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A NEW METHOD FOR MEASURING THE ELECTROLYTIC DISSOCIATION OF WATER.

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In a recent article[a] it was shown that the measurements of the velocity-coefficient of the mutarotation of glucose in acid, alkaline, or neutral solutions are accurately expressed over the whole range by the formula $k = A + B(H^{\cdot}) + C(OH')$, where k is the velocity-coefficient, A, B, and C are constants, and $H^{\cdot}$ and OH' are the concentrations of hydrogen- and hydroxyl-ions, respectively, in the solutions. For neutral solutions or pure water let the velocity-coefficient be written k_w, and the hydrogen-ion concentration which is equal for this case to that of the hydroxyl-ion be written $H_w^{\cdot}$; the above formula then takes the form, for pure water or neutral solutions, $k_w = A + (B + C)H_w^{\cdot}$. Solving this expression gives $H_w^{\cdot} = \dfrac{(k_w - A)}{(B + C)}$. This relation gives a new method for measuring the hydrogen-ion concentration or, in other words, the electrolytic dissociation of water, for the four quantities on the right-hand side of the equation can be determined experimentally by measuring the rate of mutarotation of glucose in ordinary distilled water and in acid and alkaline solutions. The first formula above is based on measurements of the rate of mutarotation of glucose in alkaline solutions by Osaka,[b] and similar ones in acid solutions by the writer,[a] and has the form, as was shown in the previous article, $k = 0.0096 + 0.258(H^{\cdot}) + 9750(OH')$, k being expressed in minutes and decimal logarithms, $H^{\cdot}$ and OH' in gram-molecules per liter, and the temperature being 25° C. The constants for glucose at 25° are therefore A = 0.0096, B = 0.258, and C = 9750. The velocity-coefficient for pure water was found at the same time to be $k_w = 0.0106$, which agrees closely with the value which Osaka found, 0.0104. The substitution of these constants in the formula preceding gives $H_w^{\cdot} = 1.0(10)^{-7}$, a value which is in close agreement with those that have been found in the past from measurements that are based on entirely different facts and principles. In the following table is recorded a list of the values for the hydrogen-ion concentration of pure water, which have been found by various investigators, together with a statement of the method by which the value was found. Those values which were later shown to be erroneous are inclosed in brackets.

[a] J. Amer. Chem. Soc., 1907, *29*:1571.

[b] Zts. physik. Chem., 1900, *35*:702.
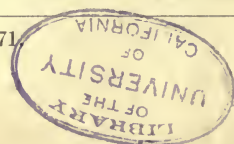
The hydrogen-ion concentration of pure water near 25° C.

$H^{\cdot}=OH'$ (gram-molecules per liter$\times 10^7$).	Temperature (°C).	Investigator.	Date.	Method of determination.
[6.0]	25	Ostwald[a]	1893	Electrical conductance of pure water.
[9.0]	?	Ostwald[a]	1893	Acid-alkali hydrogen cell.
1.1	25	Arrhenius[b]	1893	Hydrolysis of sodium acetate by ester saponification.
[0.1]	11	Wijs[c]	1893	Aqueous saponification of methyl acetate.
[6.0]	25	Bredig[d]	1893	Hydrolysis of aniline acetate from conductivity measurements.
1.2	25	Wijs[e]	1893	Aqueous saponification of methyl acetate.
0.8	18	Nernst[f]	1894	Acid-alkali hydrogen cell.
1.05	25	Kohlrausch and Heydweiller.[g]	1894	Electrical conductance of pure water.
1.2	25	Löwenherz[h]	1896	Acid-alkali hydrogen cell.
0.91	25	A.A.Noyes and Kanolt.[i]	1907	Hydrolysis of ammonium diketotetrahydrathiazole from conductivity measurements.
1.0	25	Hudson	1909	Catalysis of the mutarotation of glucose by acids and alkalis.

[a] Zts. physik. Chem., 1893, *11*:521.
[b] Ibid., 1893, *11*:823; see also Shields, ibid., 1893, *12*:184.
[c] Ibid., 1893, *11*:492.
[d] Ibid., 1893, *11*:829; see Arrhenius, ibid., 1890, *5*:19, and Walker, 1889, *4*:334.
[e] Ibid., 1893, *12*:514.

[f] Ibid., 1894, *14*:155. A new theory of this method is there given by Nernst.
[g] Ibid , 1894, *14*:330.
[h] Ibid., 1896, *20*:293
[i] Carnegie Institution of Washington, 1907, Publication 63, p 297.

The accuracy of the method which is here described for measuring the electrolytic dissociation of water depends primarily on the accuracy with which the difference k_w—A can be measured. For glucose this difference is only 10 per cent of the separate quantities, and consequently the accuracy of the method is not great, probably about 20 per cent, but from recent measurements which the writer[a] has made on the rate of mutarotation of the related sugar fructose in pure water and acid solutions, it appears that the above difference for this sugar is far greater than for glucose, being over 40 per cent of the separate quantities. Measurements on fructose will, therefore, in all probability give with closer accuracy the electrolytic dissociation of water.

[a] J. Amer. Chem. Soc., 1908, *30*:1578.

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