LXXXV.—*The Equivalent Conductivity of Solutions of Sodium Hydroxide and the Mobility of the Hydroxyl Ion.*

By HUMPHREY RIVAZ RAIKES, ALBERT FREDERICK YORKE, and FREDERICK KENNETH EWART.

THE object of the work detailed in this paper was to make use of the very pure water obtainable from stills of the type described by Bourdillon (J., 1913, **103**, 791) for determining the value of the mobility of the hydroxyl ion.

It has long been recognised that the chief impurity in conductivity water is carbon dioxide. Present as it is in extremely small quantities, its effect on the conductivity of solutions of salts and to a less degree of acids may well be regarded as negligible and the true value of the conductivity is obtained from the observed value by subtracting a " water-correction."

With hydroxides, however, the case is quite different, since slow-moving carbonate ions are substituted for mobile hydroxyl ions and in very dilute solution the conductivity is that of a carbonate and not that of a hydroxide. The observed values will thus be less than the true values and if anything a correction should be added instead of subtracted.* As, however, the determination of the value of this correction is not a simple matter, our method has been to use only water of the highest purity and to regard the whole conductivity as being due to the hydroxide.

The still used was a slightly modified Bourdillon still. It delivered, in quantity, water of specific conductivity 0·06—0·07 gemmho, and in the best experiments this had not increased beyond 0·09 gemmho after the water had been transferred to the conductivity cell.

---

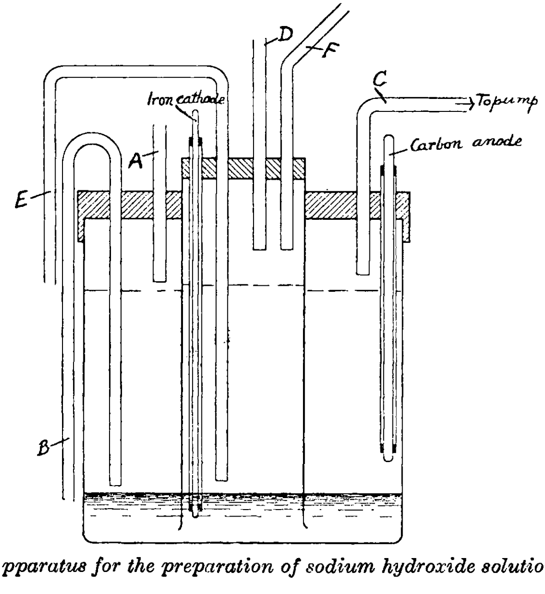
* Mr. W. F. K. Wynne-Jones has very kindly examined our figures and in one run where water of 0·599 gemmho purity was used and in which the equivalent conductivity showed a maximum at a concentration of 0·0007 mol. per litre he has shown that the application of a correction based on the assumption that the conductivity of the water was due to carbon dioxide brings the values obtained into close agreement with those found by us in water of a high degree of purity.

EXPERIMENTAL.

Preparation of Sodium Hydroxide Solutions.—The chief methods available for the preparation of pure aqueous sodium hydroxide are (i) the action of water on metallic sodium; (ii) methods involving the precipitation of the carbonate present in ordinary sodium hydroxide by means of a barium or calcium salt; (iii) the electrolysis of an aqueous solution of a sodium salt.

In the first method, the difficulty is to get rid of the scale of carbonate on the surface of the metal before submitting it to the action of water.

FIG. 1.



Apparatus for the preparation of sodium hydroxide solutions.

In the second method, it is impossible to avoid the presence in the final product of either barium or calcium. Noyes states (*Pub. Carnegie Inst.*, 1907, No. 63) that his final product contained at least 0·1% of barium sulphate.

A very pure product may be obtained, however, by the third method.

A method somewhat similar to ours for obtaining aqueous sodium hydroxide free from carbonate has been described by Jorissen and Filippo (*Chem. Weekblad*, 1909, **6**, 145).

Description of Apparatus.—The cell (Fig. 1) consisted of an outer vessel of common glass about a litre in capacity, carrying a wide glass tube of about 200 c.c. capacity which was made the cathode compartment. The tube was at first of Jena glass and later of Pyrex glass; no difference in the purity of the final product could be detected. All the glass tubing used was boro-silicate and was well steamed before being made up. The bottom of the cell was covered to the depth of about an inch with mercury, previously distilled in a vacuum.

