

<sup>3</sup> Beckmann, *Z. phys. Chemie*, **2**, 715, 1888.

<sup>4</sup> Debye, *Handbuch Radiologie*, **6**, 597, 1925.

<sup>5</sup> Rolinski, *Phys. Zeitschr.*, **29**, 658, 1928.

<sup>6</sup> (a) Williams and Krchma, *J. Amer. Chem. Soc.*, **49**, 1676, 2408, 1927. (b) Williams and Allgeier, *Ibid.*, **49**, 2416, 1927. See also Williams, *Phys. Zeitschr.* **29**, 174, 683, 1928.

---

## *pH MEASUREMENT WITH THE GLASS ELECTRODE AND VACUUM TUBE POTENTIOMETER*

By L. W. ELDER, JR., AND W. H. WRIGHT

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS

Communicated October 24, 1928

Although it has been shown that solutions of oxidizing agents and of materials which poison or are catalytically decomposed by platinum, i.e., solutions in which the ordinary hydrogen or quinhydrone electrodes are inapplicable, may be *titrated* by a number of electrometric methods,<sup>1</sup> only two of these methods involve electrodes of sufficient reversibility or reproducibility to serve in *pH measurement*. These are the antimony trioxide<sup>2</sup> and glass electrodes.<sup>3</sup>

The latter probably has the wider range of applicability, but its extensive use has been discouraged by the necessity of employing a quadrant electrometer.

Although a potentiometer involving a high capacity condenser and ballistic galvanometer has been described<sup>4</sup> as serviceable for rough measurements of potential in cells of high internal resistance, it occurred to one of us that a vacuum tube potentiometer<sup>5</sup> might be preferable.<sup>6</sup>

*The Vacuum Tube Potentiometer.*—The resistance of an average glass electrode is 50 to 100 megohms. This, therefore, represents the minimum resistance of the grid circuit if the vacuum tube potentiometer is to be suitable for measuring glass potentials without polarization. A type UV 199 tube which had given satisfactory service on a quinhydrone-AgCl cell was found to suffer serious leakage ( $10^{-7}$  amperes) unless the base were removed, the leads soldered directly to the tube terminals, and the tube kept in a well-dried atmosphere. Under these conditions, no deflection could be observed on a galvanometer of 2000 megohm sensitivity connected in the grid circuit, i.e., the current was reduced below  $10^{-9}$  amperes. A tube having a higher amplification factor, type CX 340, was tried in the hope of obtaining greater sensitivity, but its design was such that the surface leakage across its terminals was always too great.

With the galvanometer of 2000 megohm sensitivity in a series with the glass cell and grid circuit of this latter tube (CX 340), a deflection was observed corresponding to a current of  $7 \times 10^{-9}$  amperes and the potential of the glass electrode, after a preliminary rise, showed a steady decrease on standing, indicating appreciable polarization. When the grid current was less than  $2 \times 10^{-9}$  amperes, the potentials observed were constant. Therefore, the minimum tolerable value for the resistance of the grid circuit operating with a 2-volt bias is 1000 megohms. The type UX 222 tube in which the grid lead is brought out at the top of the tube, at a maximum distance from the filament and plate leads, gave satisfactory results without any special precautions. The wiring diagram is shown in figure 1. The plate potential of 19.5 v. was supplied from 13 dry cells.

Operating on a negative grid bias of 2.3 volts, the UX 222 tube drew less than  $10^{-9}$  amperes in the grid circuit and showed a sensitivity of  $\pm 1$  millivolt with a Leeds and Northrup wall type galvanometer (sensitivity  $10^{-8}$  amperes), and variable shunt in the plate circuit. The method of measurement was a modification of that proposed by Morton (Ref. 5*d*) in which an ordinary ("student type") potentiometer was connected in opposition to the cell being measured in the grid circuit. With the paraffin block switch *S* (Fig. 1) in position "a," the galvanometer was set for a certain "zero reading." Then the cell was cut in by throwing *S* to

position "b" and the potentiometer setting changed to bring the galvanometer back to its "zero" position. Thus a nearly constant current flow was maintained in the plate circuit and difficulties due to fluctuation in plate potential were minimized. The unknown potential is, of course, the difference between the "zero" and second settings of the potentiometer, which has been independently calibrated against a standard cell in the usual manner.

