

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Conductivity of Sodium Iodide Solutions at 25° and the Limiting Conductance of the Iodide Ion¹

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Introduction

Recently in connection with work in this Laboratory on reaction rates in which the changes in concentration were followed by conductance it was necessary to know the conductance of solutions of sodium iodide more accurately than could be obtained from any available data.² Since the available data are only accurate to about 0.5%, it seemed desirable to determine the conductivity of sodium iodide with greater accuracy.

Experimental

Bridge.—The slide wire bridge with marble drum and end coils was grounded according to the method of Jones.³ A slide wire bridge with Bakelite drum was used for the ground resistance. In the resistance box the 1000 and 10,000 ohm coils were Curtis coils while the 1, 10 and 100 ohm coils were bifilar wound. A variable air condenser of small capacity was used to balance the capacity in the cell. A calibrated vacuum tube oscillator similar to that described by Jones and Josephs,³ was used as a source of current and the sensitivity increased by the use of an amplifier with a low impedance output transformer. Brown tunable phones with a resistance of 120 ohms were used. The resistance measurements were made at 1110 cycles per second.

Thermostat.—The oil thermostat was grounded through the cooling coils. Its temperature was adjusted to $25 \pm 0.002^\circ$ with a thermometer calibrated by the Bureau of Standards. It maintained this temperature constant to $\pm 0.002^\circ$.

The apparatus was not as convenient as that of Jones; however, the accuracy of our resistance measurements was probably about 0.01%.

Cells.—Type B Washburn cells were used: (I) constant 2.2211, (II) constant 0.47154, (III) constant 1.7822, (IV) a modified Shedlovsky flask cell of Pyrex glass, constant 0.64474. The cell constants were determined using a solution containing 0.74625 g. of potassium chloride in 1000 g. of water (brass weights in air).⁴

Conductivity Water.—The water used was allowed to come to equilibrium with the air in the laboratory. Its conductivity varied from 0.9 to 1.2×10^{-8} ohms⁻¹ cm⁻¹.

Potassium Chloride.—The potassium chloride was purified by two precipitations from a solution in conductivity water with dry HCl and filtering without the use of paper. The moist crystals were placed in a large platinum dish and gently heated for thirty minutes to drive off moisture. It was then heated until the edges just started to melt. After cooling in a desiccator the unfused part was separated and used for obtaining the cell constants. A saturated solution of this material was neutral to phenolphthalein.

Sodium Iodide.—The sodium iodide was prepared by dissolving Baker and Adamson reagent quality sodium iodide in conductivity water to a saturated solution and

(1) From a section of a thesis presented by Percival A. Lasselle in partial fulfilment of the requirements for the Ph.D. degree.

(2) "International Critical Tables," Vol. VI, p. 235; H. C. Jones, Publications of Carnegie Institute, No. 170, p. 12.

(3) Jones and Josephs, *THIS JOURNAL*, **50**, 1058 (1928).

(4) Parker and Parker, *ibid.*, **46**, 332 (1924).

filtering to remove any suspended matter. The solution was placed in an Erlenmeyer flask fitted with a two-holed rubber stopper, previously boiled with sodium hydroxide, carrying a tube which reached almost to the bottom and a shorter exit tube. Nitrogen purified by passing through hot reduced copper, soda-lime and sulfuric acid was then passed through and the solution heated to 70° . When about one-half of the water had evaporated the solution was allowed to cool and the sodium iodide crystallized out as $\text{NaI}\cdot 2\text{H}_2\text{O}$. If concentration is carried too far or the temperature is above 65° when crystallization starts, anhydrous sodium iodide separates, forming a hard cake in the flask which is very difficult to remove. The above operation was repeated a second time and the crystals filtered off on a Buchner funnel without the use of paper. The moist crystals were dried over phosphorus pentoxide *in vacuo* at $50\text{--}60^{\circ}$ to remove water of crystallization. Since the anhydrous salt is very hygroscopic the salt could not be weighed in the usual manner. A freshly ignited porcelain combustion boat was weighed in a large Pyrex weighing bottle, after which the sodium iodide was roughly weighed into