A tightly fitting wooden cap in the outer vessel carried the cathode compartment and other accessories. The lower end of the cathode compartment dipped well below the surface of the mercury, but did not touch the bottom of the outer vessel. A tightly fitting cork in the top of the cathode compartment itself carried the accessories necessary in this compartment.

The anode consisted of a carbon rod, which was rather rapidly attacked by chlorine; it was protected as far as possible by means of a glass tube, and arranged so that its end was about 1 inch above the mercury surface.

The cathode was of iron protected by a sheath of borosilicate glass tubing; its lower end dipped into the mercury and the iron never came into contact with the solution in the cathode compartment.

At first the whole apparatus was arranged so that it could be rocked gently in order to facilitate the passage of the sodium amalgam into the cathode compartment. This rocking was, however, found to be unnecessary and was abandoned.

The current used was about 2·3 amps. when the cell could be watched, but when it had to be left this was reduced to 1·2 amps. in order to avoid the risk of heating.

Procedure when Working the Cell.—The mercury having been run into the cell, the cap was placed in position and sealed on. As an additional precaution, the whole of the outside of the cap was covered with a layer of high melting-point paraffin-wax.

The cathode compartment was washed from five to six times with fairly good conductivity water; the water being run in through *D* and syphoned out through *E*.

A normal solution of sodium chloride (Merck) made up with water of about 0·5 gemmho conductivity was run into the anode compartment through the tube *A*, so that the level of the liquid was about an inch below the end of *C*; the tube *A* was then fitted with a soda-lime tube.

A current of dry air, free from carbon dioxide and ammonia, was next passed through the cathode compartment, *via* the tube *F*, the tubes *D* and *E* during this operation carrying soda-lime tubes; after this, the tube *F* was connected to a soda-lime tube.

Finally, about 200 c.c. of pure water (0·3 gemmho conductivity) were run into the cathode compartment through the tube *D*, which was connected to the flask delivering the water, so that at no time did the latter come into contact with the atmosphere. The tubes *D* and *E* were then closed.

The current was now switched on, the hydrogen evolved at the cathode escaping through the soda-lime tube connected with *F*, and the chlorine being drawn off through *C* by means of a water pump; it was found necessary to connect the tube *A* to the air (through a soda-lime tube) in order to prevent a reduction of pressure taking place in the anode chamber, and consequent passage of the cathode liquid into the anode compartment. The exhausted brine was syphoned off through *B*.

Care was taken to keep the temperature of the cell as low as possible during the reaction, in order to prevent the solution of silica. The temperature at no time rose above 40° and was usually kept between 25° and 30°.

After the current had passed for about 6 hours, some of the sodium hydroxide in the cathode compartment was drawn off, and its strength roughly estimated. The solutions eventually used varied from $N/10$ to N. The main quantity of solution was then transferred by suction to a Jena glass flask which had been previously steamed and filled with pure air.

Thus the sodium hydroxide solution never came into contact with the air of the room at any time during its preparation. The solution was stored in this flask until required for a dilution, but was rarely kept for more than 3 days before being so used.

Purity and Analysis of the Sodium Hydroxide Solutions.—The sodium hydroxide prepared as above was invariably tested for chlorine and carbon dioxide, the former by the nephelometric method of Richards (*Amer. Chem. J.*, 1904, **31**, 235; 1906, **35**, 99), and the latter by mixing with baryta in the nephelometer by a method which enabled the solutions to be compared without any risk of contamination by carbon dioxide. The solutions never showed a greater cloudiness than a clear solution of baryta which was used as standard. Chlorine was always absent. The analysis of the solutions was carried out by means of weight titrations against hydrochloric acid, with methyl-red as indicator. The analyses were always done in triplicate and never differed by more than 1 part in 10,000. The hydrochloric acid was purified and estimated by Richards's method (*J. Amer. Chem. Soc.*, 1905, **27**, 459). Three analyses of each sample were made and the results agreed to 1 part in 20,000.

