PRINTED IN GREAT BRITAIN

214

A DIRECT READING HYDROGEN-ION METER.*

By C. G. POPE and F. W. GOWLETT. Wellcome Physiological Research Laboratories, Langley Court, Beckenham, Kent.

[*MS. received*, *19th March*, 1927.]

ABSTRACT. An apparatus giving direct readings of hydrogen-ion concentration [*p*H], for use with the hydrogen electrode and quinhydrone electrode, is described. The use of a potentiometric form of circuit and a 4 electrode thermionic valve makes it possible to standardize the apparatus before and after each *p*H reading, by means of a single vernier rheostat. Tables are given showing the accuracy with which it is possible to calibrate the instrument for each range.

Some time ago it occurred to one of us that it might be possible to devise an apparatus for reading *p*H direct from a galvanometer deflection, by using a 3 electrode thermionic valve. In an apparatus of this description the potential to be measured is applied to the grid of the valve in such a way that the grid is always at a negative potential with respect to the negative end of the filament. Under these conditions no current flows in the grid circuit and the apparatus may be considered as a galvanometer of infinitely high resistance. A potential applied to the grid causes a change in the anode current of the valve which can be measured in a suitable manner.

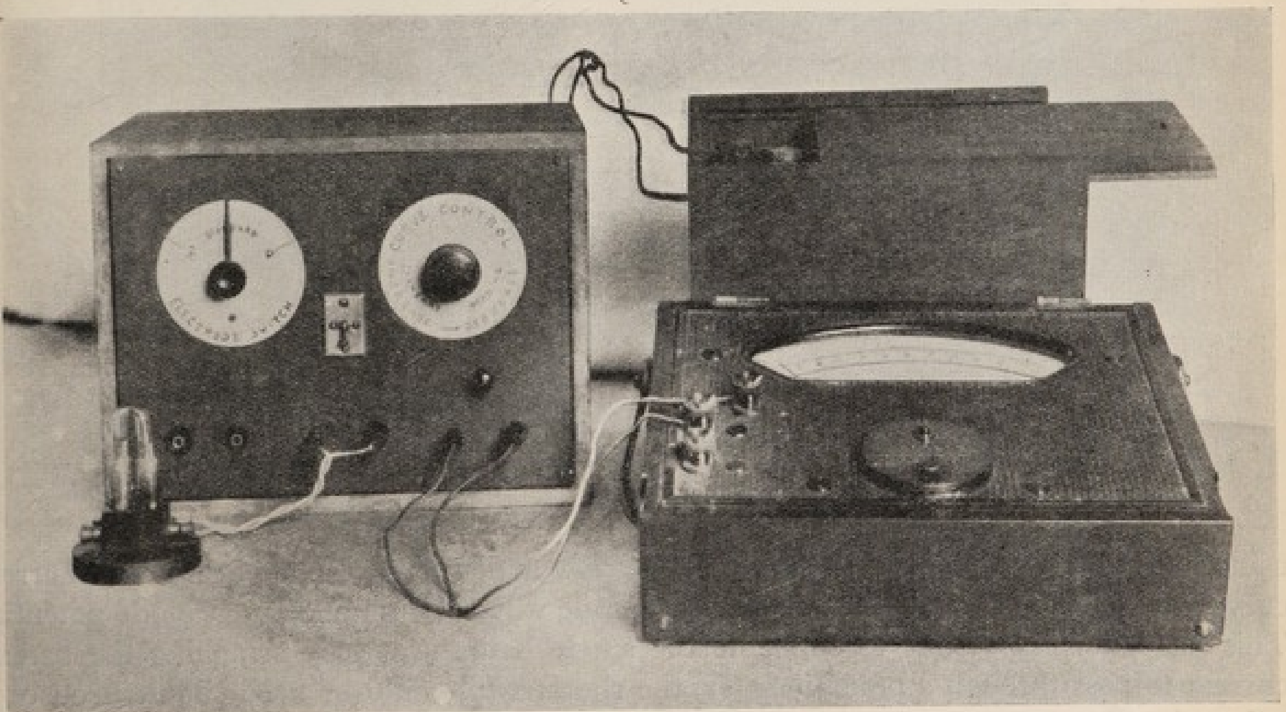


Fig. 1

After the construction of the apparatus had been commenced, our attention was drawn to the fact that a similar apparatus had been described by Goode†. Later‡, he published a description of a modified apparatus in which three 3 electrode valves were used. The change in anode current of the first valve was amplified by the two succeeding valves and the *p*H reading obtained directly on a milliameter.

