[Contribution from the Chemical Laboratory of the University of California]

# THE CONDUCTANCE OF DILUTE AQUEOUS SOLUTIONS OF THE ALKALI HYDROXIDES AT 25°

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The following measurements give moderately accurate values for the conductance of dilute aqueous solutions of the five alkali hydroxides at 25°. The data were originally obtained for the purpose of estimating the liquid potential between alkali hydroxide and chloride solutions of the same concentration, by means of the Lewis and Sargent formula.[2] The equivalent conductances at infinite dilution have also been calculated.

**The Conductivity Cell.**—Owing to the small quantity of rubidium and cesium salts available it was impossible to use the ordinary type of pipet cell. Furthermore, it is difficult to transfer alkali hydroxide solutions in air without the formation of some carbonate. By the use of the conductivity cell shown in Fig. 1, a small quantity of the hydroxide sufficed for an entire series of dilutions.

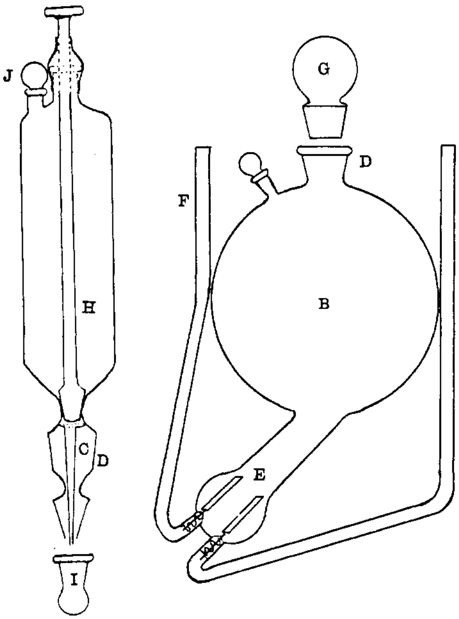

Fig. 1.

The cell consisted of two parts: a modified weight buret A of Jena apparatus glass in which the hydroxide solutions were prepared, and a conductance cell B of about 250 cc. capacity. The tip C was protected by a ground-glass cap I, which was removed when the buret tip was inserted in the ground joint DD while the solution was passing from A to B. A glass stopper G took the place of the weight buret when conductivities were being measured. The platinum electrodes E were carried at the end of a side arm set in an angle of 45°, and were connected to the electrical-measuring system by mercury leads FF. The cell was mounted in the thermostat, in a swinging frame. By a slight tilting of the cell, without removing it from the thermostat, the solution from the side arm was made to run into the bulb. Thus, the contents of the cell were thoroughly mixed and quickly brought to temperature equilibrium.

**Preparation of Solutions.**—The lithium hydroxide solution was prepared by allowing lithium amalgam to react in the buret A with conductivity water. The amalgam

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[1] The experimental work was completed in May, 1918. Dr. Scalione died at a United States Veterans' hospital in California, June 8, 1923.

[2] Lewis and Sargent, This Journal, **31,** 363 (1909).

was prepared by the electrolysis of an aqueous solution of a mixture of Kahlbaum's lithium carbonate and lithium sulfate with a mercury cathode which was stirred during electrolysis. The amalgam thus formed was introduced into A and washed twice with conductivity water. It was then allowed to react with the conductivity water and when the reaction was complete the mercury was drawn off by lifting the plug H from its ground-glass seat.

Sodium hydroxide solution was prepared from sodium which had been redistilled in a vacuum. The surface was scraped from a stick of Kahlbaum's pure sodium metal which was placed in Limb A of the distilling apparatus shown in Fig. 2. The distilling Tube A, Receiver B, and Capillary C (inside diameter, 1 mm.) were of Jena combustion glass and were fastened to connecting Tubes D and E by means of de Khotinsky cement. The bulb F was filled with electrolytic hydrogen purified by passing over a glowing platinum wire and bubbling through sodium-potassium alloy. After evacuation of the entire apparatus, the sodium was distilled from A to B by means of a small electric-resistance furnace. The Receiver B and Capillary C were warmed with a torch to prevent the distilled sodium from solidifying. Stopcocks G and H were closed, and hydrogen was admitted into the apparatus by alternately opening Stopcocks I and J. In this way a part of the liquid sodium was forced into the Capillary C. The sodium was kept in these capillaries until ready for use, when suitable lengths were cut off, tied with a loop of platinum wire and introduced into conductivity water in the weight buret where the sodium reacted quietly. When the reaction was complete, the capillary was removed through the opening J (Fig. 1).

