[CONTRIBUTION FROM THE ROGERS LABORATORY OF PHYSICS, THE ELECTROCHEMICAL LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE TRANSFERENCE NUMBERS OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION

BY M. KNOBEL, D. K. WORCESTER AND F. B. BRIGGS[1]

Received September 23, 1922

As a continuation of the work in the preceding article[2] the electromotive forces of potassium hydroxide concentration cells with transference were measured. These were of the type, $H_2 \mid KOH(c_1) \mid KOH(c_2) \mid H_2$, for which the electromotive force is given by the expression[3]

$$E_2 = 2\,n_k \frac{RT}{F}\, ln\, \frac{\alpha_1 C_1}{\alpha_2 C_2} \qquad (1)$$

where n_k is the transference number of the potassium ion, α_1 and α_2 are the mean activity coefficients of the two ions, and C_1 and C_2 the concentrations of potassium hydroxide in the two solutions, respectively. This equation combined with that for cells without transference, namely

$$E_1 = 2 \frac{RT}{F}\, ln\, \frac{\alpha_1 C_1}{\alpha_2 C_2} \qquad (2)$$

results in the equation

$$n_k = \frac{E_2}{E_1} \qquad (3)$$

thus allowing the direct calculation of the transference number.

Experimental Details

It was impossible to use hydrogen electrodes connected directly with the liquid junction because the latter would be disturbed by the slight fluctuations of pressure around

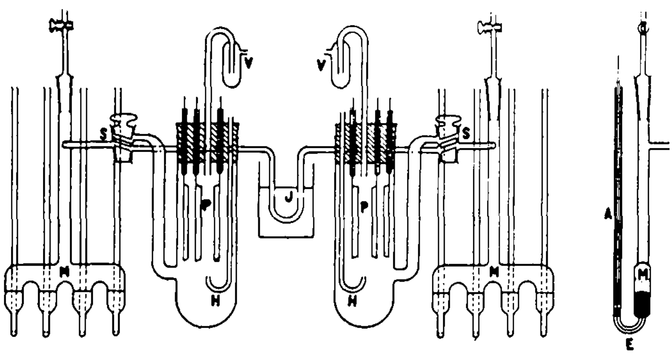

Fig. 1.

the hydrogen electrode. Resort was had to intermediate mercuric oxide electrodes. The apparatus is shown in Fig. 1. The mercuric oxide electrodes M and the hydrogen electrodes P were filled with their respective solutions of different concentration on either

[1] Credit is due to Mr. R. R. Whitehouse for a first attempt at this work. Unfortunately his results were unreliable on account of leakage currents in the thermostat.

[2] Knobel, THIS JOURNAL, 45, 70 (1923).

[3] See MacInnes and Parker, *ibid.*, 37, 1445 (1915).

side. The 3-way stopcocks S allowed for the connection across the liquid junction between the two sets of oxide electrodes or for each hydrogen electrode against its corresponding mercuric oxide electrode. The liquid junction at J was made after the electrodes had come to equilibrium by filling the surrounding vessel very slowly with potassium hydroxide solution intermediate in concentration between the two concentrations being measured. This is the method of MacInnes and Beattie.[4] Voltage measurements were made, with a carefully standardized potentiometer, every 20 minutes until the electromotive force was constant to 0.04 millivolt for over an hour. The average of the readings when it had attained this degree of constancy was taken as the electromotive force of the cell. Measurements were taken for 3 to 6 hours after setting up the cell. A check run was made on each concentration.

The solutions were made as described in the preceding article[2] by purification of the best obtainable potassium hydroxide with barium hydroxide. They were analyzed with more than sufficient accuracy when compared with the errors in the voltage measurements and were made up to round concentrations by dilution by weighing.

The entire apparatus was immersed as far as possible in a thermostat kept at 25° within 0.01°.

Results

The results obtained are listed in Table I. The first two columns give the concentrations of potassium hydroxide on the two sides of the cell. The measured electromotive force with an estimate of its precision is given in the third column.

Table I

Electromotive Forces of Concentration Cells of Potassium Hydroxide at 25°

Concentrations Gram-molecular weights per 1000 g. of water		E.m.f. Volts
3.0	0.3	0.03683±0.00003
1.0	0.1	0.03104±0.00003
0.3	0.1	0.01424±0.00003
0.3	0.03	0.02916±0.00003
0.1	0.01	0.03465±0.00015

It was impossible with the apparatus to make measurements on solutions more dilute than 0.01 N on account of the insensitivity of the galvanometer.

Equation 3 was not used in the calculation of the transference numbers, as it involves the assumption of constant transference number in integrating to obtain Equation 1. The exact equation is

$$n_k = \frac{dE_2}{dE_1} \qquad (4)$$

where the electromotive force dE is measured for an infinitesimal concentration difference, and may be used as follows. Let a curve be drawn such that each point on it has an abscissa which is the electromotive force of a cell without transference and an ordinate which is the electromotive force of a cell with transference for the same pair of concentrations. All

[4] MacInnes and Beattie, This Journal, 42, 1117 (1920).

electromotive forces are to be such as would be measured between a solution of one reference concentration (the lowest concentration was chosen) and a solution of any other concentration. The slope of this curve is then the transference number. Each electromotive force corresponds to a concentration and, therefore, the transference number at any particular concentration may be found as the slope of the curve at that point.

The values to be plotted are given in Table II. In the first column is the concentration of the solution. The second and third columns contain the electromotive forces of concentration cells, between the concentration listed and 0.01 N, with and without transference, respectively. The latter values were derived from the preceding article. When plotted carefully on a large scale it was found that all except the last point lay on a straight line, the maximum divergence being 0.00013 volt, which is about the experimental error. The slope of this line is 0.2633 and, therefore, *the transference number of the potassium ion in potassium hydroxide between the concentrations 0.03 and 3.0 N is independent of the concentration and equal to 0.2633.* We estimate the average deviation of this value to be about 0.0005 or 0.2%. For concentrations lower than 0.03 N the transference number apparently must increase for the point for 0.01 N is 5 millivolts below the straight line. This trend is in the right direction to check the value for the transference number as calculated from conductance data at infinite dilution, the latter being 0.274.

TABLE II

ELECTROMOTIVE FORCE FOR VARIOUS CONCENTRATIONS AGAINST 0.01 N

Concentration Moles per 1000 g. H_2O	E_1 With tranference	E_1 Without transference
0.03	0.01972	0.05295
0.1	0.03465	0.1106
0.3	0.04888	0.1641
1.0	0.06569	0.2278
3.0	0.08572	0.3040

Summary

The electromotive forces of concentration cells of potassium hydroxide of the type, $H_2 | KOH(c_1) | KOH(c_2) | H_2$, have been measured at 25°, for concentrations between 3.0 and 0.01 N. These values combined with those for cells without transference have been utilized to calculate the transference numbers of the potassium ion in potassium hydroxide solutions of various concentrations. The transference number of the potassium ion was found to be constant and equal to 0.2633 in the range of concentrations from 3.0 to 0.01 N and to increase with decrease in concentration.

CAMBRIDGE 39, MASSACHUSETTS