The chief difficulty we have experienced with apparatus of both types has been due to

* The apparatus was demonstrated at a Meeting of the Biochemical Society in June 1926.

† *Journ. Amer. Chem. Soc.* **44** (1922) 26.

‡ *Ibid.* **47** (1925) 2483.

changes in the potential of the anode batteries. When anode batteries of the type sold for wireless purposes were used, it was found that marked changes in the anode potential occurred, due to the breakdown of a faulty cell. Similar changes were produced by prolonged use of the apparatus. As these changes in the anode potential necessitated a re-calibration of the instrument, the apparatus was unsatisfactory for routine work. Bienfait* has published an improved form of Goode's first apparatus in which arrangements have been made to allow for control of both the anode and filament potentials.

The apparatus to be described in this paper employs one 4 electrode valve, the anode battery as such being discarded, and it is so arranged that the apparatus is standardized before and after each *p*H reading by a single vernier resistance. The chief advantage in

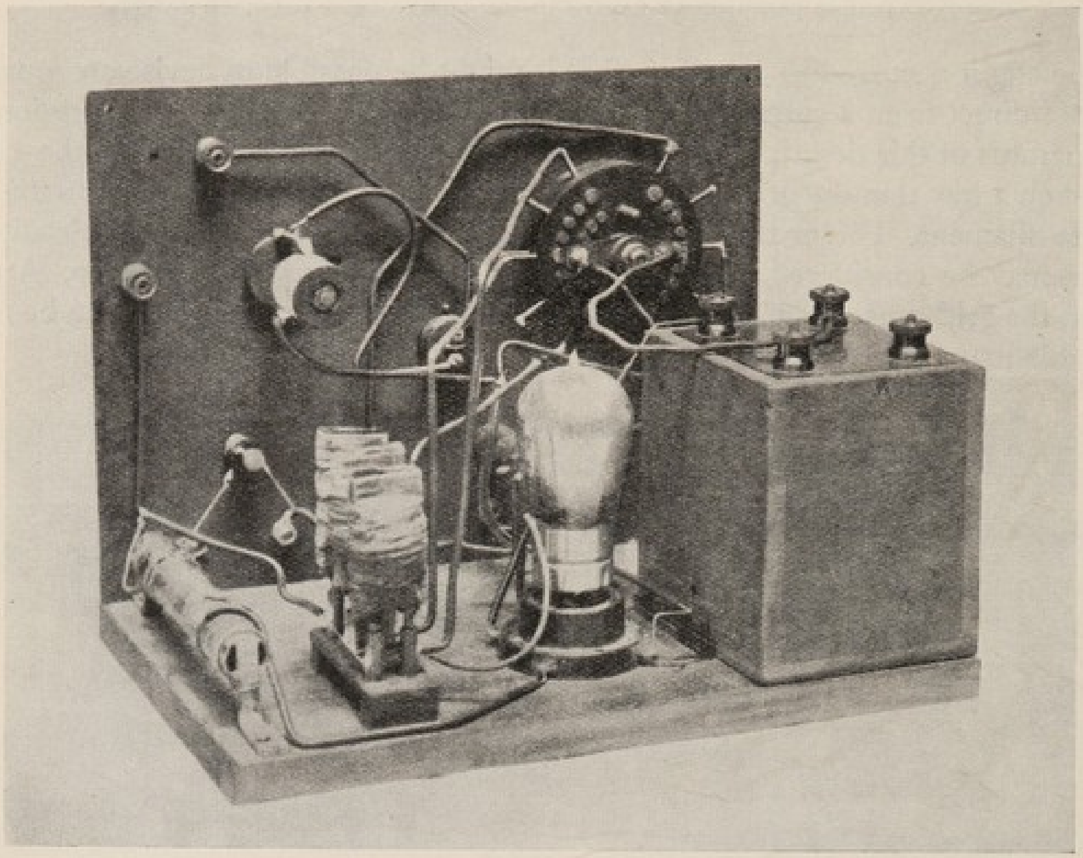


Fig. 2

using a 4 electrode valve lies in the fact that a low anode potential gives an anode current curve similar to that obtained with the 3 electrode valve at a much higher anode potential. This has made it possible to eliminate the anode battery, and by arranging the battery current to pass through a potentiometer, the rheostat (7) could be used simultaneously to adjust the filament current and the anode potential to constant values.

