REVIEW ARTICLE

INSTRUMENTS EMPLOYED IN POTENTIOMETRIC DETERMINATIONS

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Introduction

The theory, technique, and applications of potentiometric analysis are fully described in well-known textbooks, e.g., those of Britton[1] and Clark.[2] Britton[3] has contributed a review of the electrode reactions upon which potentiometric determinations are based and, in a valuable series of articles, Furman[4,5,6] has summarised recent advances in this field of work, including brief references to progress in instrumentation: as far as the author is aware, however, no comprehensive review of the history and development of instruments for use in potentiometric analysis has appeared in recent years.

The potentiometric determination of an ion consists essentially in the measurement of the voltage of a cell, the E.M.F. of which is a function of the concentration of the ion. Prior to the investigation by Haber and Klemensiewicz[7] of the electromotive properties of the glass electrode, the cells used in potentiometry were of comparatively low electrical resistance and, in measuring the E.M.F. by means of the Poggendorf potentiometer, a moving coil galvanometer served as a satisfactory null point detector. In their fundamental studies of the behaviour of the glass electrode Hughes,[8] Kerridge,[9] MacInnes and Dole,[10] Dole,[11] and MacInnes and Belcher[12] used the quadrant electrometer as a null point indicator. Ballistic methods in which the cell is allowed to charge a condenser, the capacitor being subsequently discharged through a ballistic galvanometer, have been used by Brown,[13] Morton,[14] and Britton.[15] Neither the quadrant electrometer nor the ballistic galvanometer attained general popularity in potentiometric estimations, and it was not until the invention of the thermionic valve potentiometer that the problem of measuring the E.M.F. of cells of high electrical resistance was satisfactorily solved. Due to their high sensitivity, robust construction, portability, high input resistance, and simplicity of adjustment, electronic instruments have now superseded other devices for the measurement of E.M.F.

Goode's Valve Voltmeter

Thermionic valves were first employed in the measurement of electrode potentials by Goode,[16] in 1922. The principle upon which the design of Goode's valve voltmeter is based may be described with the aid of the simplified circuit diagram of Figure 1. The filament or cathode F of the triode valve T, when heated by a current supplied by the battery B_1, emits electrons. The anode A, which takes the form of a metallic sheath surrounding the cathode, is charged positively with respect to the cathode by means of the anode battery B_2, and thus attracts the electrons

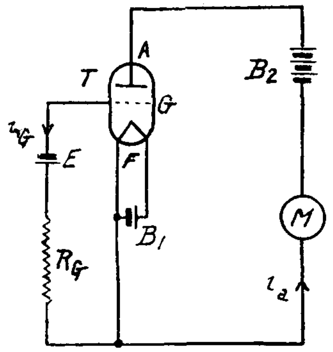

FIG. 1.

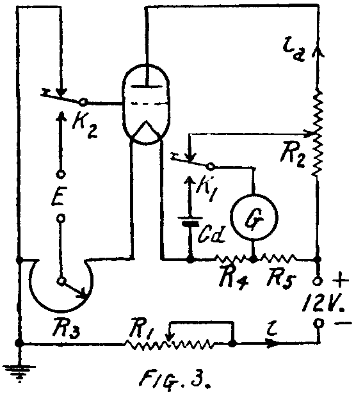

FIG. 3.

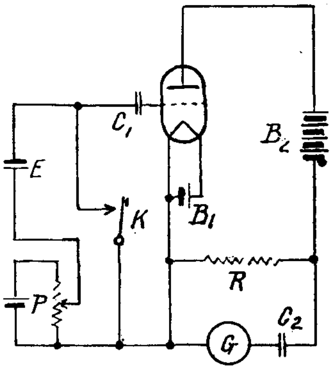

FIG. 4.

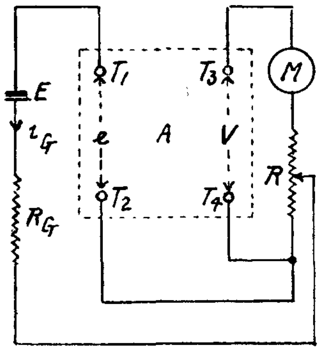

FIG. 5.

emitted by the hot cathode: the stream of electrons collected by the anode, in returning to the filament through the external circuit, sets up a unidirectional anode current i_a which actuates the microammeter or galvanometer M. In traversing the evacuated space between the cathode and anode, the electrons pass through the meshes of a perforated structure G known as the control grid. As this grid is usually charged negatively with respect to the cathode, comparatively few electrons are collected by it, and the grid current i_g flowing through the external grid circuit is extremely small by comparison with the anode current i_a: nevertheless, due to its proximity to the cathode, the grid exercises a powerful electrostatic control over the anode current which may, in fact, be reduced to zero when the grid is sufficiently negative with respect to the cathode. This effect is illustrated by the characteristic curves 1 and 2 of Figure 2, in which the anode current i_a of the ME 1400 valve is plotted for anode voltages of 30 and 45 respectively, as a function of the grid voltage V_g. It will be seen that, except at highly negative grid voltages, the relationship between anode current and grid voltage is approximately linear: the microammeter M (Fig. 1) may accordingly be calibrated in such a manner that its readings indicate directly the value of a voltage E applied to the grid circuit.

