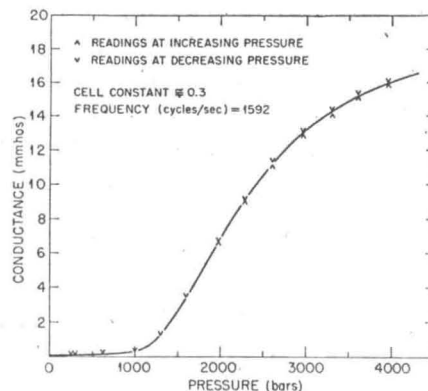


FIG. 2. Conductances of a 0.010 molal solution of KCl in H₂O at 800°C and up to 4000 bars.

Measurements were made either after filling the cell with a syringe before closure or by pressing the solution with the pressure generator into the cell after it had been evacuated. As soon as the desired temperature was attained, the pressure was decreased and increased stepwise; conductance measurements were made after each step. Figure 2 gives an example of a complete run using a 0.010 molal KCl solution at 800°C and at pressures up to 4000 bars. The symbols \blacktriangle and \blacktriangledown show the reproducibility of values upon increasing and decreasing the pressure of the fluid. An investigation of supercritical aqueous solutions of H₂SO₄ and metal sulfates is in progress; the results will be published elsewhere.

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