[CONTRIBUTION FROM THE CHEMICAL AND OCEANOGRAPHIC LABORATORIES OF THE UNIVERSITY OF WASHINGTON]

The Electrical Conductances of Standard Potassium Chloride Solutions Throughout the Temperature Range 0 to 25°

BY RAYMOND W. BREMNER AND THOMAS G. THOMPSON

Introduction

The purpose of this paper is to present certain accurately determined values of specific conductance of standard potassium chloride solutions at 5, 10, 15, and 20°. The determinations were made with an accuracy ranging from 0.001 to 0.01% for the relative values. The standard solutions were the 0.01 and 0.1 demal solutions defined and measured at 0, 18, and 25° by Jones and Bradshaw.[1]

Apparatus and Materials

Bridge Circuits.—The bridge used for the measurements was similar to that described in detail by Dike.[2] It was calibrated twice during the present work, and no appreciable change in the calibration corrections was observed.

The oscillator that supplied the current for the bridge was set at frequencies of 1008 ± 3 and approximately 2000 cycles per second by comparing with standard tuning forks. The potential difference supplied to the bridge was 0.3 volt. The potentials of the detector terminals of the bridge were increased in the ratio $^1/_{15}$ by a transformer and then amplified. Changes of 0.01 ohm could be detected easily in a bridge setting of 1000 ohms.

The cells were connected to the bridge through mercury cups suspended in opposite sides of the thermostat. The parts of the leads that ran from the mercury cups to the cells were heavily insulated to reduce any heat transfer to the cells.

The Conductance Cells.—The cells were of the Washburn pipet type, in which any capacitative shunt effect was too small to be detected by differences in rsesitance readings at 1000 and 2000 cycles per second.[3] The cells were such that their resistances when filled with solution varied from 1200 to 6000 ohms. They were platinized in the manner suggested by Jones and Bollinger[4] and by Reilly and Rae.[5]

Equilibrium Water.—The equilibrium water was prepared in the manner described by Washburn and had a specific conductance of 1.1×10^{-6} ohms.[6]

Each batch of equilibrium water was kept in thoroughly steamed and seasoned Pyrex glass-stoppered bottles. Check determinations of the conductance of each batch of water were made at 25°, and the conductances at the other temperatures were calculated from that at 25° by multiplying by the following experimentally determined factors:

Temp., °C.	0	5	10	15	18	20	25
Factor	0.45	0.55	0.65	0.76	0.83	0.87	1.00

Potassium Chloride.—The most pure potassium chloride obtainable on the market was used. It was further purified and tested in much the same manner as described by Shedlovsky.[7]

Weighing.—The balance used for weighing the dry salt was sensitive to 0.01 mg. with a 50-g. load and that used for the solutions was sensitive to 0.1 mg. with a 1200-g. load. The weights used were calibrated on each balance at several different times during the investigations.

The dry salt was weighed in a platinum crucible and the solution in a thoroughly seasoned and steamed ground glass-stoppered Erlenmeyer flask, all weighings being corrected to vacuum. The 0.01 demal solutions were prepared from weighed portions of 0.1 demal solutions, this procedure being more accurate than weighing small quantities of dry salt. All solutions were transferred to bottles similar to those used for equilibrium water immediately after they were prepared. They were accurate to 0.001%.

Experimental Procedure

Each cell was rinsed four times with the solution, allowed to stand filled for fifteen to thirty minutes and then refilled with the solution. Great care to prevent contamination by evaporation or otherwise was exercised.

After temperature equilibrium was reached, the heavily insulated portions of the leads were placed in position, and the bridge was balanced in the manner recommended by Dike.[2] The leads were then shifted to the next cell and the bridge rebalanced. In this way, the leads were shifted from cell to cell so that successive readings for each cell were taken at about five-minute intervals. This was continued until several closely agreeing values were obtained for each cell. The time required to balance the bridge after the leads were inserted was thus reduced to very few seconds, effectively eliminating any heating effects caused by electrical currents in the cells. The thermometer was read repeatedly during this process, as a check upon the temperature of the thermostat.

The resistances were checked with the oscillator set at 2000 cycles, as recommended by Jones and Bradshaw,[1] and were measured at 0, 5, 10, 15, 18, 20, and 25°, consecutively. The cells were then emptied and refilled with the same solutions and measurements again made at 25°. The averages of the values at 25° were accepted as correct and small corrections, proportional to the resistances were made at the other temperatures. The corrections were seldom as large as 0.01% of the resistance values and never greater than this.