The weights used were standardised by Richards's method (*J. Amer. Chem. Soc.*, 1900, **22**, 144) and the appropriate vacuum correction was always applied. The densities of the sodium hydroxide and hydrochloric acid solutions were taken from Landolt and Bornstein's tables.

The Conductivity Measurements.—The cell used was one designed by Hartley and Barrett and will be described in a future publication. It consisted essentially of a 1500 c.c. Jena glass beaker, to the top of which was cemented a brass ring. To this ring was attached by means of screws a silver-plated brass cover which carried the electrodes, a stirrer, and a thermometer, and was provided with two openings through one of which a stream of pure air could be passed, whilst the tip of the weight pipette was inserted through the other. These openings could be closed at will. The electrodes were coated with platinum black.

All the resistances were calibrated against Wolff standards which had been recently restandardised at the National Physical Laboratory.

The cell constant, determined in the manner described by Frazer and Hartley (*Proc. Roy. Soc.*, 1925, *A*, **109**, 355), had the value 0·1367, identical with the value obtained by Hartley and Barrett in 1909.

The Thermostat.—The temperature variation of the bath was never more than ± 0·01° and for most of the runs it did not exceed ± 0·005°.

The Weight Pipette.—The weight pipette used for adding the solution to the cell was provided with a filling arrangement which effectually prevented the contamination of the solution by the carbon dioxide of the air.

A run was carried out by adding weighed portions of stock solution to the solvent in the cell.

Cleaning and Drying the Cell.—After each run the cell was rinsed out several times with pure water, and the electrodes, thermometer, and stirrer were cleaned by means of a stream of water. The cell was then filled with about a litre of pure water, the top placed in position, and the stirrer set going for several hours. The water was changed at least once a day and stirred. When the cell was required for a run, the beaker was inverted and allowed to drain for about 6 hours; the rest of the cell was also drained. For the first two runs the beaker was finally dried by means of filter-paper; the thermometer and stirrer were dried in a similar manner. The electrodes were dried by just touching their edges with filter-paper.

It was found later that the water was of better quality if the beaker was not wiped, but if, after draining, the top was placed in position and a current of dry air passed through it for several hours, the stirrer being rotated in order to keep the air circulating. This was found to be a very effective method of drying.

The Results.—In all, seven runs were carried out at 18° and two at 10°. The figures in Tables I and II show that even in the best water the equivalent conductivity fell off in solutions less concentrated than *N*/1000. In some of the earlier runs the values obtained were quite untrustworthy.

All concentrations are given in gram-molecules per litre at the temperature of experiment (NaOH = 40).

TABLE I.

Equivalent Conductivity of Sodium Hydroxide at 18°.

Uncorrected for solvent conductivity.

Run H. 31/5/1922. $T = 18° \pm 0{\cdot}005°$. Water 0·086 gemmho.

Conc. × 10^4	0·266	0·576	0·889	2·45	7·24	17·87	29·9
Λ	171·8	185·0	189·0	200·7	205·0	208·0	208·0

Run K. 12/6/1922. $T = 18° \pm 0{\cdot}005°$. Water 0·084 gemmho.

Conc. × 10^4	2·54	5·85	11·28	22·5	48·7	99·5	170	319
Λ	208·3	211·4	214·4	213·6	211·4	209·5	207·6	203·8

Run L. 20/6/1922. $T = 18° \pm 0{\cdot}005°$. Water 0·087 gemmho.

Conc. × 10^4	10·5	22·3	41·2	76·4	158	277	545
Λ	215·0	213·7	212·0	210·1	207·9	204·9	198·1

TABLE II.

Equivalent Conductivity of Sodium Hydroxide at 10°.

Uncorrected for solvent conductivity.

Run D. 29/4/1922. $T = 10° \pm 0{\cdot}01°$. Water 0·082 gemmho.

Conc. × 10^4 ...	0·431	1·26	8·42	17·6	33·1
Λ	152·4	169·1	178·3	178·6	178·0

Run M. 22/6/1922. $T = 10° \pm 0{\cdot}01°$. Water 0·089 gemmho.

