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.

BY FRANCIS C. FRARY AND ADOLPH H. NIETZ.

Received July 28, 1915.

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.

$$k_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]},$$

where H_2CO_3 includes both free CO_2 and actual H_2CO_3.

$$k_2 = \frac{[H^+][CO_3^=]}{[HCO_3^-]}.$$

$$k_3 = \frac{k_1}{k_2} = \frac{[HCO_3^-]^2}{[H_2CO_3][CO_3^=]}.$$

$$k_4 = \frac{[HCO_3^-][OH^-]}{[CO_3^=]} = \frac{k_w}{k_2}.$$

Of these, the first has been determined by various methods, with varying results. The commonly accepted value for 25° is 1.2×10^{-14}. k_1 has been determined by Walker and Cormack[1] from the conductivity of carbon dioxide solutions, and found to be 3.04×10^{-7} at 18°. Bodländer,[2] from one of the results of Shields,[3] on a solution containing 0.0238 mols sodium carbonate per liter, calculated k_2 to be 1.3×10^{-11} at 24.2°. McCoy,[4] from the carbon dioxide tension of carbonate and bicarbonate solutions, calculates $k_2 = 6.0 \times 10^{-11}$ at 25°, assuming the correctness of Walker and Cormack's value for k_1. k_3 and k_4 can be calculated from the values of k_1, k_2, and k_w. Auerback and Pick[5] have recalculated data from the work of Koelichen,[6] at 25.2°, and obtained the value $k_2 = 6.6 \times 10^{-11}$. They also recalculated the work of Shields, from which they obtained the value of 6.4×10^{-11}, at 24.2°. From their own work, they find at 18°, $k_2 = 6.0 \times 10^{-11}$. Using $k_2 = 6.0 \times 10^{-11}$, and $k_w = 1.12 \times 10^{-14}$, they calculate at 25°

$$k_4 = \frac{k_w}{k_2} = \frac{1.12 \times 10^{-14}}{6.0 \times 10^{-11}} = 1.9 \times 10^{-4}.$$

It is to be noted that since $k_4 = \frac{[HCO_3^-][OH^-]}{[CO_3^=]}$, it forms the limiting value which $K = \frac{[NaOH][NaHCO_3]}{[Na_2CO_3]}$ tends to approach at infinite dilution.

From the data given in our paper on the hydrogen potentials of sodium hydroxide solutions, we are able to determine the hydroxyl-ion concentration of any sodium carbonate solution from its hydrogen potential. In order to be able to calculate the amount of sodium hydroxide actually

[1] *J. Chem. Soc.*, **77**, 8 (1900).

[2] *Z. physik. Chem.*, **35**, 23 (1900).

[3] *Ibid.*, **12**, 144 (1893).

[4] *Am. Chem. J.*, **29**, 437 (1903).

[5] *Arbeiten d. kais. Gesundheitsamt*, **38**, 273 (1911).

[6] *Z. physik. Chem.*, **33**, 173 (1900).

present, we need to know the extent to which it is dissociated in the presence of the sodium carbonate. It seems to be well established[1] that in a solution containing two salts having a common ion, each is dissociated to the same extent that it would be in a solution having the same concentration of the common ion. In this case the concentration of the common ion (sodium) is fixed by the dissociation of the sodium carbonate. From the data of Kohlrausch,[2] and Jones and West,[3] we constructed a curve from which the dissociation of sodium carbonate at any concentration could be determined by inspection, and have used the values of the sodium ion thus obtained in correcting for the repression of the ionization of the sodium hydroxide.

The carbonate used was prepared by heating a sample of C. P. sodium bicarbonate for an hour at 300° in an electric oven. From this a twice molar solution was made and diluted with conductivity water to the concentrations desired. It was found that if ordinary distilled water was used, especially for the more dilute solutions, irregular and false results were obtained, apparently on account of its carbon dioxide content. The hydrogen electrodes described in our paper on the single potentials of developers were used in this work, the temperature being maintained at 25° by immersion in water, and other precautions taken as previously mentioned in the paper referred to.