---

(1) Grinnell Jones and Benj. C. Bradshaw, THIS JOURNAL, **55**, 1780–1800 (1933).

(2) Paul H. Dike, *Ref. Sci. Instruments*, **2**, 379–395 (1931).

(3) Grinnell Jones and and Giles M. Bollinger, THIS JOURNAL, **53**, 411–451 (1931).

(4) Grinnell Jones and Dorothy M. Bollinger, *ibid.*, **57**, 280–284 (1935).

(5) J. Reilly and W. N. Rae, "Physico-Chemical Methods," D. Van Nostrand Company, New York, 1933, p. 706.

(6) Edward W. Washburn, THIS JOURNAL, **40**, 111 (1918).

(7) Theodore Shedlovsky, *ibid.*, **54**, 1417 (1932).

Temperature Control

The apparatus used for maintaining constant temperature consisted of a thermostated oil-bath immersed in a thermostated water-bath. Ample space was allowed for circulation in the water-bath on all sides and below the oil-bath. The temperature fluctuations of the water-bath varied from 0.01 to 0 to 0.002 at 25°, while those of the oil-bath varied from 0.004 at 0° to no change observable at 25°. The oil was a good grade transformer oil diluted with "odorless" kerosene to reduce the viscosity. The oil thermostat was a five-gallon (20-liter) tank of thin sheet copper which projected about 1.5 cm. above the liquid in the water-bath. At temperatures below the dew-point, water condensed on the projecting part and tended to run down into the oil. This condition was remedied by suspending cheesecloth covered pads of absorbent cotton in the oil to absorb the moisture at times when the oil-bath was not in use.

The lower temperatures were maintained by appropriately regulating the flow of refrigerant through a coil of copper tubing, in which difluorodichloromethane was the refrigerant. Addition of ethyl alcohol prevented ice from forming on the cooling coil in the water thermostat.

The seven exact temperatures, 0, 5, 10, 15, 18, 20, and 25°, at which the oil-bath was set were established and maintained by the use of twelve Beckmann thermometers and two fixed bulb thermometers. Seven of the former and the two latter recently had been calibrated by the Bureau of Standards to the nearest 0.001 and 0.002°, respectively.

The ice-point served as the basis to which all the temperatures were referred, ice made from equilibrium water being used. The temperatures other than 0° were then established consecutively by means of two calibrated Beckmann thermometers of unusually uniform bore. The 25° value, after passing through the five 5° intervals with Beckmann thermometers, agreed with that given by the two fixed bulb thermometers within 0.002°. Check determinations of the seven temperature values were made at several different times, both by going up and by going down the temperature scale.

The temperature of the room during the entire time that measurements were being made did not vary by more than 5°. The maximum distance that the mercury capillary column in any thermometer projected above the surface of the liquid in the thermostat was only about 1° and in most cases less than this, for every temperature except 25 and 18°. The stem temperature was always noted at each of these two temperatures and the correction applied, but it never amounted to more than 0.002°. All of the thermometer readings were made with the same lens clamped to the stem of the thermometer in the same way. It was demonstrated repeatedly that the readings were made consistently to the nearest 0.001°, throughout the work.

Experimental Results

The individual and average values of conductance at each of the temperatures are listed in Table I. These values were obtained in such a manner that the errors involved were very small. An illustration should make the method clear. A cell had been filled with 0.1 demal solution and its resistance measured at 0, 5, 10, 15, 18, 20, and 25°. Using the specific conductance data of Jones and Bradshaw and the previously determined value for water, the cell constant was calculated at 0, 18, and 25°.[1] The cell constant at intermediate temperatures for this particular run was found by plotting the known values and drawing the best line through the points, assuming the cell constant to be a linear function of the temperature. The average change in the individual cell constants obtained in this way was less than 0.01% for the 25° interval. The conductances of the 0.1 demal solution at the intermediate temperatures were then calculated, using the measured resistances and the previously determined corrections for water. In this way, a set of values was obtained from a single filling of the cell, eliminating many experimental errors. This procedure was repeated several times with each cell using different solutions. Values from each of three different cells were used in determining the average conductance of each standard solution at a given temperature.

