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

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

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 $m_{\mathrm{H}}\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$. 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 $m_{\mathrm{H}}\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$ 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 $m_{\mathrm{H}}\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$ 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 $m_{\mathrm{H}}\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$ 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

$$E = E_0 - (RT/F) \ln (m_{\mathrm{H}}/m_{\mathrm{C}})(\gamma_{\mathrm{H}}/\gamma_{\mathrm{C}})\text{''}$$

Theoretically this is an excellent suggestion, for the quantity $m_{\mathrm{H}}\gamma_{\mathrm{H}}/\gamma_{\mathrm{C}}$ would probably be numerically closer to m_{H} than $m_{\mathrm{H}}\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$ 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 $m_{\mathrm{H}}\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$ as a quantitative measure of acidity.

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[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).

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

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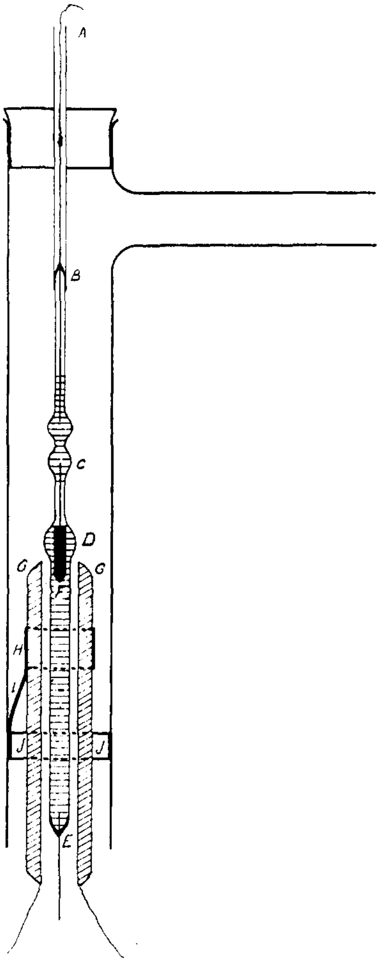
[1] Daniels and Heidt, THIS JOURNAL, 54, 2384 (1932).

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

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

starter, F, consists of an iron plunger (12.7 × 2.38 mm.) fitted with 1-mm. tungsten wire. A solenoid, G, surrounds the lower portion of the lamp and consists of 4 layers of 100 turns each of number 22 enameled, single cotton covered copper wire wound on the barrel of a number 4 cork borer, 9 cm. long. It is held in place and centered in the surrounding water jacket by the device HIJ; H is a brass collar, I is a piece of spring brass soldered to H and to J, and J is a portion of a clock spring expanding against the inner wall of the water jacket. The solenoid is connected in series with a tapping key across a 110 v. a. c. line.



To start the lamp, the cooling water is turned on so that the water jacket is completely and constantly filled with water. The lamp circuit, which is the same as that of Daniels and Heidt, is closed, and the external resistance adjusted so that 10–15 amp. flow through the lamp. The solenoid circuit is then closed momentarily with the tapping key. The resultant magnetic field snaps the starter to the lower portion of the lamp, and in so doing the tungsten draws a spark sufficiently hot to start the arc.

Attempts to use this method with lamps of finer bore have been unsuccessful, since the starting spark is hot enough to melt the tip of the tungsten to a ball which sticks in the capillary. With tubes of 2-mm. bore or more, excess heat does not accumulate in the tungsten and hence it does not melt.

CONTRIBUTION FROM THE
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COMMUNICATIONS TO THE EDITOR

THE PREPARATION OF PHENANTHRYL AMINES AND PHENANTHRYL HALIDES

Sir:

The preparation of 2- and 3-aminophenanthrenes from the corresponding phenanthrenesulfonic acids [Werner, *Ann.*, **321,** 312–321 (1902)] and from the nitrophenanthrenes [Schmidt, *Ber.*, **44,** 1488 (1910)] involves the tedious separation of the isomeric sulfonic acids and nitrophenanthrenes. By hydrolysis of the products obtained by the Beckmann rearrangement of the oximes of 2- and 3-acetylphenanthrenes we have found that the 2- and 3-aminophenanthrenes are formed in excellent yields. Since the necessary ketones are readily obtainable [Mosettig and van de Kamp, THIS JOURNAL, **55,** 3443 (1933)], the procedure constitutes a convenient practical method for making the amines. By this method we have also prepared the new 1-aminophenanthrene (m. p. 145–146°) from the new 1-acetylphenanthrene (m. p. 112–113°) and also the 9-aminophenanthrene.