[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

P_H MEASUREMENT WITH THE GLASS ELECTRODE AND VACUUM TUBE POTENTIOMETER

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In a previous communication a single tube vacuum tube potentiometer was described which gave satisfactory potential readings in acid and alkali when a suitable glass was used.[1,2] The present paper deals with a further modification of this apparatus and presents the results of a direct comparison of the vacuum tube instrument with a Lindemann quadrant electrometer. In an effort to produce a glass electrode with predictable characteristics there are also reported measurements made on five different soft glass stocks in a buffer series standardized by the hydrogen electrode. Particular interest has been centered in the slope of the line relating potential and P_H, the magnitude of the asymmetry potential,[3] and electrical resistance.

Modification of the Vacuum Tube Apparatus.—The circuit for the vacuum tube potentiometer as shown in Fig. 1 has been slightly modified. The high sensitivity galvanometer in the grid circuit is, of course, quite unnecessary for ordinary work. It was inserted only for the purpose of measuring grid leakage while testing various tubes and the effect of varying grid bias potential. Higher sensitivity can be obtained without the shunt around the plate circuit galvanometer, using the latter as a microammeter null instrument, but this arrangement restricts the choice of plate potential, which is determined by the type of galvanometer used and by the construction of the vacuum tube. With the Leeds and Northrup Type P galvanometer (Cat. No. 2239-b, 1000 meg. sensitivity) and Type CX299 tube, a plate potential of 22.5 volts was employed in most of the measurements reported below. The critical grid potential

[1] Elder and Wright, *Proc. Nat. Acad. Sci.*, **14**, 936 (1928).

[2] The wiring diagram is shown in Fig. 1. The plate potential of 19.5 volts 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} ampere in the grid circuit and showed a sensitivity of ± 1 millivolt with a Leeds and Northrup wall type galvanometer (sensitivity 10^{-8} ampere) and variable shunt in the plate circuit. The method of measurement was a modification of that proposed by Morton [*Trans. Faraday Soc.*, **24**, 14 (1928)] 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 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.

[3] W. S. Hughes, *J. Chem. Soc.*, 491 (1928).

as estimated by Goode's method[4] for a plate potential of 22.5 volts and filament potential of 2.4 volts for this type of tube is -1.5 volts with reference to the negative filament lead. Any grid bias of greater negative value will be satisfactory in eliminating grid leakage, except that a very large negative grid potential will bring the plate current down to a point where it is less sensitive to change in grid potential. -2.3 Volts is still a satisfactory value for the grid bias of this tube.

The "direct reading hydrogen ion meter" described by Pope and Gowlett[5] offers certain advantages over Goode's apparatus in that the high voltage "B" battery is eliminated and the plate circuit millivoltmeter can be calibrated readily in terms of P_H readings before and after each measurement. Both of these circuits, depending on calibration of the indicating instrument in the plate circuit, seem to be fundamentally less reliable than those of the type suggested independently by Morton[2] and Partridge[6] in which the unknown e.m.f. is measured by compensation with a calibrated potentiometer in the grid circuit.[7] The author prefers the single tube outfit since it involves less "B" battery equipment, and with the improvement in sensitivity mentioned above it is possible to measure to ± 0.5 millivolt (0.008 P_H unit). This sensitivity is more than adequate for work with the glass electrode.

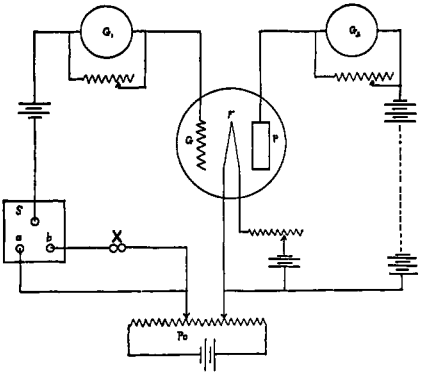

Fig. 1.—G, grid; F, filament; P, plate; G_1, high-sensitivity galvanometer; G_2, wall galvanometer; P_0, potentiometer; S, paraffin block, mercury cup switch; X, glass electrode—Ag, AgCl cell.

