ting CD to intersect the  $-6^{\circ}$  ordinate. Following are the data for the two determinations:

No.	Lampblack taken (g.).	Expansion due to freezing apparent capillary water (cm.).	Volume of 1 cm. (cc.).	Apparent capillary water per g. of lampblack (g.).
I	. o.969	4.27	0.01600	0.756
2	. 0.844	7.02	0.008148	0.727

The results show that apparent capillary water in this sample amounted to about three-fourths the weight of the carbon. The amount would undoubtedly vary with the sample of lampblack and with its treatment but it is much larger than we have found in any sample of hydrogel. It is also greater than that found previously in lampblack, but the sample used at that time contained a much smaller proportion of total water and was nearly dry to the touch, so that part of the capillary water had undoubtedly evaporated. There was sufficient water in both the present samples to make them distinctly moist, and the amounts found are probably as great as the sample is capable of absorbing.

In closing, we wish to call attention to the fact that the freezing curves for lampblack are similar to those of hydrogels. The curves differ materially in only one respect. In hydrogels, the line DF begins to curve ordinarily at a comparatively low temperature, often as low as  $-20^{\circ}$ , showing that ice begins melting at this low temperature. In the curves for lampblack, the line D'F is straight as far as we have determined it, up to about  $-6^{\circ}$ . In this case, therefore, ice when once formed does not melt again until the temperature approaches  $0^{\circ}$ .

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

## A DIRECT READING IONOMETER.<sup>1</sup>

By F. E. BARTELL. Received February 15, 1917.

Owing to the numerous applications of the hydrogen electrode for both scientific and technical purposes it has seemed desirable to construct an apparatus for the determination of ion concentration which could be easily operated, which would be reasonably accurate, and which would give readings directly in terms of ion concentration.

Two different types of direct reading potentiometers have been described and used. An apparatus devised by McClendon<sup>2</sup> reads directly in terms of ion concentration and is similar in general principles to the apparatus herein described. With the Bovie apparatus<sup>3</sup> hydrogen ion

<sup>1</sup> The term potentiometer would be a misnomer for an apparatus of this type. Ion concentration and not potential values are determined.

<sup>2</sup> McClendon. Am. J. Physiol., 38, 186 (1915).

<sup>3</sup> Bovie, J. Med. Res., 33, 295 (1915).

values are automatically plotted on cross section paper. Each of these types has the advantage over the usual potentiometer apparatus in that readings are given directly in terms of ion concentrations. Since the electromotive force increases in logarithmic ratio with increase in concentration it is necessary, in a direct reading apparatus, that given units of resistance be capable of division into logarithmic parts. In logarithmic potentiometers which have heretofore been described and used this logarithmic feature was obtained by means of a slide wire arrangement in which the contact point was moved over a fixed strip of logarithm paper. The resistance of this unit length is of necessity low; this factor, together with the slide wire contact, gives the apparatus a rather limited degree of accuracy. The higher degree of accuracy of the apparatus herein described is obtained by using a much greater unit resistance which permits the use of a series of small resistance coils of given logarithmic values, the total resistance of which (90 coils) is 1000 ohms; in addition the error due to uncertain contact is eliminated.

In constructing the ionometer to read from normal acid to normal base ( $1 \times 10^{-\circ}$  to  $1 \times 10^{-14}$ ) thirteen coils of 1000 ohms resistance each are used together with the 1000 ohm logarithmic resistance which consists of 90 different coils with resistance values arranged logarithmically. Also additional resistances may be inserted in this circuit to compensate for the potential values of KCl calomel electrodes, for electrodes other than hydrogen or calomel, etc. With a N KCl calomel electrode hydrogen electrode cell, and with a temperature of  $23^\circ$ , the formula E = $0.0587 \log 1/c + 0.283$  volt applies. A change in resistance of 1000 ohms in the resistance series is made to correspond to a ten-fold change in ion concentration  $(10^{-1}, 10^{-2}, 10^{-3}, \text{ etc.})$ . For use, then, the apparatus must be set so that each 1000 ohms resistance represents a fall in potential of 0.0587 volt. At 23° the standard cell employed in our experiments had an e.m. f. of 1.01817 volts  $1.01817 \times 1000/0.0587 = 17345$ , which is the resistance value in ohms over which a fall in potential of 1.01817 volts must exist so that each 1000 ohm resistance will have the desired fall in potential (0.0587 volt). When N KCl calomel (which is +0.283 volt) is used, 4821 ohms  $(0.283 \times 1000/0.0587)$  must be inserted to compensate for this electrode. This value must be included in the above 17345 ohms. The readings, on the dials of the ionometer, which represent a total subtended resistance of 17345 ohms (including the 4821 ohms) is  $3.0 \times 10^{-18}$ . When using a standard cell of the voltage above mentioned, 3.0 and  $10^{-13}$ are the dial readings on which one must set and balance the apparatus in order that it will read directly in terms of ion concentration.