Fig. 1 shows the complete apparatus, set up for reading *p*H by means of the quinhydrone electrode. The terminals on the left are for use with the hydrogen electrode. Fig. 2 shows the internal construction of the apparatus, and Fig. 3 the circuit in diagrammatic form. The numbers given in brackets in the text refer to Fig. 3.

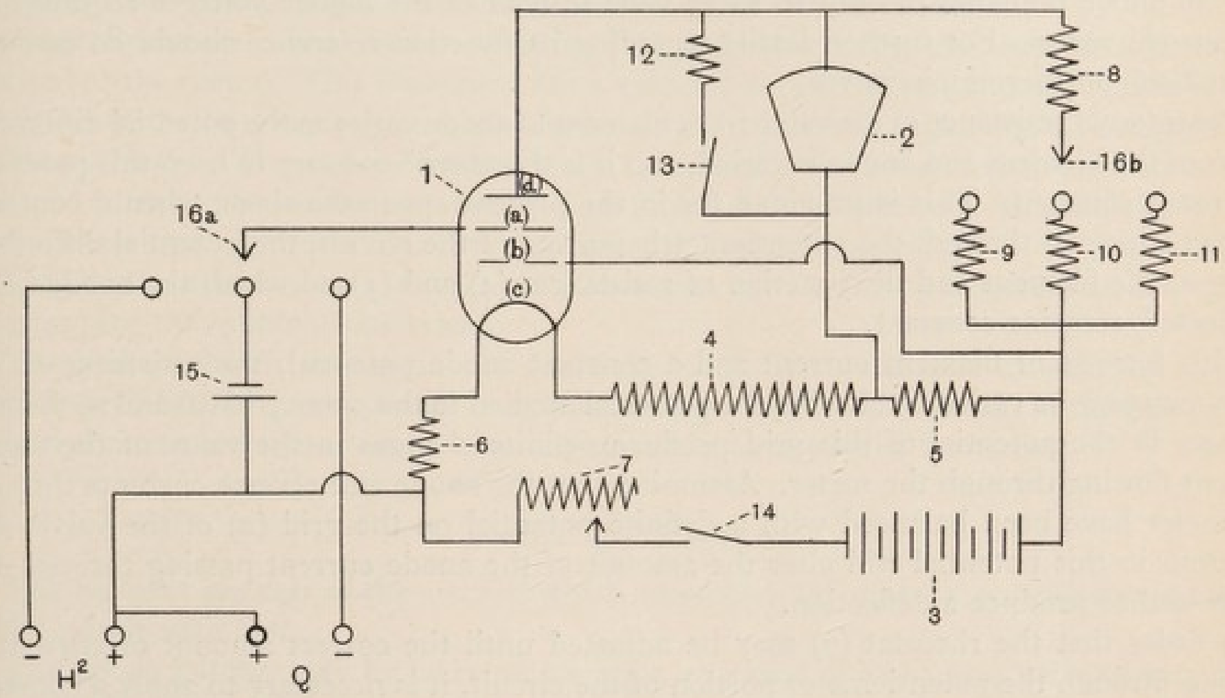
Theory of the Apparatus

The circuit operates in the following manner.

The potential of the electrode system to be measured is applied between the grid of the valve and the end of the bias resistance (6) and alters the anode current from the valve

* *Rec. trav. chim.* **45** (1926) 166.

proportionally to its magnitude. When the grid ((*a*) Fig. 3) is made more negative with respect to the filament the anode current is decreased. Now the normal anode current of the valve is of the order of twelve hundred micro-amperes, and as the milli-voltmeter gives a full scale deflection for a current of 240 micro-amperes, some method must be adopted to balance this normal anode current by passing a current of the same magnitude through the meter in the reverse direction.



