

**97.** *The Conductivity of Sodium Carbonate Solutions at 25°.*

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Hydrolysis corrections have been applied to some conductivity measurements of sodium carbonate solutions at 25°. From the corrected figures, the mobility of the carbonate ion is found to be  $69.3 \pm 0.3$ .

THE extensive hydrolysis which occurs in sodium carbonate solutions causes the conductivity to be considerably greater than would be the case with the unhydrolysed salt. This is due to the

large proportion of sodium hydroxide present, and to the high mobility of the hydroxyl ion. The figures given hitherto have not been corrected for this effect (Int. Crit. Tables, VI, 249; Landolt-Börnstein, 5th edtn., 3rd supplement, p. 1073). In the measurements reported below, the extent of the hydrolysis has been calculated, and corresponding corrections made to the conductivity figures. The results have been used to deduce a conductivity curve for unhydrolysed sodium carbonate solutions.

The conductivity measurements were made on solutions formed by addition of a stock solution from a weight pipette fitted with a soda-lime guard to conductivity water which was kept under carbon dioxide-free air. The small amount of carbon dioxide present in conductivity water was calculated from its specific conductivity (Davies, "Conductivity of Solutions", Chap. IV). This is necessary since the presence of carbon dioxide slightly modifies the main hydrolysis. The equivalent concentration range taken was from  $C = 0.001$  to  $C = 0.02$ ; the densities of these solutions were calculated from the relation  $d_4^{25} = 0.99707 + 0.054C$ , which is based on available data (Int. Crit. Tables, III, p. 82). All resistance readings showed a slight drift with time, and this was allowed for as far as possible by taking time measurements and extrapolating back to the time of addition of the stock solution. This drift was no doubt due to the adsorption of hydroxyl ions by the cell walls. Similar effects with alkaline solutions have been noted by others (Darken and Meier, *J. Amer. Chem. Soc.*, 1942, **64**, 621). Because of this trouble it was not possible to study more dilute solutions.

In order to compute the concentrations of the various ions present, the equilibria to be taken into consideration are  $\text{CO}_3'' + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3' + \text{OH}'$ , and  $\text{OH}' + \text{CO}_2 \rightleftharpoons \text{HCO}_3'$ . The first of these alone would be the only one to consider if pure water had been used, and in this case  $\text{HCO}_3' = \text{OH}'$ . The second process goes almost to completion. This follows from the relation  $K_w/K_1 = \{\text{OH}'\}\{\text{CO}_2\}/\{\text{HCO}_3'\}$ , where  $K_w = 1.008 \times 10^{-14}$  (Harned and Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 2194) and  $K_1$  (the first dissociation constant of carbonic acid) =  $4.45 \times 10^{-7}$  (Harned and Davis, *ibid.*, 1943, **65**, 2030). Since the bicarbonate and hydroxyl ions are in almost identical concentrations, it follows that the concentration of carbon dioxide is negligibly small, being about  $2.5 \times 10^{-8}$ . Accordingly, all the carbon dioxide is converted into bicarbonate. If  $m$  is the stoichiometric molarity of the carbonate,  $x$  is the concentration of carbonate which hydrolyses, and  $y$  is the concentration of carbon dioxide present in the water before the addition of the salt, then it follows that the bicarbonate concentration is given by  $\text{HCO}_3' = x + y$ , and the concentration of hydroxide is given by  $\text{OH}' = x - y$ . The actual concentrations may therefore be deduced from the relation

$$\frac{K_w}{K_2} = K_h = \frac{\{\text{OH}'\}\{\text{HCO}_3'\}}{\{\text{CO}_3''\}} = \frac{(x-y)(x+y)f_1^2}{(m-x)f_2}$$

$K_2$ , the second dissociation constant of carbonic acid, is  $4.69 \times 10^{-11}$  (Harned and Scholes, *ibid.*, 1941, **63**, 1706). The ion-activity coefficients  $f_1$  and  $f_2$  are for uni- and bi-valent ions, respectively. These were calculated from Davies's activity expression (*J.*, 1938, 2093). An approximation method was used in calculating the various ion concentrations. The resulting values of  $x$ ,  $y$ , and the total ionic strength  $I$  are given in the table.