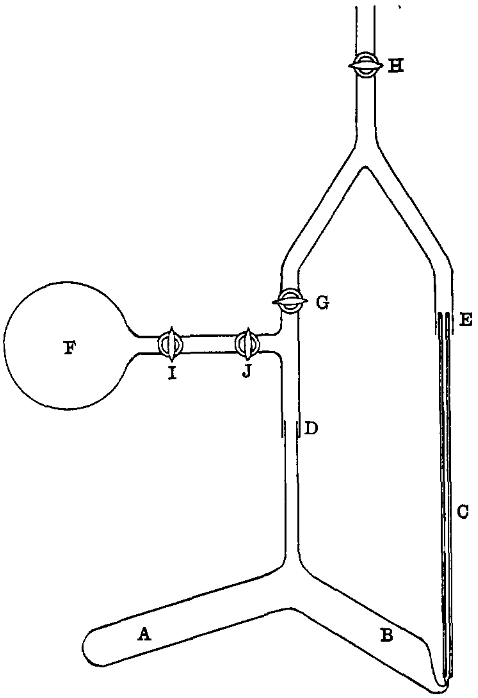

Fig. 2.

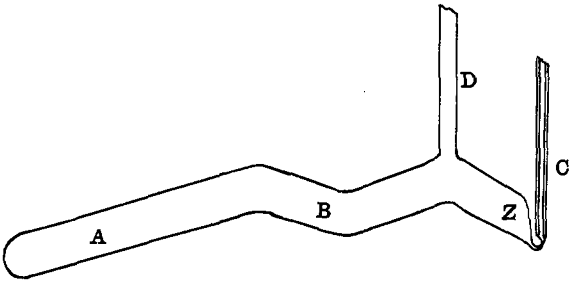

Fig. 3.

Potassium hydroxide solution was prepared from Kahlbaum's pure potassium metal in a manner similar to that used for sodium hydroxide.

For the preparation of rubidium and cesium hydroxides no pure materials were available. Respective salts of unknown origin were converted into the dichloro-iodide,[3] and the dichloro-iodide was submitted to a systematic series of 25 fractional crystallizations. The resulting final fractions, as well as the materials used in making the lithium, potassium and sodium solutions, were tested spectroscopically and found to be free of impurities. The dichloro-iodide was placed in a silver boat, and converted into the chloride by heating in a stream of dry hydrogen chloride. For the preparation of rubidium and cesium metal, 3 g. of pure calcium[4] and 4.5 g. of rubidium chloride or 6 g. of cesium chloride were placed in Limb A of the distilling apparatus (see Fig. 3) of Jena glass. After evacuation as described above, Part A was heated by an electric-resistance furnace, the metal distilling into B was redistilled from B to Z and driven up into Capillary C in a manner similar to that used for sodium and potassium. The hydroxides were prepared from the metal as previously described.

**The Electrical-Measuring System.**—The electrical-measuring system[5] consisted of a Leeds and Northrup Kohlrausch conductivity bridge with extension coils, a set of Curtis compensated resistance coils, compensating condensers, and a set of telephones tuned to 1000 cycles. A Siemens-Schuchart high-frequency generator, placed in a distant room and enclosed in a lead case to decrease the annoyance in operation, served as a source of current. All instruments were shielded from one another, where necessary, by metal partitions thoroughly grounded, and all leads were encased in armored cable. The leads from the conductance vessel were about 25 cm. long, composed of two twisted No. 14 braided copper wires soldered to heavy copper terminals. The resistance of the leads was negligible. Exceedingly satisfactory minima were obtained at all concentrations.