The results are shown in Table I. To determine the corrected sodium hydroxide concentration from the observed hydrogen potential on the hydrogen scale (E_h), the first step is to determine, from the curve described in our previous paper, the concentration of pure sodium hydroxide which would give this potential. From the curve showing the dissociation of sodium hydroxide we determine α at this concentration, and by multiplying this value by the concentration, obtain the concentration of the hydroxyl ion in the solution measured. From the curve showing the dissociation of sodium carbonate we determine α and the total concentration of sodium ion in the solution. From the curve showing the dissociation of sodium hydroxide, we now find by trial the concentration of pure sodium hydroxide which would furnish the same concentration of the sodium ion, and record α, the degree of dissociation at that concentration. As previously explained, this is the degree of dissociation of the sodium hydroxide present in the sodium carbonate solution, and by dividing the concentration of the hydroxyl ion by this figure we obtain the corrected sodium hydroxide concentration. K is then equal to the square of this concentration divided by the difference between this and the original

---

[1] Bray and Hunt, THIS JOURNAL, **33**, 681 (1911); Arrhenius, *Z. physik. Chem.*, **2**, 184 (1887); **31**, 204 (1899).

[2] Landolt-Börnstein Tabellen, 4th ed., p. 1124.

[3] *Am. Chem. J.*, **34**, 357 (1905).

TABLE I.—HYDROLYSIS OF SODIUM CARBONATE IN SOLUTION AT 25°.

Strength of soln. Molar.	v.	E_{H_2}.	E_h.	v.	Conc. NaOH calc. from E_h.	α.	Apparent OH^- conc.	α for Na_2CO_3 at given dilution.	Corresp. Na^+ conc.	NaOH conc. furnishing same Na^+ conc.	α for NaOH.	Corr. NaOH conc.	$k \times 10^5$.
2.0	0.5	—0.402	—0.684	152	0.00658	0.937	0.00616	0.174	0.696	0.940	0.738	0.00835	3.50
1.5	0.67	—0.398	—0.680	175	0.0057	0.938	0.00535	0.24	0.72	0.988	0.728	0.00735	3.62
1.0	1.0	—0.395	—0.677	200	0.00500	0.94	0.00470	0.31	0.62	0.81	0.758	0.00620	3.9
0.708[1]	1.41	—0.393	—0.675	215	0.00465	0.941	0.00437	0.355	0.504	0.64	0.784	0.00558	4.45
0.5	2	—0.390	—0.672	240	0.00417	0.943	0.00393	0.39	0.39	0.49	0.807	0.00487	4.8
0.2	5	—0.384	—0.666	300	0.00333	0.946	0.00315	0.47	0.188	0.22	0.849	0.00371	7.0
0.1	10	—0.379	—0.661	360	0.00278	0.949	0.00264	0.54	0.108	0.12	0.889	0.00297	9.1
0.05	20	—0.373	—0.655	450	0.00222	0.952	0.00211	0.60	0.060	0.0655	0.916	0.00230	11.1
0.02	50	—0.364	—0.646	625	0.00160	0.959	0.00153	0.673	0.027	0.029	0.926	0.00165	14.8
0.01	100	—0.358	—0.640	790	0.00127	0.967	0.00123	0.717	0.0143	0.0154	0.931	0.00132	17.6
0.005	200	—0.349	—0.631	1160	0.000862	0.977	0.000842	0.75	0.0075	0.0081	0.935	0.00090	19.7

[1] C. P. Na_2CO_3, dried at 300°, used for this instead of the carbonate prepared from the bicarbonate.

concentration of sodium carbonate, since obviously the concentration of the bicarbonate is the same as that of the hydroxide, while the final carbonate concentration is the original concentration minus the portion hydrolyzed.

By recalculating the results of Auerbach and Pick, according to the above-described method, for *K*, we obtained Table II.

TABLE II.

Hydrolysis of sodium carbonate in solution at 25°, from results of Auerbach and Pick. Concentrations expressed in gram-molecules and gram-ions per liter.