Goode's valve voltmeter, subsequently modified by Williams and

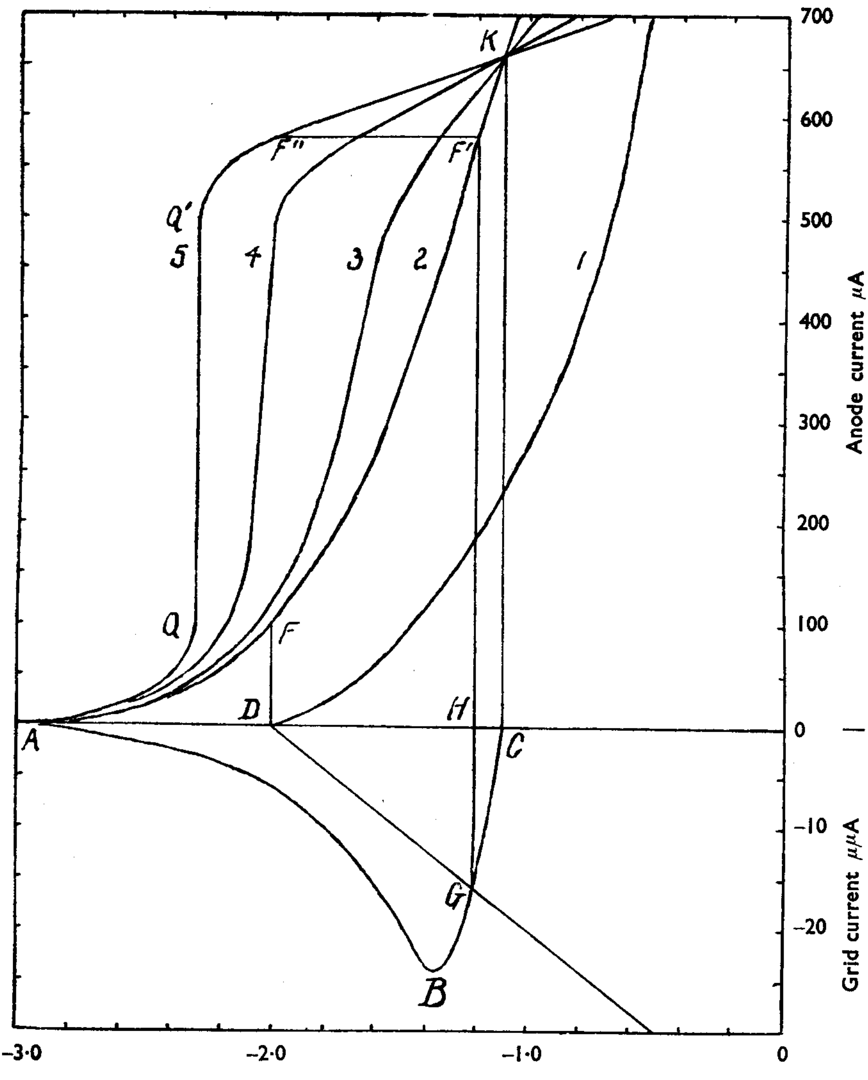

FIG. 2. Grid Voltage.

Whitenach,[17] Bienfait[18] and other workers, has been found to yield satisfactory results in the location of the end-point of potentiometric titrations. Unfortunately, the accuracy is seriously impaired by changes in the voltages of the batteries and by the gradual decline in the emission of electrons from the cathode as the valve ages.

THE VALVE POTENTIOMETER

The valve potentiometer[19] differs essentially from the valve voltmeter in that the readings are given, not by a calibrated microammeter in the anode circuit, but by a standard potentiometer in the grid circuit of the valve: the potentiometer may be calibrated with any desired degree of accuracy, and retains its calibration unimpaired by changes in valve characteristics or battery voltages. The principle of the valve potentiometer may be applied in various ways, one of which is illustrated by the simplified circuit diagram[20,21] of Figure 3.