*The Glass Electrode.*—Thin-walled bulbs were prepared from several types of soft glass stock, all of which showed little or no change in potential when placed successively in acid and alkaline solutions. Although one type of glass gave bulbs of roughly reproducible potential in any one solution, these bulbs in the course of six hours developed strong positive potentials in both acid and alkali.

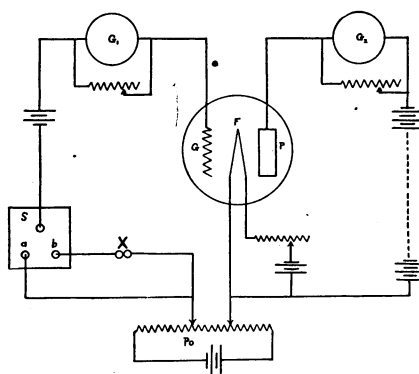


FIGURE 1

G—grid; F—filament; P—plate;  $G_1$ —high sensitivity galvanometer;  $G_2$ —wall galvanometer;  $P_c$ —potentiometer; S—paraffin block, mercury cup switch; X—glass electrode—Ag, AgCl cell.

A batch of glass was then prepared from a mixture of c.p. lime and soda and some high-grade "Ottawa" glass sand by fusion in a large nickel crucible heated in a carbon resistance furnace. Preliminary work in so-called graphite crucibles showed considerable action on the clay binder with the consequent danger of a high alumina content of the resulting glass. Hughes (Ref. 3*b*) has pointed out that the alumina content of an electrode glass must be as low as possible, and recommends a glass of the approximate composition— $\text{SiO}_2$  72 per cent,  $\text{CaO}$  8 per cent,  $\text{Na}_2\text{O}$  20 per cent. The batch was held at about  $1200^\circ\text{C}$ . for 2 hours, with frequent stirring by means of a fused quartz rod. When most of the bubbles had disappeared, the batch was drawn into small rods. On cooling the glass had a slight brown color, probably due to a trace of dissolved nickel oxide. A drop of this glass was blown into a bulb of 2 to 3 cm. diameter from the end of an 8-mm. tube of stock soft glass. Bulbs prepared in this way

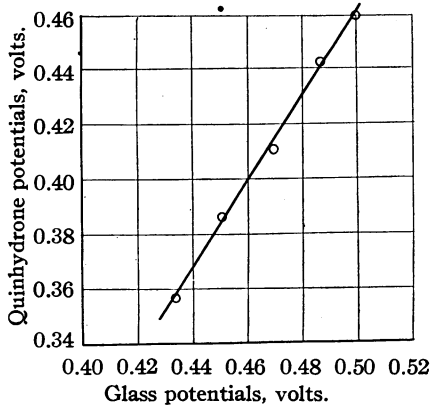


FIGURE 2

gave very constant and reproducible potentials in 1*N* HCl and showed an approximately normal hydrogen electrode function with change in pH of the electrolyte.

The *reference electrode* employed throughout was the Ag, AgCl system in normal KCl solution, prepared by the method of MacInnes and Parker<sup>7</sup> as modified by Willard and Fenwick.<sup>8</sup>

*pH Measurements.*—A complete report of the experimental results in various buffer solutions and in oxidizing media will be published

shortly. For the present we submit a comparison of quinhydrone electrode and glass electrode potentials, both measured with the vacuum tube potentiometer in the titration of normal HCl by NaOH. (Fig. 2.) We plan to study this relation in the alkaline range more in detail by working with buffers in which sufficient time may be allowed for the attainment of complete equilibrium.