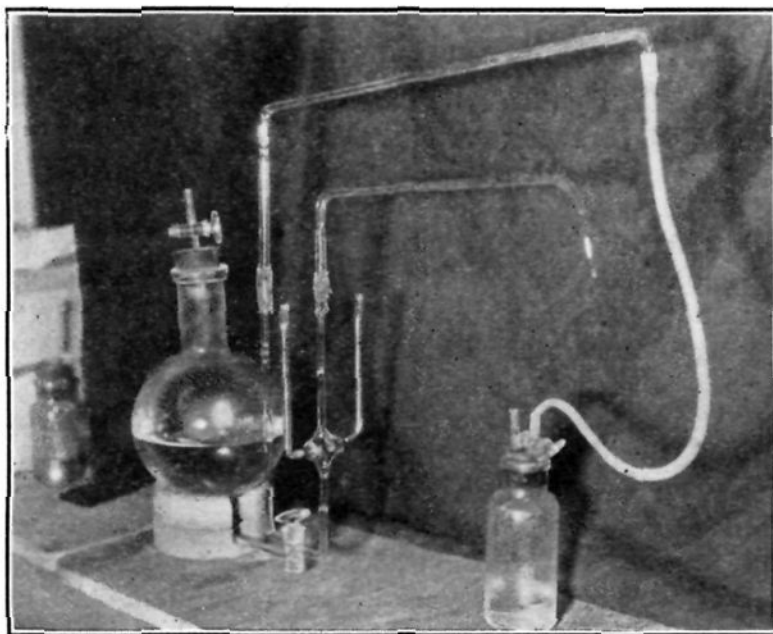


Fig. 1.

the boat. The boat was placed in a tube filled with hydrogen purified by passing over reduced nickel, through soda lime, calcium chloride and phosphorus pentoxide. The tube was then heated in an electric furnace to 250° and allowed to cool to $160\text{--}190^{\circ}$ when it was removed and quickly placed in the same weighing bottle, cooled and weighed. Since the material was transferred above its transition point it was not thought necessary to use a Richards bottling apparatus. The boat and sample were then dropped into a flask containing a weighed quantity of water sufficient to give a solution of approximately the desired normality. The density was then obtained and the normality calculated. The more dilute solutions were prepared by adding the desired amount of one of the stronger solutions from a weight pipet to a weighed quantity of "equilibrium" water.

Gravimetric analysis of the strongest solution agreed with that calculated from weight and density measurements to 0.02%. Solutions of the iodide prepared as described were neutral to phenolphthalein and showed no trace of yellow color due to iodine.

In determining the conductance of those solutions in which the flask cell was used the flask and cell were thoroughly cleaned, dried and weighed. The water to be used was then placed in the flask and weighed, after which the salt was added to the water and

the tubes connected. The ground glass joints and the stopcock were lubricated with a small amount of petrolatum which had been boiled several times with conductivity water. The cell was then placed in the thermostat, and by means of purified nitrogen the solution was forced through the cell. In order to empty the cell the two-way stopcock was reversed, and the solution drawn out by vacuum. Readings checking to 0.01% could be obtained using this cell. Fig. 1 shows the details of this cell.

All measurements on dilute solutions and most of them on the stronger solutions were made at frequencies varying from 1110 to 2950 cycles. In the case of the concentrated solutions the variation in conductance was less than the experimental error. In the case of the most dilute solution the conductance changed by slightly more than 0.01%. Thus no correction to the value at 1110 cycles was necessary.⁵

Discussion of Results

The values of the conductance are given on the basis of a 0.01 demal potassium chloride solution;⁴ the equivalent conductance being defined as $\Lambda = 1000\kappa/C$ where C is in equivalents per liter. Molecular weights were from the 1933 table.

The results of the conductance measurements are given in Table I. Column 4 of this table shows the equivalent conductance calculated by the Shedlovsky equation.⁶ The results obey this equation to 0.04 normal.

TABLE I
EQUIVALENT CONDUCTANCE OF SODIUM IODIDE AT 25°

C	Observed	Percentage deviation from curve	Calculated from Shedlovsky equation	Cell
0.17050	105.53	0.00	108.12	I
.12982	107.20	+ .04	109.25	I
.10254	108.63	+ .07	109.78	III
.09221	109.03	- .04	110.19	I
.060325	111.52	.00	111.91	I
.041222	113.51	.00	113.54	I
.024813	115.91	.00	115.76	II
.017467	117.34	+ .02	117.19	I
.013992	118.03	- .02	118.04	IV
.0091517	119.35	- .05	119.47	III
.0090983	119.54	+ .02	119.50	IV
.0087179	119.66	+ .02	119.63	II
.0045595	121.31	- .02	121.43	II
.0021304	123.24	+ .08	123.06	IV
.00070431	124.46	- .06	124.63	II
.00050250	125.32	+ .17	124.97	IV
.00023655	125.59	.00	125.57	IV
Extrapolated	126.85			

Values for calculations by Shedlovsky equation: $A = 88.84$, $B = 119$, $\Lambda_0 = 126.90$.

(5) Jones and Bollinger, *THIS JOURNAL*, **53**, 436 (1931).

(6) Shedlovsky, *ibid.*, **54**, 1407 (1932). This calculation was made at the suggestion of one of the referees. The Λ_0 found by this equation was 126.90. This value was used in calculating the equivalent conductance by the Shedlovsky equation. The Λ_0 values calculated as suggested by Shedlovsky appear to be very nearly constant in the range of dilution in which the Onsager equation holds, thus making the extrapolation to zero concentration by this method somewhat doubtful. We believe our extrapolation from Fig. 2 to be the more reliable value.

