2. The calculation of the partial pressure of hydrogen, to which the developer is equivalent, seems to be the only way in which the absolute or relative reducing power of developers can be directly measured.

3. The results obtained by the employment of this method seem to be photographically reasonable.

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THE HYDROGEN POTENTIALS OF SODIUM HYDROXIDE SOLUTIONS AND THE DISSOCIATION CONSTANT OF WATER.

By Francis C. Frary and Adolph H. Nietz.

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In connection with our work on the single potentials of developers, we noticed that the hydrogen potential (E_{H_2}) of a solution containing sodium carbonate and sulfite would change as much as thirty millivolts on adding the proper amount of hydrochinon to make a satisfactory developer. The change was in such a direction as to indicate that the hydrochinon combined with the sodium carbonate, forming a sodium salt and sodium bicarbonate, thereby decreasing the hydroxyl-ion concentration of the solution. It seemed that electrometric measurements of this nature might give us some very useful information about the reactions taking place when a developer is mixed, but in order to interpret such measurements we needed certain data not accessible in the literature.

It is evident that the mechanism of this reaction involves the hydrolysis of sodium carbonate and the reaction between the sodium hydroxide thus formed and the hydrochinon. As the sodium hydroxide is consumed, the hydrolysis must continue until the product of the bicarbonate concentration by the hydroxide concentration, divided by the concentration of the carbonate, reaches the value characteristic of the equilibrium at that temperature and dilution. In order to be able to determine the extent of the reaction, it is necessary to know both the hydrolysis constant of sodium carbonate and the hydrogen potentials corresponding to the various concentrations of sodium hydroxide. Since these were the fundamental quantities involved in the reaction under consideration, it appeared very desirable, in order to eliminate any errors inherent in the electrometric method, to use this method in their determination. As the hydrogen-ion concentration is the quantity directly susceptible of measurement by the electrometric method, it is first necessary to be able to transform a measurement of the hydrogen potential of the solution into terms of the concentration of sodium hydroxide.

A few measurements of the hydrogen potentials of sodium hydroxide solutions have been made by Lorenz and Mohn,[1] but their values do not cover a sufficient range for our purpose, and nothing is stated as to the purity of their sodium hydroxide. Since a very small quantity of carbon dioxide can have a large effect in very weak sodium hydroxide solutions, we decided to repeat their work and extend it over a somewhat wider range.

A quantity of sodium amalgam was prepared by electrolysis of a strong solution of C. P. sodium carbonate, with a cathode of purified mercury. This amalgam was thoroughly washed with distilled water and then with conductivity water, and finally decomposed by treatment with conductivity water in the presence of platinum, in an aged Jena glass flask. Special precautions were always taken in the handling of this solution to avoid contamination by carbon dioxide. This solution, after preliminary titration and dilution, was standardized gravimetrically by evaporation in platinum with an excess of hydrochloric acid, and ignition of the resulting salt. The dilute solutions, made from this one by the addition of conductivity water, were all standardized in this way. All solutions were carefully preserved in Jena glass flasks which had been thoroughly aged by steam and the determinations were made as soon as possible after mixing, to avoid contamination by the glass.

The hydrogen electrode described in the previous paper (p. 2244) was used, and all determinations were made at 25°. The results in Table I are each the mean of a number of concordant measurements, using a normal calomel electrode and a saturated solution of potassium chloride as the intermediate liquid.

TABLE I.—HYDROGEN POTENTIALS OF PURE SODIUM HYDROXIDE SOLUTIONS.

E_{H_2} is the observed potential referred to the normal calomel electrode as +0.560 + 0.0006 (t — 18), E_h is the same potential on the hydrogen scale.

Sodium hydroxide conc.			
Mols per liter.	Liters per mol.	E_{H_2}.	E_h.
1.000	1.0	—0.525	—0.807
0.507	1.97	—0.506	—0.788
0.2039	4.91	—0.484	—0.766
0.102	9.8	—0.470	—0.752
0.01057	94.6	—0.413	—0.695
0.00078	1282.0	—0.344	—0.626

In all cases the potentials listed are on the basis of the potential of the electrode minus the potential of the solution. In order to convert E_{H_2} into the values for E_h, it is necessary, according to the work of Loomis and Acree,[2] to add —0.282 volt, and the resulting values are listed under E_h in the table. Since the basis of the hydrogen scale is the hydrogen

[1] *Z. physik. Chem.*, **60**, 422 (1907).

[2] *Am. Chem. J.*, **46**, 634 (1911).

potential of a solution which is normal in respect to the hydrogen ion, E_h represents in each case the e. m. f. between a hydrogen electrode in a solution of normal hydrogen-ion concentration and a hydrogen electrode in the given solution.