The adjustable rheostat R_1, the calibrated potentiometer R_3, the filament of the valve, the standardising resitance R_4 and the resistor R_5 are connected in series, this series circuit being supplied with a current i of 100 mA. from a 12 volt source, such as an accumulator or one of the commercial 12 volt mains units now available. The voltage drop across the potentiometer due to this current provides the normal operating grid potential or "grid bias" of the valve; similarly, the voltage dropped across the series-connected resistors R_4 and R_5 supplies the anode voltage of the valve. On depressing the key K_1, the Weston or cadmium cell Cd, the E.M.F. of which is 1·0183 volt, is connected, in series with the galvanometer G, across the standardising resistance R_4 (the ohmic value of which is 10·183 ohms), and the variable rheostat R_1 is adjusted until the galvanometer is undeflected: by this means the potentiometer current and the grid, filament, and anode voltages of the valve are accurately standardised in a single operation. On releasing K_1 and adjusting the movable contact on the anode resistance R_2 until the galvanometer is again undeflected, the voltage drop across this resistance due to the anode current i_a flowing through it is counterbalanced by the equal and opposite voltage across the resistance R_5 due to the current i: during this operation, the grid is earthed via the key K_2. Finally the latter key is depressed, thereby connecting the cell E, in series with an opposing voltage derived from the potentiometer R_3, to the grid of the valve, and the potentiometer control is adjusted until the galvanometer is once more undeflected: it is clear that on the completion of this adjustment the grid is again at earth potential. It follows that the voltage impressed on the grid by the potentiometer is now equal and opposite to that of the applied voltage E: this E.M.F. may be read on the calibrated scale of the potentiometer.

With few exceptions, the instruments used in the measurement of electrode potentials since 1928 have been of the potentiometric type: amongst the many workers who have applied this principle in various ways are Stadie,[22] Dubois,[23] Partridge,[24] Elder,[25] Fosbinder,[26] Muller,[27] Harrison,[28] Greville and Maclagan,[29] and Voegtlin, de Eds and Kahler,[30] Recent developments in electronics have made it possible to stabilise the calibration of Goode's valve voltmeter, and there is at the present time a tendency to revert to this type of instrument in routine analytical work, the valve potentiometer being retained for applications in which measurements of high precision are essential. Before discussing the developments which have led to the reinstatement of the valve voltmeter, however, it is advisable to consider the modifications which are necessary in order to adapt electronic instruments for use with electrodes or non-aqueous solutions of high electrical resistance.

Grid Current

It has been pointed out that the grid current of a triode valve is extremely small by comparison with the anode current. For valves of the type used in radio receivers, the maximum grid current under normal operating conditions varies from 10^{-8} to about 5×10^{-6} amperes and, provided that the resistance of the cell does not exceed a few thousand ohms, no difficulty arises. The average resistance of a glass electrode, however, is about 10^8 ohms, and that of an electrochemical cell containing a non-aqueous solution may greatly exceed this value. Reverting to Figure 1, it is evident that if the true E.M.F. of the cell is E and its resistance R_g, the apparent E.M.F., i.e., the reading given by the instrument, is $E - i_g R_g$, where i_g is the grid current: for example, if $i_g = 10^{-8}$ amperes and $R_g = 10^8$ ohms, the error in the reading is 1 volt. Hence, unless precautions are taken to exclude grid current, or to apply corrections for its effects, the readings of the instrument are of no value.

In Figure 2, the grid current of the ME 1400 valve, when operated at an anode potential of 45 volts, is plotted as a function of the grid voltage. It will be seen that both the grid and anode currents are vanishingly small when the grid is highly negative, e.g., at the point A. As the negative potential applied to the grid is decreased, electrons are able to pass through the meshes of the grid in increasing numbers, and the anode current increases (curve 2): this increase in anode current is accompanied by a proportionate increase in grid current, which attains a maximum value at the point B. The grid current throughout this region of the characteristic curve, i.e., between the points A and B, is due mainly to the fact that the highly negative grid attracts and collects positive ions produced by the bombardment of the residual gas molecules in the incompletely evacuated glass envelope by the electron stream. With further reduction in the negative voltage applied to the grid, the latter loses its capacity for attracting positive ions and the grid current declines until, at the point C (usually known as the "contact potential point" or "free grid potential") it again becomes zero. Reduction of the negative potential of the grid beyond this point causes the latter to attract negative electrons instead of positive ions: in consequence the grid current, after passing through zero at the point C, changes sign and rapidly increases in the reverse direction. As the valve is not designed for operation under conditions of positive grid current, this portion of the characteristic curve is of no practical value, and is not shown in the diagram.