Filament temperature is probably the most important variable. Although Goode recommends the oxide-coated filament on account of its longer life, the author found that the thoriated filaments (222 and 199 types) gave approximately 1000 hours of satisfactory service, with only 0.1 ampere from the "A" battery as compared with 0.85 ampere used in Goode's 101-D and 102-D tubes. The lower current consumption is consistent with more constant filament temperature when the ordinary 60 or 100 ampere-hour storage battery is used.

[4] K. H. Goode, *J. Opt. Soc. Am.*, **17**, 65 (1928).

[5] Pope and Gowlett, *J. Sci. Inst.*, **4**, 380 (1927).

[6] H. M. Partridge, THIS JOURNAL, **51**, 1 (1929).

[7] Since this paper was submitted for publication, a description of a "balanced Wheatstone bridge circuit" which also employs the compensation principle, but makes possible the use of a high sensitivity galvanometer as null instrument, has been published by W. C. Stadie [*J. Biol. Chem.*, **83**, 477 (1929)].

When the vacuum tube and its socket are placed in a small tubulated desiccator provided with a drying agent and the leads brought out through a paraffin block in the tubulature, no difficulties are experienced from atmospheric conditions.

Comparison with the Lindemann Electrometer.—The glass cell and potentiometer were connected in series between the electrometer needle and ground, the potential readings being found from the potentiometer setting, with the electrometer functioning as a null instrument.

The electrometer readings were consistently lower than those recorded by the vacuum tube apparatus. The differences ($\Delta E'$) varied roughly between 2 and 100 millivolts, the larger differences being consistently associated with high resistances for the glass cells. Table I shows the magnitude of $\Delta E'$ for electrodes made from two different soft glasses, measured in a series of buffers. It is obvious that $\Delta E'$ is reasonably constant over the P_H range from zero to ten, and about five times as large for the high-resistance electrodes as for those of low resistance.

TABLE I

POTENTIALS OF THE CELL

$$\mathrm{Hg}\,|\,\mathrm{Hg_2Cl_2}\,|\,\text{Satd. KCl}\,\|\,\text{Buffer}\,|\,\text{Glass}\,|\,\text{1.0 } N\ \mathrm{HCl}\,|\,\mathrm{Hg}\,|\,\mathrm{Hg_2Cl_2}$$

Buffer P_H	Electrode E5 Resistance 32.6 megs. V. T.	Elect.	$\Delta E'$ (mv.)	Electrode E8 Resistance 40.2 megs. V. T.	Elect.	$\Delta E'$ (mv.)
0.02	+0.0405	+0.0340	6.5	+0.0380	+0.0350	3.0
1.96	− .0760	− .0810	5.0	− .0745	− .0790	4.5
3.89	− .1960	− .2000	4.0	− .1955	− .2000	4.5
6.02	− .3160	− .3260	10.0	− .3140	− .3210	7.0
7.92	− .4380	− .4430	5.0	− .4430	− .4500	7.0
9.95	− .5580	− .5615	3.5	− .5515	− .5545	3.0
		Average	5.7		Average	4.8

Buffer P_H	Electrode W1 Resistance 1520 megs. V. T.	Elect.	$\Delta E'$ (mv.)	Electrode W4 Resistance 1010 megs. V. T.	Elect.	$\Delta E'$ (mv.)
0.02	+0.0465	+0.0200	26.5	+0.0470	+0.0195	27.5
1.96	− .0400	− .0665	26.5	− .0540	− .0700	16.0
3.89	− .1620	− .1860	24.0	− .1720	− .2000	28.0
6.02	− .2720	− .3000	28.0	− .2820	− .3060	24.0
7.92	− .3590	− .3880	29.0	− .3665	− .3925	26.0
9.95	− .5175	− .5475	30.0	− .5350	− .5525	17.5
		Average	27.3		Average	23.7

