11.5% N_2 content dissolved in anhydrous ethyl alcohol containing 0.5% benzene. Relative molecular weights of the nitrocelluloses are calculated on the basis of Staudingers' equation $M = KcN_{sp}$, which becomes, for the following data, using 1/2-sec. cellulose nitrate as the unit: $M_x = N_{sp}/0.053$.

Also, the amount of gelling agent needed to produce a strong gel, and the concentration of cellulose nitrate in solution are related as shown in Table II.

TABLE II

Concn. "A. S." 40 sec. N. C. in anhyd. 2B EtOH, % by wt.	2	4	6	8
% gelling agent for gel	0.15	0.10	0.06	0.06
No. C_6 units per mol of Cu	5.1	15.1	44.6	59.5
Mols of Cu per C_6 unit	0.196	0.066	0.022	0.017

The correspondence, shown in Table I, between chain length of nitrocellulose and the number of C_6 units per molecule of Cu in the gel stage (assuming that the gel structure is about the same regardless of whether cellulose chains or Cu-nitrate links go to construct it) is a direct piece of evidence that the macromolecules of cellulose nitrate in solution are essentially linear or string-like.

This conception leads to a simple picture of nitrocellulose gel formation, namely, that the chain molecules are joined at points along their length by the Cu-nitrate complex formation, giving a gel structure. The greater the length of these chains, or the greater their concentration, the less gelling agent is required to give a solid gel. These data also give an approximate portrayal of a simple three-dimensional gel structure, the cellulose chains being the linear bonds cross-linked by the copper–nitrate complex.

HERCULES EXPT. STATION
WILMINGTON, DELAWARE RECEIVED MARCH 7, 1936

The Optical Rotation of *l*-Threose

BY VENANCIO DEULOFEU

The recent work of Robert C. Hockett[1] has shown values for the specific rotations of *d*-threose diacetamide ($[\alpha]_D$ −10.9° in water) and *d*-threose ($[\alpha]_D$ −12.3° in water) which are in full disagreement with values which we have published[2] for *l*-threose diacetamide ($[\alpha]_D$ −7.7° in water) and *l*-threose ($[\alpha]_D$ −24.6° in water). One must of course expect from stereochemical theory that enantiomorphic isomers will have rotations of equal magnitude but opposite signs. Undoubtedly Hockett is right in his rotations. Some time ago we measured the rotation of *d*-threose diacetamide and found $[\alpha]_D$ −10.4° in water (0.2205 g. in 5 cc. rotated −0.93° in a 2-dm. tube). A sample with an initial rotation of −9.9° in 0.3 *N* sulfuric acid (0.2238 g. in 5 cc. rotated −0.89° in a 2-dm. tube) was hydrolyzed by heating for forty-five minutes in a boiling water-bath, and the rotation changed to −15.1°. (The reading was −0.74°.) The assumption was made in calculating this last reading that all the diacetamide compound has been hydrolyzed and transformed into *d*-threose, an assumption that Hockett shows to be erroneous. That explains why, although the reading was a little inferior to the initial, the calculation gave a higher value for the rotation.

In this connection, following the same method employed for the preparation of triacetyl *l*-erythreose diacetamide,[3] we prepared triacetyl *d*-threose diacetamide melting at 176–177° (uncorr.) and found $[\alpha]_D$ + 38° in water (0.1124 g. in 5 cc. rotated +1.71° in a 2-dm. tube). It is evident that the compounds of the *l*-series must be corrected for its sign and values. The only explanation for our inversion of the sign is that an error was done when noting it. We have no explanation for the sign of rotation given by Freudenberg, which we interpreted when published as confirming our own.

(1) Hockett, THIS JOURNAL, **57**, 2260, 2265 (1935).
(2) Deulofeu, *J. Chem. Soc.*, 2458 (1929).
(3) Deulofeu, *J. Chem. Soc.*, 2973 (1932).

INSTITUTO DE FISIOLOGÍA
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A Measure of Acidity Obtained from the Electromotive Force of a Cell without Liquid Junction

BY DAVID I. HITCHCOCK

The value of hydrogen-ion determinations in many branches of chemistry has been established beyond question. The usual units of acidity, *p*H and *pa*H, as defined by Sørensen,[1] are theoretically unsatisfactory because they are based on the assumption that the concentration or activity of the hydrogen ion can be obtained by the use of a cell

(1) Sørensen, *Compt.-rend. trav. lab. Carlsberg*, **8**, 1 (1909); Sørensen and Linderstrøm-Lang, *ibid.*, **15**, No. 6 (1924).

which includes a salt bridge. Lewis and Randall[2] have indicated methods of avoiding the use of such cells, and Harned[3] has obtained exact values for the dissociation constants of weak electrolytes, in acid or alkaline solutions, by the use of the hydrogen electrode and the silver–silver chloride electrode in cells without liquid junction. It seems possible to extend the use of cells of this type to the determination of the acidity or alkalinity of aqueous solutions in general.