Observed concentrations.			
Na_2CO_3.	OH^-.	Corr. NaOH conc.	$K \times 10^5$.
0.2	0.0034	0.004	8.16
0.1	0.0029	0.00326	11.0
0.05	0.0023	0.0025	13.1
0.01	0.00113	0.00122	17.0
0.005	0.00080	0.000856	17.7
0.001	0.00034	0.000355	19.5

Comparing the values of *K* in Tables I and II, for the range common to both, it will be noticed that the agreement is as good as could be expected, especially since Auerbach and Pick used a colorimetric method depending on an electrometric determination of the hydroxyl-ion concentration in a series of known solutions according to the method of Sörensen.[1]

As previously stated, the value of k_4 is the limiting value for *K*, since it represents the ionic equilibrium involved. It is obvious that the values of *K* should approach k_4 at infinite dilution, where the substances concerned are completely dissociated, but they should not approach it at dilutions where the dissociation of any one of the constituents is far from complete. Assuming the value of 1.12×10^{-14} for k_w, the dissociation constant of water at 25°, Auerbach and Pick calculate for k_4 the value 19×10^{-5}. By reference to Table II, it will be seen that the value of *K* calculated from their work, which should approach this value as a limit, already exceeds it in solutions 0.001 molar in respect to sodium carbonate, where this salt is only about 80% dissociated and sodium hydroxide only 96%. Little is known of the dissociation of the bicarbonate, but it would certainly be less than that of the hydroxide. According to our results (Table I), *K* exceeds 19×10^{-5} for 0.005 molar carbonate solution, where the carbonate is only 75% dissociated. If we assume that the dissociation constant of water in the presence of sodium hydroxide is 1.76×10^{-14} at 25°, as determined in our previous paper, the value of k_4 becomes 28×10^{-5}, which appears much more reasonable as a limiting value for *K*, particularly if the values of *K* at various dilutions be plotted and the slope of the curve observed. The work of Auerbach and Pick therefore confirms ours over part of the range investigated

---

[1] *Biochem. Z.*, **21**, 131 (1909); **22**, 352 (1909); **24**, 381, 387 (1910).

for the values of K, and furnishes additional evidence of the trustworthiness of a higher value for the dissociation constant of water in the presence of sodium hydroxide than the one generally accepted.

MINNEAPOLIS, MINN.

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

THE REACTION BETWEEN ALKALIES AND METOL AND HYDROCHINON IN PHOTOGRAPHIC DEVELOPERS.

BY FRANCIS C. FRARY AND ADOLPH H. NIETZ.

Received July 28, 1915.

In our paper on the single potential of developers, we have mentioned noticing that the addition of hydrochinon caused a change of thirty millivolts in the hydrogen potential of a solution containing sodium carbonate and sodium sulfite. As this seemed to indicate a combination between the alkali and the reducing agent, it appeared possible to use these hydrogen potentials as a means of studying the reactions which take place when a developer is mixed. After determining the hydrogen potentials of pure solutions of sodium hydroxide and the hydrolysis constant of sodium carbonate, as described in our previous papers, we have the necessary information upon which to base our calculations of the reactions involved.

In this study we investigated four different hydrochinon developers, seven solutions of sodium hydroxide and hydrochinon, and one solution containing metol and sodium hydroxide. The composition of the developers is shown in Table I.

TABLE I.—COMPOSITION OF DEVELOPERS, GRAMS PER 1000 CC. WATER.

Dev. No.	Hydrochinon.	Sodium sulfite.	Sodium carbonate.
1	11.1	7.8	141.7
2	7.0	50.0	150.0
3	7.0	50.0	75.0
4	7.0	None	75.0

The sulfite used was an analyzed anhydrous article, and the carbonate was prepared by drying the last C. P. salt at 300°. In making a determination the hydrogen potential of the solution containing all the constituents except the metol and hydrochinon was first found as described in our previous papers. Then the complete developer was tested in the same way. Where the solution contained only sodium hydroxide and hydrochinon (or metol), reference to the curve showing the hydrogen potentials of solutions of pure sodium hydroxide gave us directly the concentration of the sodium hydroxide before and after adding the reducing agent. From the difference between these two values the amount of sodium hydroxide used up could be readily calculated.