TABLE II

DIFFERENCES IN VACUUM TUBE AND ELECTROMETER READINGS COMPARED WITH RESISTANCES OF ELECTRODES FROM GLASS STOCK E

Electrode	E2	E4	E5	E6	E8	E11	E12	E13	
$\Delta E'$, mv.	10.5	23.0	6.5	25.0	3.0	3.5	20.5	29.0	
R, megohms	139	139	32.6	190	40.2	26.0	177	326	
$\Delta E'/R$	0.075	0.165	0.199	0.131	0.074	0.135	0.116	0.089	Av. 0.123

TABLE III

DIFFERENCES IN VACUUM TUBE AND ELECTROMETER READINGS COMPARED WITH RESISTANCES OF ELECTRODES FROM VARIOUS GLASS STOCKS

Glass stock	E	CG	W	K	G1
No. of electrodes	8	12	4	5	3
Average $\Delta E'/R$	0.123	0.062	0.026	0.077	0.121
Av. R, megohms	134	256	1270	1450	40

In Table II are listed values of $\Delta E'$ for electrodes all blown from the same glass, but varying widely in resistance. The constancy of the ratio $\Delta E'/R$ as shown in the last line of this table leaves little room for doubt that the difference in apparent potential of the same glass electrode as measured by the two instruments is directly connected with the resistance of the cell as a whole. The value of this ratio, while constant for electrodes prepared from any one glass stock, varies considerably among the five varieties of glass used, as shown in Table III.[8]

The general conclusion to be drawn from the above data is that when a high-resistance cell is connected in series with the grid of a vacuum tube, the latter tends to acquire a free grid potential approximating the critical grid potential which is always more positive than the bias potential. On open circuit the difference is equal to that between the bias potential and critical grid potential, or 800 millivolts. One electrode which showed a resistance of more than 5000 megs. gave a difference of potential on the two instruments amounting to 112 millivolts. The constancy of this difference for any one electrode, however, is responsible for the fact that no error is introduced when P_H values are measured on the vacuum tube apparatus, provided that the glass electrode is checked against at least one standard buffer. Table IV shows the slope $\Delta E/\Delta P_H$ calculated from the data of Table I over the P_H range from 0.02 to 7.92. Within the limits of error indicated (average deviation of the mean of four values) the slope for Sample E agrees with the theoretical, while Sample W shows

TABLE IV

VALUES OF $\Delta E/\Delta P_H$

Electrode	$\Delta E/\Delta P_H$ on vacuum tube	$\Delta E/\Delta P_H$ on electrometer	$\Delta E/\Delta P_H$ theoretical for 25°
E5	0.0607 ± 0.0013	0.0604 ± 0.0006	0.0591
E8	.0610 ± .0021	.0615 ± .0019	.0591
W1	.0513 ± .0030	.0516 ± .0030	.0591
W4	.0523 ± .0022	.0521 ± .0038	.0591
CG	.0584 ± .0026	.....	.0591
G1	.0603 ± .0021	.....	.0591
K	.0589 ± .0022	.....	.0591

[8] Stadie has also pointed out that the free grid potential, $\Delta E'$ (see next paragraph) varies not only with the external grid resistance, but also with those factors which influence plate current, notably filament temperature.

a low value, in agreement with Hughes' results on the same glass. Average slopes for the other three glasses are also included in the table.

