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The Determination of the Pressure Dependence of Transference Numbers

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Recently, an electrical detection system for moving boundaries was described[1] that permits transference numbers to be measured precisely without the limitations imposed by the traditional optical system.[2] In this new system, the boundary is timed, as it passes probe electrodes sealed into the moving boundary tube, by the increase in the potential across adjacent probes as the boundary enters the volume between the probes. The method therefore makes use of the fact that the potential drop in the following solution behind a stable two-salt boundary must be different from that of the leading solution in front of the boundary. The potential change at each event can be detected by various electrometer circuits[1] and recorded.

The method is ideally suited to remote control operation and has been used with considerable success for high-temperature measurements.[3] In this paper we describe the adaptation of the method to measurements at high pressures.

Experimental Section

The adaptation of this method to pressure work has necessitated two substantial modifications in the conventional moving boundary apparatus. The cell was redesigned to reduce the dimensions to those imposed by the pressure vessel and the type of electrical connection to the cell and the detector itself was modified to overcome current leakage problems encountered at high pressures.

The essential features of the autogenic cell are shown in Figure 1. This type of cell was used since it imposes none of the difficulties involved in generating a boundary prior to pressurizing. A constant current is passed between the cadmium anode, situated at the bottom of the calibrated uranium glass tube (3.5-mm i.d.) containing the probe electrodes, and the Ag, AgCl cathode situated in the side arm. A flexible Teflon extension of the side arm provided a simple and effective method of transmitting pressure to the system without contaminating the electrolyte solution with the pressurizing oil. This design resulted in a cell that could fit into a 1.2-in. bore, thereby reducing the pressure vessel to one of manageable size and weight.

The electrical probes were grouped in two sets of three about 5 cm apart with a separation of 1 cm between individual probes. The cadmium anode was held firmly to a glass flange at the end of the calibrated tube by a Lucite clamp. A leak-proof seal was effected by a small rubber O-ring. The current range required for these measurements was supplied by a commerical 1500-V power supply wired for constant-current operation.[1]

(1) R. L. Kay, G. A. Vidulich, and A. Fratiello, *Chem. Instrum.*, **1**, 361 (1969).

(2) D. A. MacInnes and L. G. Longsworth, *Chem. Rev.*, **11**, 17 (1932).

(3) J. E. Smith, Jr., and E. B. Dismukes, *J. Phys. Chem.*, **67**, 1160 (1963).

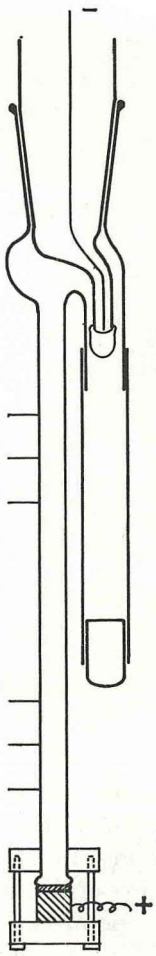

Figure 1. The high-pressure autogenic cell.

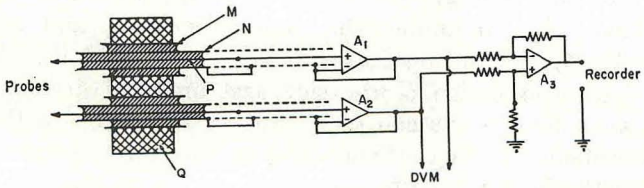

Figure 2. Schematic of the electrical system.

The main difficulty encountered in adapting the method to high-pressure work was that of connecting the probes to the electrometer through the high-pressure vessel so that a resistance to ground of greater than 10^{10} ohms was maintained, since a smaller resistance results in excessive electrode polarization at the probe electrodes owing to current leakage. The best available electrical connectors for high-pressure vessels have a resistance of about 10^8 ohms or two orders of magnitude too small. This problem was solved by using a driven-guard circuit as shown in Figure 2. The connections to the probes pass through the top of the pressure vessel Q by triaxial leads (1.5-mm o.d.) that consist of the concentric stainless steel sheaths M and N and a copper inner conductor P, the conductors being separated from each other by powdered MgO (Continental Sensing Inc.). The inner conductor is connected directly to the probes and to the inputs of FET operational amplifiers A_1 and A_2 (Burr-Brown 3038/25). These amplifiers have a gain of 1 and are used to drive the sheath N at the same voltage as the inner conductor P. Since both these leads are at the same potential, no current can flow between them and, consequently, effectively all leakage to ground from the inner conductor is eliminated. The outer sheath M is grounded and is soldered into the pressure vessel closure plug. The connections between the amplifiers and the various probe positions were made by means of small magnetic reed switches which permitted a continuously driven guard between the cell probes and the amplifier input terminals. The third amplifier A_3 in Figure 2 acts as a differential amplifier, the output from which can be recorded and the exact time of the boundary events noted. It is also possible to read the probe potentials directly across the amplifiers A_1 and A_2 with a digital voltmeter (input impedance about 10^8 ohms).