(1) Four electrode thermionic valve.
(2) Milli-voltmeter.
(3) 12 volt accumulator.
(4) Main filament circuit resistance.
(5) Reverse current resistance (filament circuit).
(6) Grid bias resistance.
(7) Vernier rheostat.
(8) Main reverse current resistance.
(9) Calibrated reverse current resistance used with the hydrogen electrode system.
(10) Calibrated reverse current resistance used when standardizing the apparatus.
(11) Calibrated reverse current resistance used with the quinhydrone electrode system.
(12) Shunt resistance for milli-voltmeter.
(13) Spring switch keeping the shunt across the milli-voltmeter until the button is depressed.
(14) Main filament circuit switch.
(15) Standard Weston cell.
(16) Double pole three way switch.

Fig. 3. Circuit Diagram

The reverse current is obtained in the following way.

The resistances (4), (5), (6) and the filament resistance (*c*) form a potentiometer circuit, the amount of current passing being controlled by the rheostat (7). If the current is kept constant, the potential differences between the ends of resistances (4), (5), (6) and the filament resistance (*c*) will be constant. It will be seen that two currents can pass through the meter (2) in reverse directions, first, from the valve filament to the valve anode (the electron stream) through the meter to the junction of resistances (4) and (5) and so back through resistance (4) to the filament; second, from the junction of resistance (4) and (5) through the meter, resistance (8) and one of (9), (10) or (11), and thence *via* resistance (5) to the junction of (4) and (5). The amount of current passing through the meter in the second manner can be controlled by adjusting the resistance values of (9), (10) or (11), and will be dealt with when considering the calibration of the apparatus.

The inner grid of the valve (*b*) is maintained at a positive potential with regard to the filament, by connecting it direct to the positive terminal of the battery (3) as shown in Fig. 3. Its function is that of reducing the "negative space charge," and so lowering the internal resistance of the valve, making it possible to obtain a typical anode current curve with an anode potential of only 10 to 15 volts instead of the higher voltages required for 3 electrode valves. For further details regarding its function reference should be made to a text-book on thermionic valves.

The internal resistance of the valve from filament to anode varies as the potential difference between the filament and anode is varied, and it is therefore necessary to keep this potential difference constant. This is provided for in the present apparatus since, when a constant current is passed through the potentiometric portion of the circuit, the potential difference between the filament and the junction of resistances (4) and (5), to which the anode (*d*) is connected, remains constant.

With a constant filament current and a constant anode potential, the resistance of the valve may now be varied by altering the potential applied to the outer grid (*a*) and so definite changes in the potential of this grid produce definite changes in the value of the anode current flowing through the meter. Assuming that the anode and reverse currents through the meter have been balanced with a definite potential on the grid (*a*) of the valve, any variation in this potential will alter the amount of the anode current passing through the meter and so produce a deflection.

In order that the rheostat (7) may be adjusted until the correct amount of current is flowing through the potentiometer portion of the circuit, it is necessary to apply a constant and easily reproducible voltage to the grid (*a*) of the valve, and then to adjust rheostat (7) until a certain reading on the milli-voltmeter is obtained. The voltage for this purpose is obtained from the Weston cell as shown in Fig. 3. The standardization of the apparatus by means of a known voltage will be dealt with in greater detail under "calibration."

Components

Valve. The valve used in this apparatus is a 4 electrode Osram valve, type D.E. 7. It requires a filament voltage of 1·8 to 2·0 volts, and consumes a current of 0·4 ampere. The valve should show no grid current (outer grid) when the potential applied to the outer grid is zero volts, and the anode current should diminish by at least 300 micro-amperes when the potential on the outer grid is reduced from zero to $-$ 0·7 volt.

Battery. The battery consists of 6 Exide D.T.G. two volt cells connected in series. These cells are capable of supplying the current of 0·4 ampere although they are of small size (rated at 20 ampere hours).

Meter. The instrument is a unipivot milli-voltmeter by the Cambridge Instrument Company, Ltd., used on the 0·0024 volt range; the resistance is 10 ohms and the current required for full scale deflection 240 micro-amperes. As the scale is divided into 120 divisions the instrument gives a convenient reading of *p*H from 0 to 12.