The effect on the performance of a valve voltmeter of including an electrochemical cell of high resistance in the grid circuit is most readily demonstrated by a graphic method. The characteristic of the ME 1400 valve, when operated at an anode potential of 45 volts with zero grid resistance, is represented by curve 2 of Figure 2. Normally the grid is maintained at an average potential of -2 volts with respect to the cathode by means of an accumulator or other source of E.M.F.; this negative "grid bias" is represented by O D, and the corresponding anode current is given by D F, viz., 100 μA. The effect on the anode current of the inclusion of a high resistance in the grid circuit may be investigated by drawing, from the point D, a load line of slope equal to $-1/R_g$, where R_g is the value of the grid resistance: for example, the load line D G, which has a slope of 20 $\mu\mu$A./V., corresponds to a value of $R_g = 5 \times 10^{10}$ ohms. At the point G the load line intersects the grid current characteristic, and the grid current at this point is given by G H, viz., 16 $\mu\mu$A. The applied E.M.F. of -2 volts represented by O D is now partially offset by the opposing voltage drop due to the flow of grid current through the grid resistance. This voltage drop is given by D H, viz., 0·8 volt: the resultant or true E.M.F. between the grid and cathode is thus only $-1{\cdot}2$ volt, and is represented by O H. It will be seen that the effect of introducing a resistance of 5×10^{10} ohms into the grid circuit is to increase the anode current from a value given by F D, viz., 100 μA., to the much higher value represented by F′H, i.e., 580 μA. It is also clear that, with an applied E.M.F. of -2 volts, the error introduced into the reading of the thermionic voltmeter by the inclusion of a resistance of 5×10^{10} ohms in the input circuit is that represented by D H, viz., 0·8 volt, corresponding to a percentage error of 40 per cent. in the reading.

By drawing, from various points along the grid voltage axis, a number of load lines parallel to D G, and noting their points of intersection with the grid current characteristics, curve 5 (in which the anode current is plotted as a function of the applied voltage in the presence of a grid resistance of 5×10^{10} ohms) has been constructed: for example, the point F″ on this curve was obtained by drawing a line F′F″ through F′ equal in length and parallel to D H. Anode characteristic curves corresponding to values of $R_g = 2 \times 10^{10}$ (curve 4) and $R_g = 10^{10}$ (curve 3) are also included in the figures. If the grid current were constant for all values of grid voltage, these curves would be parallel to the normal characteristic (curve 2), and the simple addition of a constant correction would suffice to compensate for the effect of the grid resistance on the calibration of the instrument: however, due to the curvature of the grid characteristic, the anode characteristics 3, 4 and 5 are convex with respect to the normal characteristic, and no such simple correction can be applied. The convexity of the characteristics increases rapidly with the value of the grid resistance and, if the latter exceeds 5×10^{10} ohms, the grid loses control over the anode current. It is, of course, true, that resistances of this magnitude are only occasionally encountered in potentiometric determinations. The ME 1400 valve, however, is one of a type known as "electrometer valves" in which, by methods described later in this review, grid current is very greatly reduced: during the early development of the valve potentiometer, such valves were unknown, and effects similar to those described above were obtained with glass electrodes having resistances as low as 10 megohms.

Early Attempts to Minimise Errors Due to Grid Current

The effects of grid current on the performance of thermionic voltmeters and potentiometers have been discussed in general terms by Metcalf and Thompson,[31] Morton,[32] Nottingham[33] and others. One of the earliest attempts to adapt the valve potentiometer for use with the glass electrode was that of Stadie,[22] who pointed out that, when this method is used, the grid voltage is restored to a predetermined value on the completion of each adjustment: on the assumption that the grid current is constant at constant grid voltage, a simple correction can be applied to compensate for the voltage drop across the glass electrode due to the flow of grid current across the glass membrane. Unfortunately, slight changes in cathode temperature or anode current due to decline in the battery voltages or other causes may produce considerable changes in grid current, even when the grid is maintained at constant potential. Moreover, as Morton[34] has pointed out, the glass electrode has an exceptionally high temperature coefficient of resistance, and the changes in its resistance (and therefore in the voltage dropped across it due to grid current) resulting from fluctuations in ambient temperature may vitiate the measurements: for these and other reasons, Stadie's method has not been generally adopted.

Morton[32] proposed a circuit arrangement in which the effects of grid current were eliminated by a "sum and difference" method: the device was in some respects inconvenient, and failed to gain general acceptance.

A method which has been more widely adopted is that in which, when using the valve potentiometer, the operating grid potential is adjusted to the "contact potential point," e.g., to the point C in Figure 2. At this point the grid current is zero, and the inclusion of a high resistance in the grid circuit has no effect on the anode current, the value of which is given by C K: it is for this reason that the anode characteristics 2, 3, 4 and 5 intersect at the point K. The method, which has been used by a number of workers, notably Garman and Droz,[35] is inconvenient in that, in order to provide for adjustment of the mean grid voltage to the contact potential point, an additional control (which usually takes the form of an auxiliary potentiometer) is required, and frequent readjustment of this control is necessary: further, as the contact potential point lies in the steepest part of the grid current characteristic, slight errors in adjustment lead to errors in measurement of considerable magnitude.