It is evident that from these results we may calculate directly the hydrogen-ion concentration in the sodium hydroxide solutions by means of the formula

$$E_h = 0.05909 \log 1/c',$$

where c' represents the hydrogen-ion concentration in the sodium hydroxide solution at 25°.

In order to convert these values into the corresponding concentrations of the hydroxyl ion, it is only necessary to know the dissociation constant of water. It is obvious that this constant will be involved in every measurement of the hydrolysis of sodium carbonate, and in all other measurements of the alkalinity of a solution. The hydroxyl-ion concentration of any pure sodium hydroxide solution can easily be determined from its degree of dissociation as indicated by conductivity measurements, which have been very accurately made by various authors. To determine k_w, the dissociation constant of water, it is only necessary to substitute in the above equation the value of $c' = k_w/[\mathrm{OH}]$, giving us

$$E_h = 0.05909 \log [\mathrm{OH}^-]/k_w.$$

The conductivity data used for the calculation of the dissociation of the sodium hydroxide, with their sources, are shown in Table II.

TABLE II.—CONDUCTIVITY OF SODIUM HYDROXIDE SOLUTIONS AT 18°.

v (liters per gram-equivalent).	λ_v at 18.	Determined by	v (liters per gram-equivalent).	λ_v at 18.	Determined by
1	157.0	Foster[1]	200	203	Kohlrausch[2]
2	174.1	Foster[1]	500	204.5	Foster
10	195.4	Foster[1]	1000	208	Kohlrausch
50	197	Kohlrausch[2]	5	210[3]	Goldsmith and Larsen[4]
100	200	Kohlrausch[2]			

Arrhenius[5] gives the temperature coefficients of the conductivity of sodium hydroxide for temperatures between 18° and 40° as 0.0202 for $v = 2$ and $v = 10$, and 0.0213 for $v = 100$. No more complete data on temperature coefficients has been found, and most of the work on the conductivity of sodium hydroxide appears to have been done at 18°. We have therefore calculated the conductivity and degree of ionization from the above values. The results so obtained are undoubtedly a very

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

[2] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," p. 160.

[3] At 25°.

[4] *Z. physik. Chem.*, 71, 453 (1910).

[5] *Ibid.*, 9, 339 (1892).

close approximation, and when the dissociation is plotted as a function of the dilution a smooth curve is obtained.

Recent determinations of the conductivity of the ions give, for 25°, $Na^+ = 50.5$, $OH^- = 196$, from which the equivalent conductivity of sodium hydroxide at infinite dilution is 246.5. Table III shows the ionization as calculated from the figures in Table II; the temperature coefficients c and the value for $\lambda_\infty = 246.5$.

TABLE III.—IONIZATION OF SODIUM HYDROXIDE AT 25°.

v.	λ_v at 18°.	c.	λ_v at 25°.	$\alpha = \lambda_v/\lambda_\infty$.
1	157.0	0.0202	179.2	0.727
2	174.1	0.0202	198.7	0.806
5	.....	......	210.3	0.853
10	195.4	0.0202	223.0	0.905
100	200	0.0213	230.0	0.933
200	203	0.0215	233.6	0.948
500	204.5	0.0215	235.3	0.955
1000	208	0.0215	239.3	0.971

α represents the fraction ionized. These results were carefully plotted on a large scale, so that interpolation from the curve would be as close as the above values would warrant. We assume complete ionization at $v = 2000$. The curve also indicates this.

Applying the above data to our determinations of the hydrogen potentials, we obtain the results shown in Table IV.

TABLE IV.

Ionization constant of water in the presence of sodium hydroxide, and the hydrogen potentials corresponding to various hydroxyl-ion concentrations in sodium hydroxide solutions. Concentrations in gram-molecules or gram-ions per liter.

NaOH.	α.	OH.	E_h.	$k_w \times 10^{14}$.
1.000	0.727	0.727	—0.807	1.60
0.507	0.805	0.408	—0.788	1.88
0.2039	0.852	0.1737	—0.766	1.89
0.102	0.9025	0.0920	—0.752	1.73
0.01057	0.933	0.00986	—0.695	1.71
0.00078	0.983	0.0007667	—0.626	1.95

We feel justified in omitting the last value from the average for k_w, on account of the difficulty of making accurate determinations in such dilute solutions, and the relative size of the error introduced by a small unavoidable absorption of carbon dioxide. The average of the first five values gives $k_w = 1.76 \times 10^{-14}$ at 25°.