**The Temperature Control.**—A large water thermostat 100 × 50 × 50 cm. was automatically regulated to within ±0.02° at 25°. A grounded copper tank with rounded ends, 30 × 20 × 30 cm., provided with an efficient stirrer, was filled with kerosene and placed in the water thermostat. A small automobile headlight lamp was placed in this tank, and the current was hand-regulated so that the bath remained constant at 25° within ±0.002°. This method of temperature control is more satisfactory than a completely automatically controlled thermostat. A Baudin thermometer, carefully standardized, was used in standardizing the thermometers in the bath.

**Cell Constant.**—1.4912 g. (weighed in air) of Kahlbaum's potassium chloride, recrystallized to a constant conductance, and powdered and dried to constant weight, was dissolved to make two liters of solution at 25°. This solution, according to Kohlrausch, with temperature coefficients of Deguine, and as used by Bray and Hunt,[6] has a specific con-

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[3] Wells and Wheeler, *Z. anorg. Chem.*, **1**, 442 (1892); **2**, 257 (1892).

[4] Hackspill, *Compt. rend.*, **141**, 106 (1905).

[5] The more modern arrangement of Randall and Scott [THIS JOURNAL, **49**, 636 (1927)] is more satisfactory.

[6] Bray and Hunt, *ibid.*, **33**, 781 (1911).

ductance of 0.0014142 mho. From the work of Parker and Parker,[7] we calculate the standard of Bray and Hunt to be 0.152% too high. The original results have been corrected by this amount. Atomic weights of 1926 and vacuum corrections have been used.

**Conductivity Measurements.**—The conductance Cell B, the electrodes of which had been previously platinized, was thoroughly steamed out and dried by means of a current of air free from carbon dioxide. A weighed quantity of conductivity water (approximately 50 g.) was introduced into Cell B and, as a check, the specific conductance of the water was measured ($0.7 - 0.8 \times 10^{-6}$ mho). A little of the previously prepared hydroxide solution in A was run to waste and a weighed portion of the concentrated hydroxide solution was then allowed to run into B. The contents of the cell were mixed by tilting the cell in the thermostat, and as equilibrium was reached the conductance was measured and another weighed portion of concentrated hydroxide solution was added to the solution in Cell B and the conductivity determined as before.[8] The mixing and attainment of temperature equilibrium were rapid so that the dilute hydroxide solutions did not remain in contact with the glass long enough to dissolve an appreciable amount. After the last addition of hydroxide, all or a portion of the solution in Cell B was weighed out for analysis. In some cases a portion of this solution was placed in the pipet Cell A and used for the preparation of the more dilute hydroxide solutions. From the analysis of the final solution in B, the weight of conductivity water originally present, and the weight of each portion of solution run out from Cell A, the concentration at each dilution was calculated.

**Analysis of End Solution.**—The weighed portions of the end solutions were titrated with approximately 0.03 *M* hydrochloric acid solution from a weight buret, a mixture of *p*-nitrophenol and methyl red being used as an indicator. The hydrochloric acid solutions were prepared by passing pure hydrochloric acid into the conductivity water and were accurately standardized[9] with sodium carbonate which had been fused in a stream of carbon dioxide.

**The Conductance Data.**—The results of the measurements are given in Tables I–V, inclusive. Col. 1 gives the concentration in moles per kilogram of solution, Col. 2 the concentration in grams per kilogram of water, Col. 3 the specific conductance, $k$, Col. 4 the "molal conductance,"[10] $1000\ k/m$, Col. 5 the density, Col. 6 the concentration in moles per liter, Col. 7 the equivalent conductance, $\Lambda$, and the last column, the quotient

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[7] Parker and Parker, This Journal, **46,** 312 (1924).

[8] In cases in which the air of the laboratory contains much carbon dioxide, the transfer of solution can be made out of doors.

[9] (a) Richards and Hoover, This Journal, **37,** 95, 108 (1915). (b) Randall and Scalione, *Met. Chem. Eng.*, **13,** 787 (1915).

[10] Randall and Vanselow, This Journal, **46,** 2418 (1924).

of the equivalent conductance by the conductance ratio of hydrochloric acid. The densities for the solutions of lithium, sodium and potassium hydroxides were interpolated from values given by Ruppin.[11] No actual measurements have been made on rubidium and cesium hydroxides.