The Impulse-type Valve Electrometer

The circuit diagram of Figure 4 will serve to illustrate the basic principles of this device, which was described by Morton[36] in 1931. A blocking condenser C_1 is connected in series with the grid, which is thus effectively isolated, in so far as direct current is concerned, from the external grid circuit: the latter includes the glass electrode cell E, which is connected in series with an adjustable opposing voltage derived from the calibrated potentiometer P, and the short-circuiting key K. A second blocking condenser C_2, of much greater capacitance, is connected, in series with the galvanometer G, across a high resistance R included in the anode circuit of the valve: since the galvanometer is isolated, by the capacitor C_2, from the anode circuit, it is unaffected by the slow changes in anode current (due mainly to the gradual decline in the voltages of the batteries B_1 and B_2) which would otherwise cause drift of the electrical zero of the instrument. Electrons accumulate on the isolated grid until the latter attains the contact potential indicated by O C in Figure 2, the potential thereafter being automatically maintained at this value. It should be pointed out that the condenser C_1 is virtually in series with the grid-cathode capacitance of the valve, and the combined capacitance is exceedingly small. On depressing the key K, no effect will be observed when the E.M.F. of the cell E is exactly counterbalanced by the opposing voltage derived from the potentiometer P: if this condition does not obtain, the condenser C_1 and the grid acquire a transitory charge due to the unbalanced E.M.F., and the resultant sudden increase in anode current produces a ballistic throw of the galvanometer pointer. The process of measurement thus consists in adjusting the potentiometer P until there is no transient deflection of the pointer on depressing the key.

A discussion of the design of multi-stage amplifiers suitable for use in conjunction with impulse-type electrometers is beyond the scope of the present review: details are given by Fox and Groves,[37] Morton,[38] Chun-Yu Lin,[39] Dole,[40] Ellis and Kiehl,[41] and Goodhue.[42] Using this method, Chun-Yu Lin claims recently to have obtained a sensitivity of 100,000 μA/V., as compared with an average of 100 μA/V. for commercial *p*H meters.

THE ELECTROMETER VALVE

The electrometer valves manufactured in this country were originally intended for use in the measurement of ionisation and photoelectric currents, and credit for their application in 1930 to the determination of glass electrode potentials is due to Harrison.[28] In designing these valves, various expedients have been adopted with a view to minimising grid current, which may by these means be reduced to less than 10^{-14} ampere. For example, the cathode of the E T 1 valve is placed centrally, with the grid and anode on either side: by this means the grid is removed from the electron stream, and the internal resistance of the valve is reduced to such an extent that an adequate performance is obtained with an anode potential of 4 to 6 volts. As this is below the ionisation potential of the residual gas molecules within the valve, the most prolific source of grid current, viz., the production of positive ions as a result of the bombardment of the molecules by the electron stream, is thereby removed. Other manufacturers achieve similar results by producing "electrometer tetrodes" in which a positively charged screen grid is interposed between the cathode and the control grid: this positively-charged grid serves the additional purpose of repelling the positive ions which are emitted by the hot cathode and which would otherwise be attracted to the control grid. In yet another type, developed in America, the anode takes the form of a perforated structure situated between the cathode and the control grid: "inverted triodes" of this type have been used in glass electrode measurements by Cherry.[43] Double electrometer valves specially designed for high zero stability have been described recently by Derbyshire[44] and Little.[45]

By comparison with the valves used in radio reception, electrometer triodes and tetrodes are both costly and inefficient, and it is not surprising that many attempts have been made to adapt normal broadcast receiving valves for use as substitutes. Adaptations of this kind have been described by Johnson,[46] Johnson and Neitzert,[47] Gabus and Poole[48] and others, but the circuits are intended for use with American valves which are not readily obtainable in this country.

Any of the circuit arrangements previously described may be adapted for use with electrometer triodes merely by readjustment of the grid, cathode, and anode voltages to the values recommended by the valve manufacturers: in the case of the impulse-type electrometer (Fig. 4), the condenser C_1 may be omitted. If it is desired to use an electrometer tetrode, somewhat more elaborate modification of the circuit arrangement is necessary: for this type of valve, the circuits described by Du Bridge and Brown,[49] Barth,[50] and Penick,[51] which possess exceptionally high zero stability, are of especial value.