Resistance Measurement.—A Leeds and Northrup Type R galvanometer (Cat. No. 2500-b 2000 megohm sensitivity) was roughly calibrated by a 10-megohm grid leak, showing a sensitivity of 2040 megohms. Using these calibration data and the same source of potential (1.5 volts), the resistances of the various glass cells were calculated directly from the observed deflections, making corrections for the resistance of the electrolyte from blank measurements. The lower resistances can be taken as reliable to ± 1 megohm, but the higher values are proportionately uncertain and this fact may be responsible for the variations in $\Delta E'/R$ shown in Table III.[8]

Glass Stocks.—The symbols used in this paper indicate the following soft glasses: E, a special glass made in this Laboratory as described in the preceding paper (ref. 1, p. 938); CG, Corning soft glass G8, Corning Glass Co., Corning, N. Y.; W, Wood Bros. "white flint," Wood Bros. Glass Co.,[3] Barnsley, Yorkshire, England; K, Kimball machine drawn tubing, Kimball Glass Co., Vineland, N. J.; Gl, unidentified.[9]

Asymmetry Potential.—As pointed out in the preceding paper,[1] an electrode for P_H measurement must be reversible and readily reproducible, or else it must be frequently checked against one or more standard buffers. The latter procedure is recommended by Kerridge for the glass electrode.[10] In the hope of finding conditions under which a glass electrode could be made reproducible, the effects of strenuous polarization and of annealing on the asymmetry potential have been studied. The latter has been described by Hughes.[3] Its value is given by the difference between the potentials of the following two cells.

Cell 1. $\mathrm{Hg} \mid \mathrm{Hg_2Cl_2} \mid \text{Satd. KCl} \parallel \text{1.0 } N \text{ HCl} \mid \text{Glass} \mid \text{1.0 } N \text{ HCl} \mid \mathrm{Hg} \mid \mathrm{Hg_2Cl_2}$

Cell 2. $\mathrm{Hg} \mid \mathrm{Hg_2Cl_2} \mid \text{Satd. KCl} \parallel \text{1.0 } N \text{ HCl} \mid \mathrm{Hg} \mid \mathrm{Hg_2Cl_2}$

Repeated measurements of Cell 2, after one or two hours' standing to allow diffusion to set up a constant junction potential, show a value of the e.m.f. of 0.0315 volt.[11]

[9] This glass, taken from our laboratory soft glass stock, was traced to Glasco Products, Chicago, Ill., who described it as their "special cut glass." A sample which was kindly sent to the author by the above firm as a first approximation to the original shows the following properties: asymmetry potential, +0.0125; $\Delta E'/R$, 0.178; slope, 0.0510; average resistance high, about 300 to 400 megohms for electrodes of the bulb type. Further efforts are being made to duplicate the original sample.

[10] Kerridge, *Biochem. J.*, 19, 611 (1925).

[11] From the data of Scatchard [THIS JOURNAL, **47**, 696 (1925)] on the cell, Hg, Hg_2Cl_2 | Satd. KCl || HCl, 1.0008 M | AgCl, Ag with flowing junction, and from the data of Gerke [*ibid.*, **44**, 1684 (1922)] on the cell Ag, AgCl | Cl^- | Hg_2Cl_2, Hg, the value of the e.m.f. of Cell 2 is calculated to be 0.0295. The difference of 2 millivolts is probably due to the fact that Scatchard's measurements refer to a cell with flowing junction, whereas the cell measured by the author had a diffusion junction.

TABLE V

ASYMMETRY POTENTIALS

Electrode glass	Controls untreated	Treated Electrodes Polarized neg.	Polarized pos.	Annealed	Prepd. by method of MacInnes and Dole
E	+0.0049 ± 0.0011	+0.0098	+0.0030	+0.0035	.....
CG	− .0413 ± .0040	+ .0035	− .0410	− .1055	+0.0010
W	− .0144 ± .0033	.....	.....	.....	.....
G1	− .0103 ± .0024	.....	.....	− .0615	.....
K	− .0640 ± .0062	.....	.....	− .1550	+ .0045

On account of the free grid potential effect which is observed in using the vacuum tube apparatus, all the above measurements (Table V) were made on the Lindemann electrometer.