The plot of these data is shown in Fig. 2. The broken line shows the value of the equivalent conductance calculated from the Onsager equation using the extrapolated value of the equivalent conductance.

$$\Lambda = \Lambda_0(1 - \alpha\sqrt{c}) - \beta\sqrt{c} \quad (1)$$

$$\text{or } \Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c} \quad (2)$$

$$\text{where } \alpha = \sqrt{2} \left[\frac{5.78 \times 10^{-6}}{(DT)^{3/2}} \right] = 0.2280 \quad (3)$$

$$\text{and } \beta = \sqrt{2} \left[\frac{58.0}{(DT)^{1/2}\eta} \right] = 59.91 \quad (4)$$

In the above equations D , the dielectric constant of water, has the value given by Drake, Pierce and Dow⁷ and η , the viscosity of water, has the value given in the "International Critical Tables" for 25°.

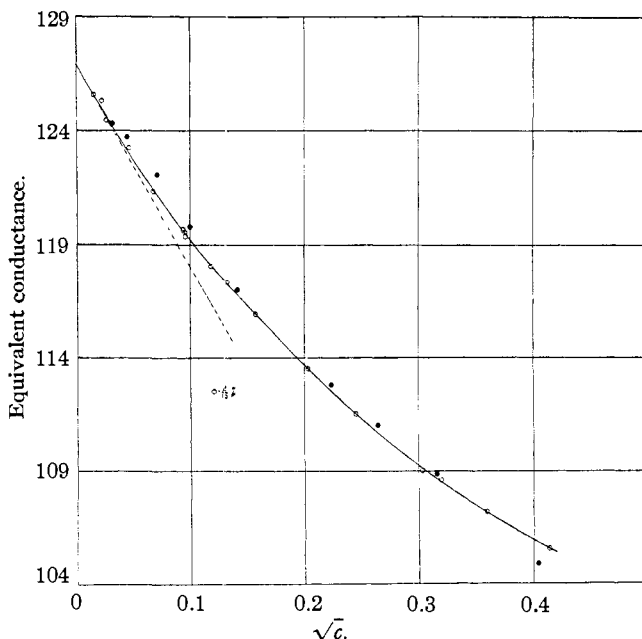


Fig. 2.—○, Lasselle and Aston; ●, Jones.

The slope of the curve in dilute solution is -85.0 while that calculated from the Onsager equation is -88.8 . The error in the extrapolated value is probably not greater than 0.1% .

The conductance of iodide ion obtained by subtracting 50.10 ohm^{-1} , the value for Na^+ obtained by MacInnes, Shedlovsky and Longworth,⁸ from the extrapolated equivalent conductance is 76.75 .

By extrapolating a plot of the data on potassium iodide at 25° from the "International Critical Tables," which seem to be accurate to about 0.05% ,

(7) Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

(8) MacInnes, Shedlovsky and Longworth, *THIS JOURNAL*, **54**, 2758 (1932).

in such a manner that the curve up to 0.001 N had the slope required by the Onsager equation, and subtracting the value of K^+ obtained by MacInnes, Shedlovsky and Longworth,⁸ the limiting conductance of the iodide ion was found to be 76.73. Both of the values depend upon the four series of transport numbers of Longworth⁹ used to calculate $\Lambda_0 Cl^-$.

The densities of the solutions are given in Table II. Column 4 gives the values calculated from the Root¹⁰ equation using the first two terms only: $D = D_0 + c_1N + c_2N^{3/2}$, where $D_0 = 0.99707$ and $c_1 = 0.1118$.

TABLE II
DENSITY OF SODIUM IODIDE SOLUTION AT 25°

C	Experimental	Percentage deviation	Calculated from Root equation
0.17050	1.01610	-0.002	1.01613
.12982	1.01186	+ .009	1.01158
.10254	1.00877	+ .018	1.00853
.09221	1.00754	+ .010	1.00737
.060325	1.00392	- .029	1.00381
.057015	1.00361	+ .009	1.00344
.041222	1.00175	.000	1.00167
.024813	0.99983	- .010	0.99977
.017467	.99861	- .036	.99902
.013992	.99856	- .008	.99863
.0091517	.99805	- .005	.99809
.0090958	.99803	- .006	.99807
.0087179	.99802	.000	.99804
.0045595	.99751	.000	.99758
.00070431	.99708	.000	.99714
Average deviation, %		.008	

Summary

The equivalent conductance and densities of sodium iodide solution have been determined. The conductance results obey the Onsager equation up to about 0.002 normal, and the Shedlovsky modification of it to 0.04 normal.

The limiting equivalent conductance was found to be 126.85 ohms⁻¹ \pm 0.05%.

The limiting equivalent conductance of the iodide ion was found to be 76.75 ohms⁻¹ \pm 0.05%.

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(9) Longworth, THIS JOURNAL, **54**, 274 (1932).

(10) Root, *ibid.*, **55**, 850 (1933).