Resistances. The resistances (4) and (5) may be considered as one resistance, with a tapping which is placed at a point to give about $\frac{1}{7}$th of the total resistance. It was made by winding No. 25 S.W.G., D.S.C., Eureka wire on an insulated steel tube. It has been found that the temperature of this resistance does not exceed about 30° C. when carrying 0·4 ampere. Resistances (9), (10) and (11) are wound with No. 34 S.W.G., S.C.C., Eureka wire, on ebonite bobbins. Resistance (8) is also wound with the same wire. In the case of (9), (10) and (11) the ebonite bobbins are made to plug into holders in order that they may be removed easily for calibration purposes or for altering the range of the instrument for any special purpose. The value in ohms of these resistances will be considered later when dealing with the calibration of the instrument.

Vernier Rheostat. The controlling rheostat (7) is of the Vernier type, with a total resistance value of about 6 ohms. It is essential that this rheostat shall give very smooth control and be capable of fine adjustment, since it is the only control used in setting the instrument to give standard readings. A suitable rheostat may be obtained from the Presland Electric Supplies Ltd., Hampton on Thames. (The Woodhall Vernier Rheostat.)

Shunt Resistance. The shunt resistance (12) and switch (13) are used as a protective device for the meter. This resistance has a value of about 2 ohms, and the circuit is kept closed until the button, seen immediately below the curve control in Fig. 1, is depressed.

Rotary Switch. The rotary switch (16) is a double pole three way switch which connects the grid of the valve to the standard cell or to the desired electrode terminals (16*a*) and at the same time connects the correct resistances in the meter circuit (16*b*), viz. resistance (10) when the standard cell is in circuit, resistance (9) for the hydrogen electrode system and (11) for the quinhydrone system.

The switch shown in Fig. 2 was originally made for a different circuit and appears therefore, to be more complicated than is necessary. Of the studs shown in the photograph only the extreme end and centre ones on each side form part of the circuit.

Method of Calibration

The filament portion of the circuit, which resembles an ordinary potentiometer circuit, will be dealt with first.

The anode battery may be taken as having a potential of from 11·4 volts to 13·2 volts, according to its condition of charge. Under these circumstances a resistance of a value varying from 28·4 to 33 ohms will pass a current of 0·4 ampere, which is required for the valve. Since the valve filament takes 0·4 ampere at 2·0 volts its resistance is 5 ohms. It will be seen that resistances (4), (5), (6) and (7) should have a value varying between 23·5 and 28 ohms, the variations being obtained by means of the rheostat (7). If the grid bias resistance (6) has a value of 0·75 ohm there will be a difference of potential of about 0·3 volt between its ends, which is sufficient to ensure that the grid is always at a slightly negative potential with respect to the filament.

The value for the combined resistance (4) and (5) is about 22 ohms, of which 19 ohms is included in (4) and 3 ohms in (5). Thus the potential difference between the ends of resistance (5) is about 1·2 volts. The circuit was arranged in this manner in order to keep the combined resistance of (8) and either (9), (10) or (11) high (*i.e.* 1000 ohms approximately) compared with the resistance of the meter. The ratio obtained is approximately 1000 ohms to 10.

The General Principle of Calibration of the Meter

The object of calibrating is to obtain the condition where the change in E.M.F. for a difference of one *p*H unit, when applied to the grid of the valve, causes a change in the anode current so that a deflection of exactly 10 divisions is produced on the meter.

The change in anode current for a given grid potential variation may be greater or less than the required amount. In this case it is necessary to alter the slope of the anode current curve by varying the filament temperature. Increasing the filament temperature by reducing the resistance at (7) makes the anode curve steeper and *vice versa*.

The apparatus is calibrated by applying known potentials by means of a potentiometer. A variable resistance box (reading to say 10,000 ohms) is used in place of resistances (9), (10) and (11), these resistances afterwards being wound to the value shown by the variable resistance box. When a given range has been calibrated by applying known potentials to the grid, some method of standardizing the apparatus before and after each pH reading is necessary. For this purpose a known E.M.F. is applied to the grid, and the filament temperature (which is the only variable) is adjusted by means of the rheostat until a predetermined meter reading is obtained. The known E.M.F. may be obtained from a standard Weston cell as shown in Fig. 3, or more simply by connecting the grid directly to the negative end of the valve filament.

Calibration for the Hydrogen Electrode System

Using the saturated calomel half cell at a temperature of 18° C., the change in potential from pH 0–12 is from 0·2503 to 0·9427 volt, and the apparatus is arranged to read 0–120 divisions on the scale of the milli-voltmeter when this range of voltages is applied to grid (*a*). This is done by adjusting the value of the resistance at (9) in the following manner.

