

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.

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### The Optical Rotation of *l*-Threose

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The recent work of Robert C. Hockett<sup>1</sup> has shown values for the specific rotations of *d*-threose diacetamide ( $[\alpha]_D -10.9^\circ$  in water) and *d*-threose ( $[\alpha]_D -12.3^\circ$  in water) which are in full disagreement with values which we have published<sup>2</sup> for *l*-threose diacetamide ( $[\alpha]_D -7.7^\circ$  in water) and *l*-threose ( $[\alpha]_D -24.6^\circ$  in water).

(1) Hockett, *This Journal*, **57**, 2260, 2265 (1935).

(2) Deulofeu, *J. Chem. Soc.*, 2458 (1929).

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  $[\alpha]_D -10.4^\circ$  in water (0.2205 g. in 5 cc. rotated  $-0.93^\circ$  in a 2-dm. tube). A sample with an initial rotation of  $-9.9^\circ$  in 0.3 *N* sulfuric acid (0.2238 g. in 5 cc. rotated  $-0.89^\circ$  in a 2-dm. tube) was hydrolyzed by heating for forty-five minutes in a boiling water-bath, and the rotation changed to  $-15.1^\circ$ . (The reading was  $-0.74^\circ$ .) 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,<sup>3</sup> we prepared triacetyl *d*-threose diacetamide melting at  $176-177^\circ$  (uncorr.) and found  $[\alpha]_D +38^\circ$  in water (0.1124 g. in 5 cc. rotated  $+1.71^\circ$  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.

(3) Deulofeu, *J. Chem. Soc.*, 2973 (1932).

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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, *pH* and *paH*, as defined by Sørensen,<sup>1</sup> 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).