TABLE I

CONDUCTANCE OF AQUEOUS LITHIUM HYDROXIDE AT 25°

| Concn., moles per kg. of soln. | Concn., moles per kg. of $H_2O$ | $k$, mhos per cc. × $10^3$ | $\frac{1000\,k}{m}$ | $D^{25}_{4}$ | $c$, moles per liter | Equiv. cond., $\Lambda$ | $\frac{\Lambda}{\alpha(\text{HCl})}$ |
|---|---|---|---|---|---|---|---|
| 0.001394 | 0.001394 | 0.3232 | 231.8 | 0.9971 | 0.001390 | 232.5 | 235.1 |
| .002923 | .002923 | .6758 | 231.1 | .9972 | .002915 | 231.8 | 235.8 |
| .004961 | .004961 | 1.1392 | 229.6 | .9972 | .004947 | 230.2 | 235.5 |
| .006152 | .006152 | 1.4016 | 227.8 | .9973 | .006136 | 228.3 | 234.3 |
| .007398 | .007398 | 1.6767 | 226.5 | .9973 | .007378 | 227.3 | 233.8 |
| .01129 | .01129 | 2.545 | 225.4 | .9974 | .01126 | 226.0 | 234.1 |
| .01394 | .01394 | 3.129 | 224.4 | .9975 | .01391 | 225.0 | 233.9 |
| .02703 | .02705 | 6.021 | 222.5 | .9978 | .02697 | 223.1 | 235.0 |

TABLE II

CONDUCTANCE OF AQUEOUS SODIUM HYDROXIDE AT 25°

| Concn., moles per kg. of soln. | Concn., moles per kg. of $H_2O$ | $k$, mhos per cc. × $10^3$ | $\frac{1000\,k}{m}$ | $D^{25}_{4}$ | $c$, moles per liter | Equiv. cond., $\Lambda$ | $\frac{\Lambda}{\alpha(\text{HCl})}$ |
|---|---|---|---|---|---|---|---|
| 0.0009123 | 0.0009123 | 0.2195 | 240.5 | 0.9971 | 0.0009097 | 241.2 | 243.2 |
| .001394 | .001394 | .3361 | 241.1 | .9971 | .001390 | 241.7 | 244.4 |
| .002232 | .002232 | .5339 | 239.2 | .9971 | .002226 | 240.8 | 244.4 |
| .002557 | .002557 | .6126 | 239.5 | .9972 | .002550 | 240.2 | 244.0 |
| .005216 | .005216 | 1.2392 | 237.5 | .9973 | .005202 | 238.1 | 243.7 |
| .006907 | .006907 | 1.634 | 236.5 | .9974 | .006889 | 237.0 | 243.5 |
| .008591 | .008591 | 2.021 | 235.2 | .9975 | .008570 | 236.0 | 244.3 |
| .009772 | .009772 | 2.299 | 235.3 | .9975 | .009748 | 235.9 | 243.7 |
| .01910 | .01912 | 4.441 | 232.2 | .9979 | .01906 | 232.6 | 243.3 |
| .04721 | .04730 | 10.803 | 228.4 | .9992 | .04717 | 228.6 | 243.9 |

