

time serve for the transmission of pressure at the temperature of the electric arc except the gases. There is, therefore, a second serious reason for discontinuing such investigations within a permanent building, due to the unavoidable danger, not only to the building but to the experimenter, which accompanies experiments under high gas pressures and which makes it preferable to conduct such experiments in the open. After long and painstaking trials, however, I feel great confidence in the possibility of maintaining constant gas pressures of more than 10,000 atmospheres in the presence of the strongest electric currents, and hope to undertake such investigations with an apparatus constructed especially for this purpose in the immediate future. It is hardly worth while at this time and with the limited experimental material now at hand, to enter upon a discussion of the important consequences for the atomic theory if these preliminary conclusions are consistently borne out. To this subject I therefore plan to return at a more appropriate time.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEP'T OF AGRICULTURE.]

A NEW METHOD FOR MEASURING THE ELECTROLYTIC DISSOCIATION OF WATER.

BY C. S. HUDSON.

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In a recent article¹ 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

$$k = A + B(H') + C(OH')$$

where k is the velocity coefficient, A , B , and C are constants, and H' 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' ; the above formula then takes the form, for pure water or neutral solutions

$$k_w = A + (B + C)H_w'$$

Solving this expression gives

$$H_w' = (k_w - A)/(B + C).$$

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

¹ THIS JOURNAL, 29, 1571 (1907).

glucose in alkaline solutions by Osaka,¹ and similar ones in acid solutions by the writer¹ and has the form, as was shown in the previous article,

$$k = 0.0096 + 0.258(H') + 9750(OH'),$$

k being expressed in minutes and decimal logarithms, H' and OH' in mols. per liter, and the temperature being 25°. 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 $H_w^* = 1.0(10)^{-7}$, 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 enclosed in brackets.

THE HYDROGEN-ION CONCENTRATION OF PURE WATER NEAR 25°.

$\frac{H_w^*}{OH_w'}$ mols. liter $\times 10^7$.	Temp.	Investigator.	Date.	Method of determination.
[6.0]	25°	Ostwald ²	1893	Electrical conductance of pure water.
[9.0]	?	Ostwald ²	1893	Acid-alkali hydrogen cell.
1.1	25	Arrhenius ³	1893	Hydrolysis of sodium acetate by ester saponification.
[0.1]	11	Wijs ⁴	1893	Aqueous saponification of methyl acetate.
[6.0]	25	Bredig ⁵	1893	Hydrolysis of aniline acetate from conductivity measurements.
1.7	25	Wijs ⁶	1893	Aqueous saponification of methyl acetate.
0.8	18	Nernst ⁷	1894	Acid-alkali hydrogen cell.
1.05	25	Kohlrausch and Heydweiller ⁸	1894	Electrical conductance of pure water.
1.2	25	Löwenherz ⁹	1896	Acid-alkali hydrogen cell.
0.91	25	A. A. Noyes and Kanolt ¹⁰	1907	Hydrolysis of ammonium diketotetrahydrathiazole from conductivity measurements.
1.0	25	Hudson	1909	Catalysis of the mutarotation of glucose by acids and alkalis.

¹ *Z. physik. Chem.*, **35**, 702 (1900).

² *Ibid.*, **11**, 521.

³ *Ibid.*, **11**, 823. See also Shields, *Ibid.*, **12**, 184.

⁴ *Ibid.*, **11**, 492.

⁵ *Ibid.*, **11**, 829. Arrhenius, *Ibid.*, **5**, 19, and Walker, **4**, 334.

⁶ *Ibid.*, **12**, 514.

⁷ *Ibid.*, **14**, 155. A new theory of this method is there given.

⁸ *Ibid.*, **14**, 330.

⁹ *Ibid.*, **20**, 293.

¹⁰ Pub. **63**, Carnegie Institution of Washington, 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 ten per cent. of the separate quantities, and consequently the accuracy of the method is not great, probably about twenty per cent., but from recent measurements which I have made on the rate of mutarotation of the related sugar fructose in pure water and acid solutions,¹ it appears that the above difference for this sugar is far larger than for glucose, being over forty per cent. of the separate quantities. Measurements on fructose will therefore, in all probability, give with closer accuracy the electrolytic dissociation of water.

LIQUID CHLORINE.

BY F. M. G. JOHNSON AND D. MCINTOSH.

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Among the liquefied gases which have been studied chlorine has received comparatively little attention. Knietsch² has measured its vapor pressure, and its density at various temperatures, while Grumach³ has made a measurement of its molecular surface energy.

We thought it of interest to repeat their work and make a further study of this substance. We have measured:

1. The vapor pressure;
2. The density and its variation with temperature;
3. The molecular surface energy;
4. Chlorine as a conducting solvent.

The apparatus employed can be understood from the accompanying figures. Fig. 1 shows the method used for obtaining constant temperatures, and consists of a Dewar flask containing ether. This is closed by a rubber stopper through which passes the bulb of a constant-volume hydrogen thermometer, a modified form of Ramsay and Shields' apparatus for measuring capillary rise, which was also connected to the pressure apparatus, and the tubes necessary to keep the temperature constant. This is effected by blowing liquefied air into bulb A. The ether was kept stirred by a vigorous air current.

The chlorine was prepared by dropping hydrochloric acid on solid potassium permanganate. The gas was purified by washing with water, passing through a tube containing copper sulphate, and was dried with phosphorus pentoxide. It was then liquefied with solid carbon dioxide and ether, and fractionally distilled three times, the middle portion being retained. It was finally liquefied in the capillary apparatus and density bulb,

¹ THIS JOURNAL, 30, 1578 (1908).

² *Ann.*, 259, 124 (1890).

³ Landolt and Börnstein.