Set the rotary switch (16) to the H_2 electrode terminals and connect a potentiometer to these terminals so that its negative lead goes to the grid of the valve. Apply a potential of 0·2503 volt from the potentiometer to the outer grid. In the position which will finally be occupied by resistance (9) connect the variable resistance box; adjust the resistance box until the reverse current is about equal to the anode current from the valve. Great care must be taken to prevent damage to the meter during these balancing operations. The shunt (12) across the meter must not be removed by depressing the button (13) until it is obvious that the anode current is almost balanced by the reverse current. The meter should be so connected that increasing the reverse current increases the meter reading.

Now make adjustments by means of the rheostat (7) (controlling filament temperature and therefore the slope of the anode current curve); at the same time adjusting the resistance at (9) by means of the resistance box until, with a potential of 0·2503 volt on the grid, the meter reads 0, and with a potential of 0·9427 volt it reads 120 divisions. As the anode current curve is not an absolute straight line, it is then advisable to apply to the grid the potential for pH 7·0, and by very slight alteration of the rheostat and resistance box adjust until the meter reading is exactly 70 divisions. The lowest and the highest readings may not quite fit the meter scale, but the deviations should be very slight. Table I shows the results

Table I. *Calibration Table showing results obtained with the present apparatus for the Hydrogen Electrode System.*

H_2 electrode—Sat. Calomel Cell. $T = 18°$ C.

E.M.F. applied to grid	Corresponding pH	Meter reading divisions		Error in pH
0·2503	0	0·9		+ 0·09
0·3080	1	10·0		0·00
0·3657	2	20·0		0·00
0·4234	3	30·0		0·00
0·4811	4	40·0		0·00
0·5388	5	50·0	Standard	0·00
0·5965	6	60·0	reading	0·00
0·6542	7	70·0	60 divisions	0·00
0·7119	8	80·0		0·00
0·7696	9	90·0		0·00
0·8373	10	100·2		+ 0·02
0·8550	11	110·9		+ 0·09
0·9427	12	122·0		+ 0·20
0·2503	0	0·0	Standard	0·00
0·8550	11	110·0	reading	0·00
0·9427	12	120·2	59 divisions	+ 0·02

The standard can be adjusted to 59 as shown to correct the 0, 11 and 12 pH readings when these are used.

btained with the present apparatus, and gives the method used to correct the end readings. resistance coil having the value in ohms indicated by the variable resistance box can be onstructed and substituted for it.

The "standard" resistance coil (10) can now be calibrated. Connect the variable re-istance box in the position to be occupied by resistance (10). Apply the constant voltage f the Weston cell to grid (*a*) by turning the switch (16) to the standard position. Adjust he resistance box until the meter reads about 60 divisions with the button (13) depressed, are being taken to protect the meter by means of the shunt until the anode and reverse urrents are about balanced. Now apply a definite potential to the H_2 terminals by means f the potentiometer, *e.g.* that for *p*H 7·0, and adjust the rheostat (7) until the meter reads xactly 70 divisions, having of course turned switch (16) to the H_2 position. Rotate switch 16) back to the standard position and adjust the resistance box only until the meter reads o divisions (or other convenient reading).

When using the apparatus for measuring *p*H this procedure is reversed; the switch (16) s set at "standard" and the rheostat (7) adjusted until the reading of 60 divisions, or such ther value as may have been chosen, is obtained. The instrument then reads correctly, nd by applying the E.M.F. for any *p*H from 0 to 12 to the H_2 terminals and rotating switch 16) to the "H_2 position," the correct reading on the meter is obtained. In practice this standard reading" is taken before and after each *p*H reading, and any adjustment necessary, ue to a drop in the potential of the battery (3), is made by means of the rheostat (7).

The resistance (10) may now be wound to the value shown by the variable resistance ox, and inserted in its proper position.

Calibration for the Quinhydrone Electrode System

The system used is based on Veibel's* quinhydrone half cell, and is as follows:

$T = 18°$ C.