TABLE III

CONDUCTANCE OF AQUEOUS POTASSIUM HYDROXIDE AT 25°

| Concn., moles per kg. of soln. | Concn., moles per kg. of $H_2O$ | $k$, mhos per cc. × $10^3$ | $\frac{1000\,k}{m}$ | $D^{25}_{4}$ | $c$, moles per liter | Equiv. cond., $\Lambda$ | $\frac{\Lambda}{\alpha(\text{HCl})}$ |
|---|---|---|---|---|---|---|---|
| 0.0005934 | 0.0005934 | 0.15654 | 263.8 | 0.9971 | 0.0005917 | 264.6 | 266.1 |
| .0008111 | .0008111 | .21495 | 265.0 | .9971 | .0008087 | 265.9 | 267.8 |
| .001179 | .001179 | .3124 | 265.0 | .9972 | .001175 | 265.7 | 268.3 |
| .002151 | .002151 | .5675 | 263.8 | .9973 | .002145 | 264.5 | 268.3 |
| .003490 | .003490 | .9144 | 262.0 | .9973 | .003481 | 262.7 | 267.7 |
| .005444 | .005444 | 1.4125 | 259.5 | .9975 | .005430 | 260.1 | 266.4 |
| .006471 | .006471 | 1.6723 | 258.4 | .9976 | .006455 | 259.0 | 265.9 |
| .007442 | .007442 | 1.9155 | 257.4 | .9976 | .007424 | 258.0 | 265.4 |
| .009472 | .009472 | 2.434 | 257.0 | .9978 | .009451 | 257.6 | 266.0 |
| .014412 | .01442 | 3.689 | 255.8 | .9981 | .01438 | 256.5 | 266.7 |
| .05044 | .05058 | 12.84 | 253.9 | 1.0007 | .05048 | 250.9 | 268.1 |

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[11] Ruppin, *Z. physik. Chem.*, **14**, 467 (1894).

TABLE IV

CONDUCTANCE OF AQUEOUS RUBIDIUM HYDROXIDE AT 25°

| Concn. moles per kg. of soln. | Concn. moles per kg. of $H_2O$ | $k$, mhos per cc. $\times 10^3$ | $\frac{1000\,k}{m}$ | $D^{25}_4$ | $c$, moles per liter | Equiv. cond., $\Lambda$ | $\frac{\Lambda}{\alpha(HCl)}$ |
|---|---|---|---|---|---|---|---|
| 0.002124 | 0.002124 | 0.5663 | 266.6 | 0.9973 | 0.002118 | 267.3 | 271.2 |
| .002489 | .002489 | .6612 | 265.7 | .9973 | .002482 | 266.3 | 270.5 |
| .003132 | .003132 | .8312 | 265.4 | .9974 | .003124 | 266.0 | 270.8 |
| .004217 | .004217 | 1.1147 | 264.3 | .9975 | .004206 | 265.0 | 270.6 |
| .007411 | .007411 | 1.9402 | 261.8 | .9978 | .007394 | 262.4 | 269.9 |
| .009306 | .009307 | 2.425 | 260.6 | .9980 | .009287 | 261.2 | 269.6 |
| .011615 | .01162 | 3.022 | 260.1 | .9982 | .011594 | 260.7 | 270.1 |

TABLE V

CONDUCTANCE OF AQUEOUS CESIUM HYDROXIDE AT 25°

| Concn., moles per kg. of soln. | Concn., moles per kg. of $H_2O$ | $k$, mhos per cc. $\times 10^3$ | $\frac{1000\,k}{m}$ | $D^{25}_4$ | $c$, moles per liter | Equiv. cond., $\Lambda$ | $\frac{\Lambda}{\alpha(HCl)}$ |
|---|---|---|---|---|---|---|---|
| 0.000695 | 0.000695 | 0.18346 | 263.8 | 0.9972 | 0.000693 | 264.5 | 265.5 |
| .001541 | .001541 | .4070 | 264.1 | .9973 | .001537 | 264.8 | 268.0 |
| .002332 | .002332 | .6189 | 265.4 | .9974 | .002332 | 265.9 | 269.9 |
| .004091 | .004091 | 1.0800 | 264.0 | .9976 | .004081 | 264.5 | 270.0 |
| .006172 | .006173 | 1.634 | 264.6 | .9979 | .006159 | 265.2 | 272.1 |
| .008391 | .008392 | 2.210 | 263.4 | .9982 | .008376 | 263.9 | 272.0 |
| .01041 | .01042 | 2.728 | 261.8 | .9985 | .01039 | 262.6 | 271.5 |
| .02729 | .02739 | 6.952 | 253.8 | 1.0007 | .02731 | 254.6 | 268.2 |
| .06495 | .06541 | 16.292 | 249.1 | 1.0057 | .06532 | 249.4 | 268.4 |