*Discussion.*—The difficulties which result from an attempt on the part of the average analytical chemist to set up and operate a quadrant electrometer are manifold. Electrostatic shielding is necessary and the switches must be operated through elaborate insulating devices in order to avoid errors introduced by the body capacity of the operator, etc.

On the other hand, we have found that the only precaution which must be taken when a vacuum tube potentiometer is employed is that the instrument must be mounted in a dry atmosphere.

We have also been able to make satisfactory glass potential measurements in humid summer weather under conditions which would have proved hopeless for the quadrant electrometer. This may be due to the fact that the electrostatic field associated with the 2.3-volt grid circuit is so small in comparison with that present in the vicinity of the electrometer vane (50 volts) that stray atmospheric charges are not so readily collected in the former case.

<sup>1</sup> N. H. Furman, *J. Am. Chem. Soc.*, **44**, 2685, 1922; *Trans. Am. Electroch. Soc.*, **43**, 79, 1923; Van der Meulen and Wilcoxon, *J. I. E. C.*, **15**, 62, 1923; Popoff and McHenry, *J. I. E. C.*, **20**, 534, 1928; W. T. Richards, *J. Phys. Chem.*, **32**, 990, 1928; Closs and Kahlenberg, *Trans. Am. Electroch. Soc.*, preprint, Sept. 24, 1928.

<sup>2</sup> E. J. Roberts and F. Fenwick, *J. Am. Chem. Soc.*, **50**, 2125, 1928.

<sup>3</sup> W. S. Hughes, (a) *J. Am. Chem. Soc.*, **44**, 2860, 1922; (b) *J. Chem. Soc.*, **1928**, 491; F. J. Watson, *Chem. Eng. Min. Rev.*, **20**, 59, 1927; Kerridge, *Biochem. Journal*, **19**, 611, 1925.

<sup>4</sup> Jones and Kaplan, *J. Am. Chem. Soc.*, **50**, 1845, 1928; C. E. Davis and G. M. Davidson, *Ibid.*, **50**, 2053, 1928; Beans and Walden, *Ibid.*, **50**, 2673, 1928.

<sup>5</sup> (a) Goode, *J. Am. Chem. Soc.*, **44**, 26, 1922; (b) Treadwell, *Helv. Chim. Acta.*, **8**, 89, 1925; (c) Williams and Whitenack, *J. Phys. Ch.*, **31**, 519, 1927; (d) C. Morton, *Trans. Faraday Soc.*, **24**, 14, 1928; (e) E. Linde, *Svensk. Kem. Tidskrift*, **39**, 285, 1927.

<sup>6</sup> After most of this work had been completed (August 12th) the authors learned that H. M. Partridge has carried out similar measurements of glass cell potentials with a vacuum tube potentiometer, at New York University.

<sup>7</sup> MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1449, 1915.

<sup>8</sup> Willard and Fenwick, *Ibid.*, **44**, 2508, 1922.

---

## CHEMICAL REACTION IN THE INTERFEROMETER U-GAUGE

BY CARL BARUS

DEPARTMENT OF PHYSICS, BROWN UNIVERSITY

Communicated November 6, 1928

1. *Apparatus.*—To determine in how far the run of a chemical process would be reproduced by the apparatus in question, the absorption of the oxygen of the air by phosphorus was tested. This, besides being rather brutal treatment of the gauge, is also unfortunately a complicated reaction—unless the air is quite dry; for there will be a heat reaction from the absorption of water vapor by the  $P_2O_5$  produced, as well as the heat reaction of oxidizing phosphorus; but it does very well for the present purposes and leads to an astonishing result. The apparatus is shown in the insert *a*, figure 1, where *m*, *m'* are the (shallow) pools of mercury of the U-gauge, *v* and *v'* the closed air volumes, communicating respectively with the Dewar flasks, *D* and *D'* (450 cm.<sup>3</sup> capacity). Each contains a