Negative Feedback

During the period 1934–1945, thermionic electrometers and other *p*H-measuring devices were described by Mouquin and Garman,[52] Goyan, Barnes and Hind,[53] Penther, Rolfson and Lykken,[54] Penther and Rolfson,[55] Buras Jun. and Reid[56] and other workers. Throughout this period, important advances were made in the general theory and practice of electronics, and the outstanding feature of the post-war period has been the application of new principles established by electronic engineers to the instruments used in potentiometry. Of these, perhaps the most important is the development of negative feedback, which has rendered possible the reinstatement of Goode's valve voltmeter in a greatly improved form.

Both negative and positive feedback have been used, for various purposes, over a period of many years: in 1932, for example, the writer[38] applied positive feedback to a potentiometer recorder in order to enhance the sensitivity. It is only within recent years, however, that the value of negative feedback (or degeneration, to use an alternative term) as a means of stabilising the calibration of a thermionic voltmeter has been fully appreciated. The underlying principles have been discussed by Tellegen and Henriquez,[57] Lewis,[58] Farren[59] and other authors, and may be explained with the aid of Figure 5, in which A represents an amplifier, such as a valve voltmeter, to the output terminals T_3 and T_4 of which a microammeter M, in series with a load resistance R, is connected. The combination of the microammeter M and its series resistance R constitutes a voltmeter, the readings of which indicate the output voltage V. The glass electrode cell (represented in the diagram as a source of voltage E in series with a high resistance R_g) is connected, in opposition to a voltage αV obtained by feeding back a fraction α of the output voltage V, to the input terminals T_1 and T_2. Using the notation of the diagram, and ignoring for the present the influence of the grid current i_g and resistance R_g in the input circuit, we have

$$V = \mu e \quad \ldots \quad (1)$$

where μ is the voltage amplification provided by the amplifier. But

$$e = E - \alpha V \quad \ldots \quad (2)$$

hence

$$V = \mu(E - \alpha V) \text{ or } V = \mu E/(1 + \mu\alpha) = E/(\frac{1}{\mu} + \alpha) \quad \ldots \quad (3)$$

Evidently when μ is sufficiently great, equation (3) reduces to

$$V = E/\alpha \quad \ldots \quad (4)$$

and if, in addition, the whole of the output voltage V is fed back to the input circuit (an arrangement which is known as a "cathode follower" circuit)—we have

$$\alpha = 1 \text{ and } V = E \quad \ldots \quad (5)$$

As the term μ has disappeared from equations (4) and (5) it follows that under these conditions the output voltage V and the calibration of the microammeter M are independent of changes in the characteristics of the valves and therefore also of changes in the voltage of the power supply to the amplifier.

Deflection *p*H meters in which the principle of negative feedback has been applied are now obtainable commercially, and various circuits have been described; one of the most recent is that of Thorp.[60] As Sowerby[61] and other authors have shown, negative feedback is also valuable as a means of increasing the input resistance of a valve voltmeter or *p*H meter.

The Feedback Potentiometer

The simple theory of the feedback potentiometer[62] may be explained with the aid of the circuit diagram of Figure 5. It has been shown above that, on the application of a voltage E to the input terminals T_1 and T_2, the output voltage V indicated by the microammeter M is given by

$$V = E/(\frac{1}{\mu} + \alpha) \quad \ldots \quad (6)$$

If now the voltage E increases by an amount δE, the output voltage will also increase, but may be restored to its former value by increasing the feedback factor α (by means of a sliding contact on the potentiometer R) by an amount $\delta\alpha$ such that the relationship

$$V = (E + \delta E)/(\frac{1}{\mu} + \alpha + \delta\alpha) \quad \ldots \quad (7)$$

is satisfied. From (6) and (7) we have

$$\delta\alpha V = \delta E \quad \ldots \quad (8)$$

that is, the increment in feedback voltage is equal to the increment in applied voltage. Assuming that the potentiometer R has been suitably calibrated with any desired degree of accuracy, its readings give directly the E.M.F. of the cell or *p*H value of the solution: as the term μ does not appear in equation (8), it follows that, even if the amplifier consists of a single stage of low voltage amplification, the readings are independent of the valve characteristics. In order to permit of accurate adjustment, the microammeter is replaced in practice by a standardising resistance, across which a galvanometer is connected in series with a Weston cell: the process of measurement consists in adjusting the potentiometer R until the galvanometer is undeflected.

Zero Stability

It has been pointed out that a prolific source of inconvenience and error in the use of electronic *p*H meters is drift of the electrical zero of the indicating instrument as a result of slow changes in valve characteristics or supply voltage. Using two independent lines of approach, electronic engineers have in recent years made striking progress in the design of D.C. amplifiers and thermionic electrometers of high zero stability.