To obtain the corrected conductivity figures, a mixture rule was used:

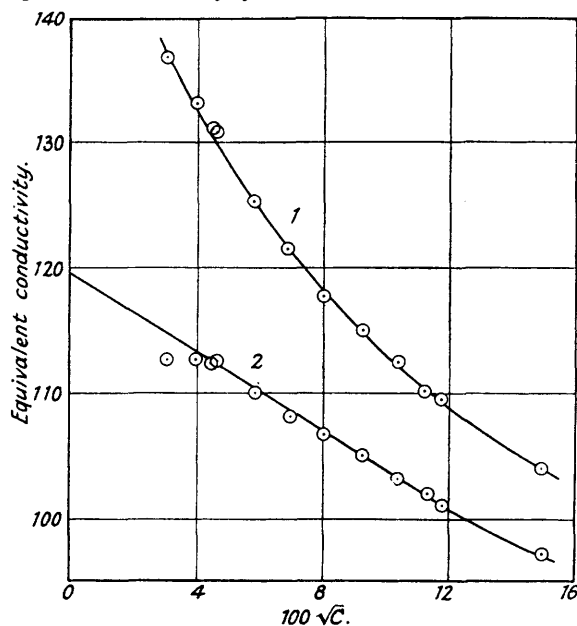
$$\Lambda_{(\text{obs.})} = \Lambda_{(\text{corr.})}(m-x) + \frac{1}{2}\Lambda_{\text{NaOH}}(x-y) + \frac{1}{2}\Lambda_{\text{NaHCO}_3}(x+y)$$

The conductivity of sodium hydroxide was taken from the data of Darken and Meier (*loc. cit.*), and that of sodium hydrogen carbonate was derived from that for potassium hydrogen carbonate (Shedlovsky and MacInnes, *J. Amer. Chem. Soc.*, 1935, **57**, 1705) and for sodium and potassium chlorides (Shedlovsky, *ibid.*, 1932, **54**, 1411). These give, for sodium hydrogen carbonate,

Run.	$10^6 y$ .	$10^6 C$ .	$10^6 x$ .	$10^5 I$ .	$\Lambda_{(\text{obs.})}$ .	$\Lambda_{(\text{corr.})}$ .
1	2.0	1130.8	249.6	144.7	136.7	112.5
2	4.9	1642.8	314.0	215.0	133.1	112.5
3	2.9	2061.3	358.9	273.8	131.1	112.3
4	2.5	2169.2	369.8	288.5	130.7	112.5
3	2.9	3503.0	484.9	477.0	125.3	110.3
5	4.2	4937.6	583.2	682.3	121.5	108.7
2	4.9	6562.1	676.5	916.7	118.2	106.9
5	4.2	8624.1	779.5	1216	115.1	105.1
5	4.2	10865	875.6	1542	112.5	103.2
6	6.2	12850	950.6	1835	110.5	101.9
2	4.9	13940	989.9	1992	109.6	101.4
6	6.2	22437	1243	3241	103.9	97.3

$\Lambda = 94.58 - 81.6C^{\frac{1}{2}}$ . Since the solutions contained ions of mixed valencies, ionic strengths were used instead of concentrations in calculating the conductivities of the sodium hydroxide and the sodium hydrogen carbonate. The corrected conductivities for sodium carbonate are shown in the table. Extrapolation of the corrected conductivity figures leads to a  $\Lambda_0$  value

Equivalent conductivity of sodium carbonate solutions at 25°.



1, Experimental curve. 2, Corrected curve.

of  $119.4 \pm 0.3$ , so, with allowance of 50.1 for the mobility of the sodium ion (Shedlovsky, *loc. cit.*), the mobility of the carbonate ion is  $69.3 \pm 0.3$ . Up to  $C = 0.005$ , the corrected curve shown in the figure, where  $\Lambda$  is plotted against  $C^{\frac{1}{2}}$ , is represented by  $\Lambda = 119.4 - 152C^{\frac{1}{2}}$ . The limiting Onsager equation is  $\Lambda = 119.4 - 174C^{\frac{1}{2}}$ . These two equations are thus sufficiently close to indicate that the corrections are of the right order.

#### EXPERIMENTAL.

"AnalaR" Sodium hydrogen carbonate was heated at 265° in a platinum dish, and the resulting carbonate dissolved in conductivity water. The hydrogen carbonate was reprecipitated by carefully washed carbon dioxide, filtered off, and heated at 265° till it reached constant weight (Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis", p. 547). The conductivity apparatus has been described previously (this vol., p. 422).

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