The cylindrical pressure vessel was machined from Type 17-4PH stainless steel with an O-ring closure and was pressurized from the side. It had an overall length of 18 in., with walls 0.65 in. and a working space of 1.2-in. diameter, 10-in. long. The pressurizing oil was Marcol 52 (Humble Oil). An air-driven pump was used to pressurize the vessel initially with the final adjustment being made by a hand generator. The exact pressure was read from a calibrated Heise gauge. Temperature control was maintained by keeping the pressure vessel in an oil bath regulated to 0.003°. It was necessary to allow the cell to stand for 1 hr after the initial pressurizing in order to permit the heat developed in this adiabatic process to dissipate.

Data reported here are restricted to a maximum pressure of 2 kbars although our pressure system can be carried to over 3 kbars. At higher pressures, the platinum probe electrodes developed small leaks and the method had to be abandoned.

Results

The volumes between the probe electrodes in the transference cell were obtained from six calibration runs at 1 atm assuming the value[4] of T^+(0.02 M aqueous KCl, 25°) = 0.4901.

The observed transference numbers for KCl in aqueous solutions of KCl at 0.02 M and 25° are given in the second column of Table I as a function of pressure. The values of $T_P{}^+$ in the third column result after a correction for the compressibility of glass[5] and of water.[6] At pressures above 1 kbar, the Tait

(4) L. G. Longsworth, *J. Amer. Chem. Soc.*, **54**, 2741 (1932).
(5) J. Adams, *ibid.*, **53**, 3769 (1931).

Table I: Observed and Corrected Cation Transference Numbers for 0.02 *M* Aqueous KCl

Pressure, bar	T_{obsd}^+	T_P^+
500	0.4757	0.4852 (4)
1000	0.4636	0.4811 (1)
1500	0.4548	0.4793 (5)
2000	0.4464	0.4770 (2)

equation as given by Owen[7] was used to obtain the density of water. At 0.02 *M* the difference between the compressibility of water and the solution can be neglected. Also, no volume or solvent conductance corrections were made since they both should be negligible.[4] Two runs were carried out at each pressure. Each number in parentheses in the last column of Table I gives the total difference in the 4th decimal place in T_P^+ obtained in the two runs. These results are compared to the only other data[8] with comparable precision in Figure 3.

Discussion

The results summarized in Figure 3 clearly confirm the previous measurements of Wall and Berkowitz[8] which extend only to 1 kbar, although our reproducibility appears to be much better. Wall and Berkowitz determined the boundary velocity be measuring the fractional change in the ac resistance with time between electrodes situated at the top and bottom of the cell, a method that required the current to be interrupted during the resistance measurements. They estimate the total error in their method to be 0.6%, whereas we claim at most 0.1%. The true accuracy of the data will best be decided when both transference and conductance data are available for two salts with a common ion.

The most significant difference in the two sets of data is the fact that T_P^+ does not show a continuous linear decrease with pressure as the previous results[8] indicated. Our data indicate that the change in T_P^+ levels off at higher pressures. It should be noted that T^+(KCl, aq) decreases both with increased pressure and increased temperature[3,9] and under both these circumstances the degree of hydrogen bonding in water is known to decrease. These high-pressure data confirm our previous conclusions[9] that the structural excess mobility of the potassium ion is greater than that for the chloride ion. Consequently, as the degree of hydrogen bonding or structure in the water decreases with increased temperature and pressure, the potassium ion becomes progressively slower with respect to the chloride ion.

Since water does not begin to act like other liquids until pressures above 2 kbars are reached, we wished to extend these transference measurements above this pressure limit of our present cells. For this purpose, we are designing a cell in which the moving boundary will be detected by impedance changes detected at metal film electrodes fused onto the outside of the glass walls.

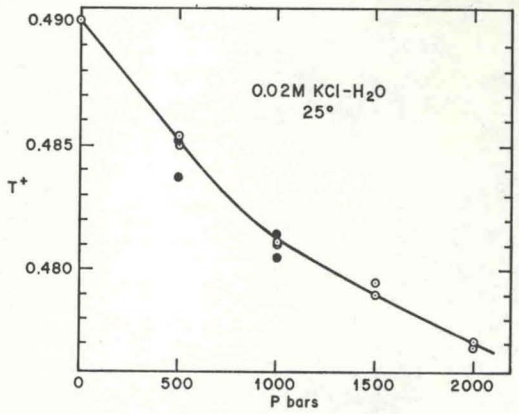

Figure 3. Cation transference numbers for 0.02 *M* KCl in aqueous solution at pressures up to 2 kbars: ○, this work; ●, ref 8.

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(6) G. S. Kell and E. Whalley, *Phil. Trans. Roy. Soc. London, Ser. A*, **258**, 565 (1965).
(7) B. B. Owen, *J. Chem. Educ.*, **27**, 59 (1944).
(8) F. T. Wall and J. Berkowitz, *J. Phys. Chem.*, **62**, 87 (1958).
(9) R. L. Kay and G. A. Vidulich, *ibid.*, **74**, 2718 (1970).