Conc. × 10^4 ...	9·74	18·9	36·7	73·5	144	285
Λ	179·2	178·2	177·0	176·6	175·1	173·0

Fig. 2 gives the graph of equivalent conductivity plotted against the square root of the concentration, and it will be seen that for solutions more concentrated than *N*/1000 the points lie on straight lines up to a concentration of *N*/30. The equations to these lines are :

$$\text{at } 18°,\ \Lambda_{18} = 217 - 75{\cdot}7\sqrt{c}$$
$$\text{and at } 10°,\ \Lambda_{10°} = 180{\cdot}2 - 44{\cdot}2\sqrt{c},$$

c being the concentration of the solution in gram-molecules per litre at the temperature of experiment.

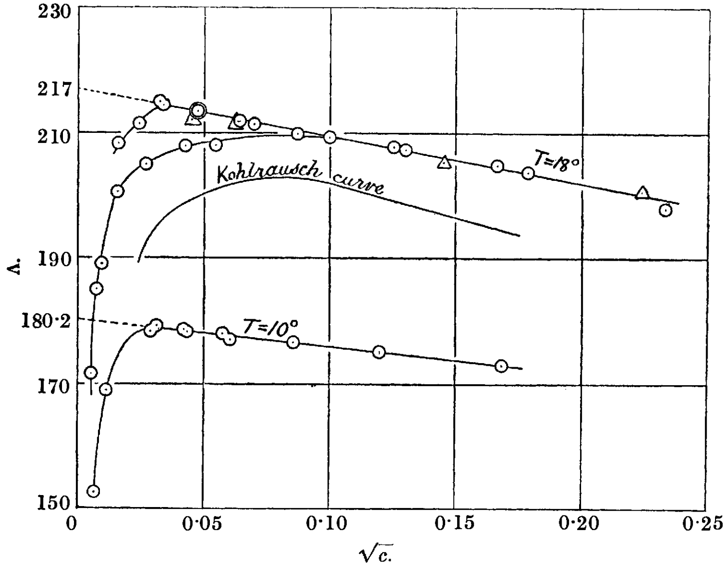
Noyes (*loc. cit.*), whose sodium hydroxide was estimated by himself to contain 0·1% of barium sulphate, gives four values for the equivalent conductivity which lie about 0·5% below our values (see Fig. 2).

For comparison, the values obtained by Kohlrausch (*Wied. Ann.*, 1885, **26**, 197) are also plotted in Fig. 2.

The Temperature Coefficient of Equivalent Conductivity between 10° and 18°.—The temperature coefficient calculated from the above figures is 4·60. The value obtained by Noyes (*loc. cit.*) for the range 18—100° was also 4·60.

The Mobility of the Hydroxyl Ion.—The mobility of the sodium ion at 18° being taken as 43·4 (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 479), the mobility of the hydroxyl ion becomes 173·6 at 18°.

FIG. 2.



The points marked △ are those of Noyes; the concentrations have been recalculated to gram-mols. per litre.

If the mobility of the sodium ion as calculated by Washburn (*J. Amer. Chem. Soc.*, 1918, **40**, 158) is taken to be 43·23, the value for the hydroxyl ion becomes 173·8.

On the somewhat untrustworthy assumption that the transport number of the hydroxyl ion in sodium hydroxide has the same value at 18° and 10°, the mobility of the hydroxyl ion at 10° is, using the Noyes and Falk value for the sodium ion, 144·2, and using the Washburn value, 144·3.

Summary.

The equivalent conductivity of solutions of sodium hydroxide has been measured at 18° and 10° and the values for infinite dilution found to be 217·0 and 180·2, respectively.

Using Washburn's value for the mobility of the sodium ion, the mobility of the hydroxyl ion is found to be 173·8 and 144·3 at the two temperatures.

The authors wish to express their indebtedness to the Research Fund Committee of the Chemical Society for assistance in purchasing a part of the apparatus used for the still, to the authorities of Balliol and Trinity Colleges for permission to use their laboratory, and in particular to Brigadier-General H. Hartley for his continued interest and advice during the course of the work.

EXETER COLLEGE, OXFORD. [*Received, November* 21*st*, 1925.]