To operate the apparatus, first connect the standard cell E, then throw in the resistance, R, needed to compensate for the auxiliary electrode which is to be used. Next, set the pointer arms A and B on the values which have been calculated from the values of the standard cell used  $(3 \times 10^{-13})$ in this case). The external balancing resistance,  $r_1$ ,  $r_2$ ,  $r_3$ ,  $r_4$ , is then so adjusted that no deflection is noted in the galvanometer, G. The apparatus is now in balance and ready to be used for direct reading. The solution to be tested (*i. e.*, cell of hydrogen electrode and calomel electrode) is now connected and by moving the pointer arms A and B on the read-



ing dials the resistances are adjusted until no deflection, or minimum deflection, is obtained with the galvanometer. When this balance is reached the readings on the dials give directly the hydrogen-ion concentration. Readings are made directly to 0.01 of the large units and may, by noting galvanometer deflection, be estimated to  $\pm 0.001$  of the large units, as for example,  $4.23 \pm (0.01) \times 10^{-7}$ .

To test the accuracy of the apparatus in actual work a series of measurements were made in which an Otto Wolff potentiometer and the above described instrument were used.<sup>1</sup> Col. I gives volt readings of the potentiometer; Col. II, the H ion concentration calculated from volt readings; Col. III, readings of the ionometer.

The apparatus has been used for a variety of experimental work in this laboratory and has proven very satisfactory for the determination of

<sup>1</sup> The limit of accuracy in reading depends largely on the galvanometer used. With a sufficiently sensitive galvanometer readings can be made to within  $\pm 0.001$  of the large units. The table represents a single series of measurements in which but ordinary care was observed in making readings.

I.	II.	III.
0.30727	$3.859 \times 10^{-1}$	$3.85 \times 10^{-1}$
0.30070	$4.994 \times 10^{-1}$	$5.00 \times 10^{-1}$
0.40916	$7.092 \times 10^{-3}$	7.09 × 10 <sup>-3</sup>
0.51105	$1.303 \times 10^{-4}$	$1.31 \times 10^{-4}$
0.61377	$2.317 \times 10^{-6}$	$2.32 \times 10^{-6}$
0.71630	$4.153 \times 10^{-8}$	$4.16 \times 10^{-8}$
0.92261	$1.270 \times 10^{-11}$	$1.27 \times 10^{-11}$
1.0230	$2.474 \times 10^{-14}$	2.48 × 10 <sup>-14</sup>

hydrogen-ion concentration. Its advantages can be readily appreciated inasmuch as conversion tables and calculations are not needed, and readings can be both quickly and accurately obtained.

The writer wishes to acknowledge his indebtedness to Eberbach and Son Company of this city who so kindly undertook the construction of this apparatus.

ANN ARBOR, MICH.

## [CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ARMOUR & COMPANY.] THE PREPARATION OF HYDROCHLOROPLATINIC ACID BY MEANS OF HYDROGEN PEROXIDE.

By PAUL RUDNICK AND R. D. COOKE.

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In the preparation of hydrochloroplatinic acid, for use as a reagent in the determination of potassium or for other purposes, such as determinations of atomic weights of platinum and chlorine, many writers<sup>1</sup> have emphasized the necessity for completely removing nitric acid and for completely oxidizing the hydrochloroplatinic acid formed. If the nitric acid is not completely removed by repeated evaporation with concentrated hydrochloric acid, nitrosoplatinic chloride (PtCl<sub>4</sub>(NO)<sub>2</sub>) is formed, which eventually contaminates the product and compounds made from it. The directions usually given for the removal of nitrates seem to be somewhat vague and uncertain in their results. On the other hand, the solution in nitrohydrochloric acid and evaporation with hydrochloric acid results in the formation of hydrochloroplatinous acid (H<sub>2</sub>PtCl<sub>4</sub>), which , must be oxidized to hydrochloroplatinic acid  $(H_2PtCl_6)$ . This has always been accomplished, so far as the literature shows, by saturating the solution with chlorine and heating to expel the excess. The objection to the presence of either of these compounds is very well stated by J. W. Mellor,<sup>2</sup> who says:

"Dissolve the gray powder at as low a temperature as possible in hydrochloric

<sup>1</sup> T. Knösel, Ber., 6, 1159 (1873); G. Krause, Z. Anal. Chem., 14, 184 (1875); E. Dulliver, Compt. rend., 84, 444 (1877); H. Precht, Z. Anal. Chem., 18, 509 (1879); J. S. Stas, Chem. News, 73, 5 (1896); H. W. Wiley, THIS JOURNAL, 19, 258 (1897); Chem. News, 75, 214 (1897).

<sup>2</sup> J. W. Mellor, "Quantitative Inorganic Analysis," 240 (1913).