Au	*p*H 2·0 buffer Sat. Quinhydrone	Sat. KCl Agar bridge	*p*H *X* Sat. Quinhydrone	Au

In this case, when the *p*H of *X* is 2·0 the E.M.F. will be zero, while at *p*H 0 it will be - 0·1154 volt, and at *p*H 9, − 0·4039 volt.

The apparatus used for the quinhydrone electrode may be seen in Fig. 1. It consists f an ebonite base, drilled with two holes. These contain mercury which makes contact o the two terminals. Two lengths of glass tube, 70 mm. long by 6 mm. internal diameter, ave short lengths of platinum wire fused into their ends, the wire inside the tubes being eavily gold plated. Connexion between the two tubes is made by means of a U-tube apillary filled with agar saturated with KCl. One tube contains the standard buffer olution saturated with quinhydrone and the other the solution whose *p*H is being deter-nined, also saturated with quinhydrone.

Place the variable resistance box in the position to be occupied by resistance (11) and otate the switch (16) to the quinhydrone position. Adjust the resistance box and rheostat 7) until the meter reads 20 divisions with zero E.M.F. applied to the quinhydrone electrode erminals, and 120 divisions when the E.M.F. is 0·5570 volt. (The negative lead of the poten-iometer goes to the grid of the valve.) Now apply the E.M.F. for *p*H 7·0 and make small djustments with the rheostat (7) and the variable resistance box until the meter reads xactly 70 divisions. With the meter reading exactly 70 divisions, rotate switch (16) to he standard position and note the reading obtained. (The standard reading will of course e different from that for the hydrogen electrode system.) This is the standard reading

* *Journ. Chem. Soc.* (Sept. 1923) 2203.

for this particular quinhydrone electrode system, and should be obtained by adjustment with rheostat (7) before each reading with the quinhydrone electrode and also checked after each reading.

The resistance (11) should be wound to the value shown by the variable resistance box.

In using the quinhydrone apparatus described, the terminal from the tube containing the liquid whose *p*H is being determined is connected to the grid, *i.e.* to the terminal marked *Q*– in Fig. 3.

The calibration values for this electrode system, obtained with the present apparatus, are shown in Table II. The small error in the readings at *p*H 0 to 3 can be corrected by lowering the standard reading as shown.

Table II. *Calibration Table showing the results obtained with the present apparatus for the Quinhydrone Electrode System.*

E.M.F. applied to grid	Corresponding *p*H	Meter reading divisions		Error in *p*H
+ 0·1154	0	1·0		+ 0·10*
+ 0·0577	1	10·5		+ 0·05*
0·0000	2	20·3		+ 0·03*
– 0·0557	3	30·0	Standard	0·00
– 0·1154	4	40·0	reading	0·00
– 0·1731	5	50·0	72 divisions	0·00
– 0·2308	6	60·0		0·00
– 0·2885	7	70·0		0·00
– 0·3462	8	80·0		0·00
– 0·4039	9	90·1		+ 0·01

* By adjusting the standard reading to 71 instead of 72 divisions *p*H 0 to 3 gave correct readings. The calibration was not continued above *p*H 9, as this represents the upper limit at which the quinhydrone electrode is of service for the determination of *p*H.

When using the apparatus it is only necessary to adjust the rheostat (7) to make good any drop in the potential of the battery (3), and of course when changing from the hydrogen electrode system to the quinhydrone electrode system, where the "standard reading" values may be, as in the case of the present apparatus, 60 and 72 divisions respectively.

The values given in this paper for the various resistances are only approximate, since they were those required for a particular valve, and will differ, although possibly only slightly, for other valves. The actual calibration is however, quite simple, and although only two systems are described it is obvious that many variations may be introduced for the measurement of various ranges of E.M.F.

The apparatus described has been in almost daily use for a period of nearly 12 months. During this time no significant alteration affecting the accuracy of the readings has taken place. Certain precautions should, however, be taken in use. All contacts should be kept perfectly clean, otherwise unwanted resistance may be introduced into the circuit which would affect the readings. The apparatus should be kept in a room of fairly even temperature, as large temperature variations will upset the values of the resistances. When replacing a discharged battery by a fully charged one, great care should be taken to see that the rheostat (7) is so adjusted that almost the whole of its resistance is in circuit. Unless this is done, too heavy a current will be passed through the valve filament, with a risk of altering the characteristic curve of the valve.