We shall make no great error if we assume that the density of these latter hydroxides bear the same relation to the densities of their respective chlorides as the densities of potassium and sodium chloride bear to their hydroxides. The densities of the chlorides were taken from the data of Baxter and Wallace.[12]

**Conductance at Infinite Dilution.**—Because of the peculiar nature of the hydroxides it is impossible, without elaborate precautions, to obtain data with an average deviation of less than 0.2%, nor is it possible to carry the measurements to extreme dilutions. It is impossible, therefore, to use a primary method of obtaining the value of the limiting conductance.[13]

We have used the method of Randall,[14] in which the conductance ratio of a salt is assumed provisionally to be the same as that of a salt of the same type whose limiting conductance has been accurately determined. The various values of the equivalent conductance were divided by the conductance ratios of hydrochloric acid as read from a curve which com-

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[12] Baxter and Wallace, THIS JOURNAL, **38,** 70 (1916).

[13] See (a) Storch, *Z. physik. Chem.*, **19,** 13 (1896). (b) Noyes, THIS JOURNAL, **30,** 335 (1908). (c) Noyes and Falk, *ibid.*, **34,** 462 (1912). (d) Bates, *ibid.*, **35,** 519 (1913). (e) Kraus and Bray, *ibid.*, **35,** 1315 (1913). (f) Washburn, *ibid.*, **40,** 107, 122 (1918). (g) Kraus, *ibid.*, **42,** 1 (1920).

[14] Randall, *ibid.*, **38,** 788 (1916).

bined the limiting value and data in dilute solutions of Parker,[15] and of Bray and Hunt.[6] The quotients thus obtained are given in the last columns of Tables I–V. When plotted against the square root of the concentration there appears to be no trend to the results. We may, therefore, take the conductance ratios to be the same as those of hydrochloric acid, within the limits of the experimental error, and take the arithmetical means as the values of the limiting conductances, whence we find, for lithium hydroxide, $\Lambda_\infty = 234.7$; for sodium hydroxide, $\Lambda_\infty = 243.9$; for potassium hydroxide, $\Lambda_\infty = 266.8$; for rubidium hydroxide, $\Lambda_\infty = 270.4$; for cesium hydroxide, $\Lambda_\infty = 269.5$. Comparison with the curve for iodic acid given by Kraus and Parker[15,16] and extrapolation to $c = 0$ gave approximately the same results.

No other measurements of the conductances of the alkali hydroxides have been made at 25°. We have plotted the ratios of the equivalent conductance to the conductance ratio of hydrochloric acid for the results given by Kohlrausch[17] for potassium hydroxide, by Foster[18] for sodium hydroxide, and by Heydweiller[19] for lithium, sodium, potassium and rubidium hydroxides in solutions below 0.25 *N* at 18°. Heydweiller's most dilute solution is 0.1 *N*. The values of the ratios for the various salts do not contradict the assumption that the conductance ratios of the hydroxides are the same as those of hydrochloric acid, within the experimental error. The values given above are probably correct to about two units. Heydweiller[19] also gives results up to 4 *N*, and values in concentrated solutions of lithium hydroxide are given by Kohlrausch[17] at 15°, for sodium hydroxide at 18° by Bousfield and Lowry,[20] and for sodium and potassium hydroxides by Kohlrausch[17] at 15°, and by Loomis[21] at 18°.

## Summary

The conductances of dilute solutions of the alkali hydroxides were measured at 25°. The conductance ratios were found to be the same as those of hydrochloric acid within the limits of the experimental error.

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[15] Parker, THIS JOURNAL, **45,** 2017 (1923).

[16] Kraus and Parker, *ibid.*, **44,** 2429 (1922).

[17] Kohlrausch, *Ann. Physik Chem.*, [3] **6,** 1, 145 (1879).

[18] Foster, *Phys. Rev.*, **8,** 257 (1899).

[19] Heydweiller, *Ann. Physik,* [4] **48,** 681 (1915).

[20] Bousfield and Lowry, *Trans. Roy. Soc. London,* **204A,** 253 (1904).

[21] Loomis, *Ann. Physik Chem.*, [3] **60,** 547 (1897).