Considerable work has been done on the dissociation of water, both by conductivity methods, methods depending on hydrolysis of complex salts, and by measurement of potentials in the acid-alkali cell. Ostwald[1] made use of the acid-alkali cell as early as 1893, but his results have since

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[1] *Z. physik. Chem.*, **11**, 521 (1893).

been superseded by other determinations. Lorenz and Böhl,[1] in 1909 obtained for k_w at 25° the value 1.21×10^{-14}. Löwenherz,[2] in 1896, used the acid-alkali cell and obtained for 0.1 *N* acid and alkali the value 1.42×10^{-14} and for 0.01 *N* acid and akali 1.16×10^{-14}. The lowest value at this temperature appears to be that of Kanolt[3] (1907), whose result, obtained by the hydrolysis of a complex organic salt, is 0.82×10^{-14}. Löwenherz's value 1.42×10^{-14} is the highest found in the literature, although Wijs[4] obtained 1.4×10^{-14} by the catalysis of ester hydrolysis by water.

Although our value for k_w at 25° is somewhat higher than the one usually accepted (1.2×10^{-14}) the fact that concordant results were obtained over such a wide range of dilutions indicates that this value has a real significance in the connection in which we wish to use it. From what is known regarding the behavior of such strong electrolytes as sodium hydroxide, it would not be surprising if their presence caused a somewhat abnormal dissociation of the water. If there is any inherent error in the electrometric method as here applied, due to contact potentials or to an uncertainty in the values assumed for the calomel electrode and the normal hydrogen electrode, these errors are included in our value for k_w; and by using it we shall eliminate their effect in the electrometric determinations of the concentration of the hydroxyl ion.

From this constant, it is possible to calculate the hydrogen·potential (E_h) of a sodium hydroxide solution of any concentration; and plotting a number of such points together with our determinations and those of Lorenz and Mohn, we obtain a curve of which Fig. 1 is a reduced copy.

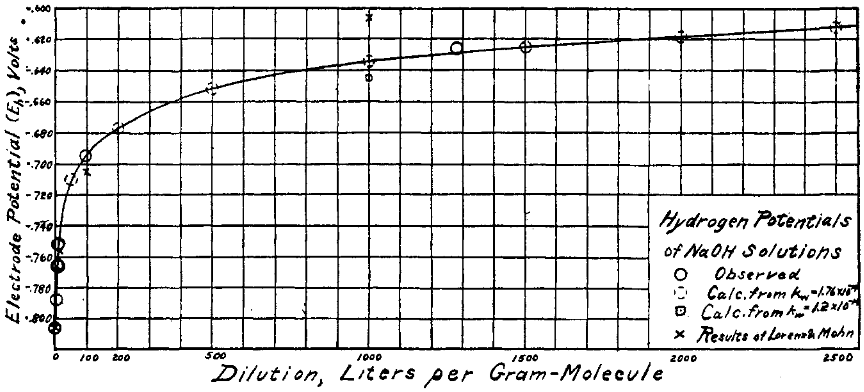

Fig. 1.—Hydrogen potentials of sodium hydroxide solutions.

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[1] *Z. physik. Chem.*, 66, 733 (1909).

[2] *Ibid.*, 20, 293 (1896).

[3] THIS JOURNAL, 29, 1414 (1907).

[4] *Z. physik. Chem.*, 14, 189 (1894).

It will be noticed that all of our results, even including the one at a dilution of $v = 1282$, are in good agreement. If the constant $k_w = 1.2 \times 10^{-14}$ is used for plotting the curve, it is found to lie under the one shown, agreeing fairly well with the value of Lorenz and Mohn at $v = 100$, but passing through the point shown by the square at $v = 1000$, and evidently farther from their results at that dilution than from ours.

Since the purpose of this work was to enable us to accurately determine the concentration of sodium hydroxide in dilute solutions, an approximately 0.1 *N* solution of pure sodium hydroxide in conductivity water was made, the hydrogen potential of this solution determined and its concentration calculated. The solution was thus found to be 0.103 *N*, while a gravimetric standardization showed it to be 0.1028 *N*. Such an agreement, within 0.2%, is sufficiently accurate for our purposes.

These values for the dissociation of water and the hydrogen potentials of dilute solutions containing the hydroxyl ion have therefore been used for the work on the hydrolysis of sodium carbonate and the reactions between this salt and various developing agents, as described in the following papers.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE HYDROLYSIS OF SODIUM CARBONATE IN SOLUTION.

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For our work on the reactions between sodium carbonate and different developing agents, it was necessary to know the hydrolysis constant *K* in the equation

$$K = \frac{[\mathrm{NaOH}][\mathrm{NaHCO_3}]}{[\mathrm{Na_2CO_3}]},$$

where the concentrations of the different substances include both the ionized and un-ionized portions. It is evident that *K* will vary with the dilution, since it involves not only several ionic equilibria, but also the degrees of dissociation of the three compounds. For any definite dilution and temperature, however, the value of *K* can be experimentally determined.

As far as we have been able to find, no one has ever investigated this value *K*, although a number of authors have worked upon the ionic equilibria involved. The latter are

$$k_w = \frac{[\mathrm{H^+}][\mathrm{OH^-}]}{[\mathrm{H_2O}]},$$

where H_2O is generally assumed = 1.