Treatment of Electrodes

Polarization.—To test the reversibility of the phase boundary equilibrium at a glass surface, a number of the electrodes listed in Table V were connected across a source of 110 volts d. c. by means of platinum wires and left in the circuit for fifteen to twenty hours. The electrolyte used was 1 *N* hydrochloric acid, inside and out. As shown in the table, the electrodes whose inside connection was positive (anodic polarization) came back after about three days to a value which agrees with the average for the control electrodes within the limits of variability of the latter. Measurements repeated after nine days on the same electrodes showed no further variation beyond these limits. Those electrodes whose inside connection was negative (cathodic polarization) showed an appreciably higher potential after three days, the potential again being constant for the six days subsequent. Thus it appears that the passage of hydrogen ion into the outer surface of glass is the less reversible process.

Annealing.—On the assumption that the asymmetry potential may be due, at least partly, to a difference in total surface energy between the inner and outer surfaces of the glass bulb, it was thought that a mild annealing process, tending to reduce mechanical strains, might also affect the asymmetry potential. The electrodes in question were put in an oven immediately after they were blown (with one exception, *viz.*, CG83) and heated to 120° for fifteen to twenty hours. The surprising results are shown in Table V.

With one exception (E8) all the electrodes which were annealed showed potentials from 50 to 100 millivolts low as compared to the average of the controls. The potentials listed in the table for Glass CG were read nine days after annealing and are about thirty millivolts more positive than they were one day after annealing. Thus there is a slow continuous drift back to the normal value as represented by the control electrodes. From these experiments it appears that whatever effect annealing may have on reducing mechanical strain is overshadowed by some other effect, the nature of which is still obscure.

Method of Preparation.—Unless otherwise indicated all the electrodes were prepared as thin-walled bulbs blown from 10 to 14-mm. tubing. MacInnes and Dole have described an alternative method for preparing very thin glass membranes which seems to offer decided advantages.[12] Electrodes were prepared by this method from the two glass stocks which showed the highest asymmetry potentials among the untreated electrodes (CG and K). In each case the electrodes so prepared had asymmetry poten-

[12] MacInnes and Dole, *Ind. Eng. Chem. Analytical Edition*, **1**, 57 (1929).

tials no greater than the probable uncertainty of the controls. It is interesting to note that one of these, K4, has a resistance of the order of 5000 megohms, while CG813 measures only 5.7 megohms.

P_H Measurement by the Glass Electrode without the Use of Standard Buffers.—Since the asymmetry potential seems to be specific for any one stock of glass and independent of age or resistance, it is suggested that the above data might be employed in measuring an unknown P_H with an electrode prepared from one of the glasses listed.

For example, the P_H of a solution in which an electrode prepared from the Corning glass and filled with 1.0 N hydrochloric acid shows a potential against saturated calomel of the value "E" is given as

$$P_H = 0.085 - \frac{E - (-0.0413 + 0.0315)}{0.0581}$$

Summary

The vacuum tube potentiometer as described by Elder and Wright has been modified with a view to increasing the sensitivity and simplicity of the apparatus.

Comparative measurements on the vacuum tube potentiometer and Lindemann electrometer show that the apparent potentials of high resistance glass cells measured on the former instrument include a free grid potential which is constant over the P_H range from zero to ten, and directly proportional to the glass cell resistance.

Four commercial stock soft glasses and one laboratory preparation were studied in a series of buffers which had been standardized by the hydrogen electrode.

The asymmetry potentials of electrodes of the bulb type measured in 1 N hydrochloric acid are constant for any one glass stock and vary from 5 millivolts for the laboratory preparation to 64 millivolts for one of the commercial stocks.

The effect of anodic polarization by 110-volt d. c. for fifteen to twenty hours disappeared completely after three days. Cathodic polarization by the same applied voltage for the same time produced a polarization potential of 40 to 50 millivolts after three days which persisted for six days more.

Annealing for fifteen to twenty hours at 120° caused a decrease in potential which was variable and very slow in disappearing.

The asymmetry potentials of electrodes prepared by the method of MacInnes and Dole were uniformly low, irrespective of the glass used.

Methods are suggested whereby the data presented in this paper could be used for P_H measurement by the glass electrode without employing standard buffers.

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