Such a cell will operate reversibly, giving a stable and reproducible electromotive force within a reasonable time, in almost any solution which is sufficiently buffered to stabilize the hydrogen electrode, provided that the concentration of chloride ion is not less than about 0.01 *M*. The electromotive force is given by the exact thermodynamic equation

$$E = E_0 - (RT/F) \ln m_H m_{Cl} \gamma_H \gamma_{Cl}$$

Since most soluble chlorides are believed to be completely dissociated, a value of m_{Cl} for almost any aqueous solution may be obtained by analysis. Values for the constant E_0 have been determined by Harned and Ehlers.[4] A single measurement of electromotive force and a single analysis will therefore give a value for the product $m_H\gamma_H\gamma_{Cl}$. The negative logarithm of this quantity should be more useful than *p*H or *pa*H as a quantitative measure of the acidity of a solution because it is based on a more reproducible measurement and because the product of activity coefficients is thermodynamically definite.

If the solution does not contain chloride ion, values of $m_H\gamma_H\gamma_{Cl}$ may be obtained after the addition of known small amounts of a soluble, neutral chloride to three or four samples of the solution. An extrapolation of the logarithms of these values should yield a value of $m_H\gamma_H\gamma_{Cl}$ for the original chloride-free solution.

The silver chloride electrode has been used not only in acid and alkaline solutions of crystalloidal electrolytes[3] but also in acid protein solutions[5] and in blood serum.[6] It would not be applicable in solutions capable of forming silver compounds less soluble than the chloride, but other electrodes could be used in such cases. For solutions containing carbon dioxide it would be desirable to replace the hydrogen electrode by a glass electrode, as was done by MacInnes.[7]

The most logical unit of acidity is probably m_H, but its value is not given by electrometric methods except in special cases. The choice of $m_H\gamma_H\gamma_{Cl}$ as a unit of acidity involves an arbitrary definition. Dr. George Scatchard has suggested that "a definition which is much more significant for some purposes could be obtained if an electrode reversible to another univalent cation could be used. Then

$$E = E_0 - (RT/F) \ln (m_H/m_C)(\gamma_H/\gamma_C)"$$

Theoretically this is an excellent suggestion, for the quantity $m_H\gamma_H/\gamma_C$ would probably be numerically closer to m_H than $m_H\gamma_H\gamma_{Cl}$ would be. Practically it might be difficult to find a suitable electrode which would not react with some constituent of the solution. In some cases, as Roberts[8] has suggested in another connection, an electrode of thallium amalgam might be used.

Experiments have been planned to test the value of $m_H\gamma_H\gamma_{Cl}$ as a quantitative measure of acidity.

(2) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 409.

(3) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930); also later papers.

(4) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

(5) Hitchcock, *J. Gen. Physiol.*, **5**, 383 (1923); **16**, 357 (1932).

(6) Farr, *Yale J. Biol. Med.*, **3**, 515 (1931).

(7) MacInnes and Belcher, THIS JOURNAL, **55**, 2630 (1933).

(8) Roberts, *ibid.*, **56**, 878 (1934).

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A Simple Method for Starting the Daniels–Heidt Capillary Mercury Arc Lamp

BY LYNN D. WILSON

In the course of photochemical experiments in progress in this Laboratory it was necessary to devise a means of starting the Daniels–Heidt capillary mercury arc lamp[1] when it is surrounded by a reaction cell. The Hoffman–Daniels spark method[2] was found inapplicable when a line voltage of only 110 v. d. c. is available. The carbon resistor method of Hollaender and Stauffer[3] was discarded since several violent explosions resulted from its use. Hence the following magnetic method was devised.

In the accompanying figure the lamp, BCDE, is cemented at B with de Khotinsky cement to a short length of glass tubing, AB. B to D is 2-mm. bore quartz tubing and D to E 4 mm. bore. The

(1) Daniels and Heidt, THIS JOURNAL, **54**, 2384 (1932).

(2) Hoffman and Daniels, *ibid.*, **54**, 4226 (1932).

(3) Hollaender and Stauffer, *Science*, **78**, 62 (1933).