(1) Reverting to the impulse-type valve electrometer (Fig. 4), it is clear that if the key K is replaced by a mechanical interruptor or vibrator operating at a suitable frequency, the unbalanced E.M.F. due to the glass electrode cell E and potentiometer P will be applied intermittently to the grid circuit, giving rise to an alternating current in the anode circuit which may be amplified by a conventional A.C. amplifier and, after rectification, used to operate a D.C. indicating or recording instrument. Successive stages in the amplifier may be isolated, in so far as direct current is concerned, by means of blocking condensers or transformers, thereby eliminating drift due to slow changes in the anode currents of the intermediate stages. The design of a high-insulation vibrator suitable for use with glass electrodes is by no means a simple problem, but *p*H meters operating on this principle have been produced. As an alternative to the use of a vibrator, the capacitance of the condenser C_1 may be varied at a convenient frequency, e.g., by using as one of its plates a vibrating diaphragm or reed. The latter method had been developed, under the name of the dynamic condenser electrometer, by Palevsky,[63] Thomas and Finch[64] and other workers, and has been applied to the measurement of glass electrode potentials by Kraus.[65]

(2) Methods of reducing zero drift by using two triodes of similar type in a balanced bridge circuit have been used for many years, the earliest being those of Brentano,[66] Wynn-Williams,[67] and Brentano and Ingleby.[68] A more recent circuit of this type, developed by Schmitt[69] and Richter,[70] has been modified for use in the measurement of glass electrode potentials by Buras and Reid.[56] The exacting requirements, as regard zero stability, of the amplifiers used in encephalography and electrocardiography have led to the extension of the balanced bridge method to multi-stage amplifiers by Offner,[71] Matthews,[72] Miller,[73] Parr and Walter,[74] Johnston[75] and many other workers.

Prinz[76] has recently described an ingenious method, based on negative feedback principles, of automatically compensating a D.C. amplifier for zero drift and input current, and has suggested the application of the device to *p*H-measuring instruments.

THE TREND OF FUTURE DEVELOPMENT

Reference has been made to a number of recent advances in electronics which may have an important bearing on future progress in potentiometric instrumentation. These include (1) the principle of negative feedback, (2) the dynamic condenser electrometer, and (3) the development of biological amplifiers of extremely high zero stability and voltage amplification. The intelligent application of these new devices may lead to striking improvements in the performance of instruments used in potentiometry. In order to meet the need for portable radiation detectors suitable for use in Civil Defence, miniature electrometer valves with very modest power requirements are now in production: this has made possible the construction of miniature *p*H meters, the power consumption of which may be no greater than 50 mW, as compared with 1,200 mW for the instrument illustrated in Figure 3. It may be anticipated that the present trend towards the development of compact apparatus of economical power consumption will continue.

In conclusion the author regrets that, owing to the limited scope of this review, it has not been found possible to describe the work of numerous investigators, some of whom have made valuable contributions to the development of potentiometric instrumentation.

REFERENCES

1. Britton, *Hydrogen Ions*, 1942, London: Chapman and Hall, Ltd.
2. Clark, *The Determination of Hydrogen Ions*, Baillière, Tindall and Cox.
3. Britton, *J. sci. Instrum.*, 1946, **23**, 89.
4. Furman, *Industr. Engng. Chem., Anal. Ed.*, 1930, **2**, 213.
5. Furman, *ibid.*, 1942, **14**, 367.
6. Furman, *Anal. Chem.*, 1950, **22**, 33.
7. Haber and Klemensiewiez, *Z. Phys. Chem.*, 1909, **67**, 385.
8. Hughes, *J. Amer. chem. Soc.*, 1922, **44**, 2860.
9. Kerridge, *Biochem. J.*, 1925, **19**, 611; *J. sci. Instrum.*, 1926, **3**, 404.
10. MacInnes and Dole, *J. Amer. chem. Soc.*, 1930, **52**, 29; *Industr. Engng. Chem., Anal. Ed.*, 1929, **1**, 57.
11. Dole, *J. Amer. chem. Soc.*, 1931, **53**, 4260; *J. Chem. Phys.*, 1934, **2**, 862.
12. MacInnes and Belcher, *J. Amer. chem. Soc.*, 1931, **53**, 3315.
13. Brown, *J. sci. Instrum.*, 1924, **2**, 12.
14. Morton, *ibid.*, 1930, **7**, 187.
15. Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 531.
16. Goode, *J. Amer. chem. Soc.*, 1922, **44**, 26; 1925, **47**, 2483.
17. Williams and Whitenach, *J. phys. Chem.*, 1927, **31**, 519.
18. Bienfait, *Rec. Trav. chim. Pays-Bas*, 1926, **45**, 166.
19. Morton, *Trans. Faraday Soc.*, 1928, **24**, 14.
20. Morton, *J. sci. Instrum.*, 1932, **9**, 289; British Patent No. 396,817.
21. Morton and Best, *J. Soc. chem. Ind.*, 1933, **52**, 6T.
22. Stadie, *J. biol. Chem.*, 1929, **83**, 477.
23. Dubois, *ibid.*, 1930, **88**, 729.
24. Partridge, *J. Amer. chem. Soc.*, 1929, **51**, 1.
25. Elder, *ibid.*, 1929, **51**, 3266.
26. Fosbinder, *J. phys. Chem.*, 1930, **34**, 1299.
27. Muller, *Z. Elektrochem.*, 1930, **34**, 1299.
28. Harrison, *J. chem. Soc.*, 1930, 1528.