TABLE I

MEASURED SPECIFIC CONDUCTANCES OF STANDARD POTASSIUM CHLORIDE SOLUTIONS

	5°	10°	15°	20°
		0.1 demal solution		
Meas. val.	0.0082017	0.0093130	0.0104616	0.0116434
	17	3	24	37
	19	5	24	44
	19	6	25	47
	23	7	29	48
Average	0.008201_9	0.009313_4	0.010462_5	0.011644_2
		0.01 demal solution		
Meas. val.	0.00089146	0.00101446	0.00114200	0.00127357
	46	48	1	59
	55	56	3	59
	63	56	4	59
	66		4	60
Average	0.0008915_5	0.0010145_2	0.0011420_3	0.0012735_9

Interpolation Formulas for Specific Conductance

In 1875, Kohlrausch and Grotrian found that the conductance of a dilute solution may be represented as a function of the temperature by the equation of a parabola.[8] The equation of Kohlrausch and Grotrian is

$$K = K_0(1 + at + bt^2)$$

in which K is electrical conductance, t is temperature, and a, b are constants found by experiment. This equation has been used since by many in-

---

[8] J. Kohlrausch and O. Grotrian, *Pogg. Ann. Phys. Chem.*, **230**, 215–239 (1875).

vestigators for purposes of interpolating and extrapolating various conductance data. It was used by Parker and Parker to calculate the conductances of standard potassium chloride solutions at other temperatures, after having measured them at 0°.[9]

The applicability of this equation to the experimental data on 0.1 demal potassium chloride solution was tested. The constants a and b were evaluated by the method of least squares and the conductances at each temperature calculated by use of the resulting equation. The deviations of the observed from the calculated values were as high as 0.077% whereas the expected deviations were not greater than 0.01%.

Very little work on exact temperature coefficients, particularly at higher temperatures, has been reported. That which has been done indicates that a point of inflection occurs in each conductance–temperature curve.[10,11] Moreover, the point of inflection is in accord with the most recent theoretical considerations.[12] It is impossible for the curve represented by the above equation to contain a point of inflection and it is therefore inconsistent with the known facts.

The Debye–Hückel–Onsager equation for limiting conditions recently has been applied to new data on potassium chloride solutions by Clews.[11] He found this equation to hold for 0.01 normal solutions up to 30° and to be inapplicable to 0.1 normal solutions.

For these reasons, a cubic equation was used. The proposed equation is

$$L = a + bt + ct^2 + dt^3$$

$$L_{0\cdot 1\mathrm{D}} \times 10^6 = 7137.60 + 208.312t + 0.99077t^2 - 0.006964t^3$$

$$L_{0\cdot 01\mathrm{D}} \times 10^6 = 773.637 + 23.0485t + 0.110384t^2 - 0.0006446t^3$$

The constants a, b, c, and d were evaluated by the method of least squares.

When these equations were applied, the calculated values of specific conductance of standard potassium chloride solutions at different temperatures showed remarkable agreement with the observed values given in Table I and with the values obtained by Jones and Bradshaw.[1] For the 0.1 demal solution, the deviations of the observed from the calculated values at the different temperatures averaged 0.006%, and for the 0.01 demal solution, less than 0.001%.

Conclusions

1. The values of the specific conductances of 0.1 demal and 0.01 demal standard potassium chloride solutions have been measured at 5, 10, 15, and 20°.
2. An interpolation formula that will reproduce these results and the results of Jones and Bradshaw at 0, 18, and 25° within 0.01% for 0.1 demal potassium chloride solution and within 0.001% for 0.01 demal potassium chloride solution has been proposed and the constants evaluated for these concentrations.
3. The proposed formula, unlike that of Kohlrausch and Grotrian, predicts a point of inflection in each temperature–conductance curve.

SEATTLE, WASHINGTON RECEIVED AUGUST 25, 1937

---

[9] Henry C. Parker and Elizabeth W. Parker, THIS JOURNAL, **46**, 312–335 (1924).

[10] "International Critical Tables," Vol. V, p. 229.

[11] C. J. B. Clews, *Proc. Roy. Phys. Soc.* (London), **46**, 764–771 (1934).

[12] Hans Falkenhagen, "Electrolytes," Oxford University Press, 1934, p. 200.