29. Greville and Maclagan, *Trans. Faraday Soc.*, 1931, **27**, 211.
30. Voegtlin, de Eds and Kahler, *Amer. J. Physiol.*, 1929, **91**, 225.
31. Metcalf and Thompson, *Phys. Review*, 1930, **36**, 1489.
32. Morton, *J. chem. Soc.*, 1931, 2983.
33. Nottingham, *J. Franklin Inst.*, 1930, **209**, 287.
34. Morton, *J. chem. Soc.*, 1934, 256.
35. Garman and Droz, *Industr. Engng. Chem. Anal. Ed.*, 1939, **11**, 398.
36. Morton, *J. chem. Soc.*, 1931, 2977.
37. Fox and Groves, *J. Soc. chem. Ind.*, 1932, **51**, 7T.
38. Morton, *J. chem. Soc.*, 1932, 2469.
39. Chun-Yu-Lin, *J. sci. Instrum.*, 1944, **21**, 48.
40. Dole, *The Glass Electrode*, Chapman and Hall, Ltd., 1941, 60.
41. Ellis and Kiehl, *Rev. sci. Instrum.*, 1933, **4**, 131.
42. Goodhue, *Iowa State Coll. J. Sci.*, 1935, **10**, 7.
43. Cherry, *Trans. electrochem. Soc.*, 1937, **72**, 33.
44. Derbyshire, *Electronic Engn.*, 1946, **18**, 277.
45. Little, *ibid.*, 1947, Nov., 365.
46. Johnson, *Phys. Review*, 1936, **50**, 170.
47. Johnson and Neitzert, *Rev. sci. Instrum.*, 1934, **5**, 196.
48. Gabus and Poole, *ibid.*, 1937, **8**, 196.
49. Du Bridge and Brown, *ibid.*, 1933, **4**, 532.
50. Barth, *Z. Physik.*, 1934, **87**, 399.
51. Penick, *Rev. sci. Instrum.*, 1935, **6**, 115.
52. Mouquin and Garman, *Industr. Engng. Chem., Anal. Ed.*, 1937, **9**, 287.
53. Goyan, Barnes and Hind, *ibid.*, 1940, **12**, 485.
54. Penther, Rolfson and Lykken, *ibid.*, 1941, **13**, 831.
55. Penther and Rolfson, *ibid.*, 1943, **15**, 337.
56. Buras, Jun. and Reid, *ibid.*, 1945, **17**, 120.
57. Tellegen and Henriquez, *Wireless Engr.*, 1937, **14**, 409.
58. Lewis, *J. sci. Instrum.*, 1938, **15**, 353.
59. Farren, *Wireless Engr.*, 1938, **15**, 23.
60. Thorp, *Electronic Engn.*, 1945, Sept., 671; *Instrum. Practice*, 1947, **1**, 132.
61. McG. Sowerby, *J. sci. Instrum.*, 1944, **21**, 42.
62. Morton, *Trans. Faraday Soc.*, 1948, **44**, 588: British Patent No. 593,920.
63. Palevsky, Swenk and Grenchik, *Rev. sci. Instrum.*, 1947, 298.
64. Thomas and Finch, *Electronic Engn.*, 1950, **22**, 395.
65. Kraus, Holmberg and Borkowski, *Anal. Chem.*, 1940, **22**, 341.
66. Brentano, *Nature, Lond.* 1926, **108**, 532.
67. Wynn-Williams, *Trans. Camb. phil. Soc.*, 1927, **23**, 811.
68. Brentano and Ingleby, *J. sci. Instrum.*, 1939, **16**, 81.
69. Schmitt, *ibid.*, 1938, **15**, 136.
70. Richter, *Electronics*, 1943, Nov., 112.
71. Offner, *Rev. sci. Instrum.*, 1937, **8**, 20.
72. Matthews, *J. Physiol.*, 1934, **81**, 28 P.
73. Miller, *Electronics*, 1941, **14**, 27.
74. Parr and Walter, *J. Instn. elect. Engrs.*, 1943, **90**, 129.
75. Johnston, *Wireless Engr.*, 1947, **24**, 231.
76. Prinz, *J. sci. Instrum.*, 1947, **24**, 328.