CCCCXV.—*The Determination of Glass-electrode Potentials by Means of Valve Potentiometers.*

By CHARLES MORTON.

THE thermionic valve potentiometer was introduced by the writer in 1928 (*Trans. Faraday Soc.*, **24**, 14), and has been applied to the determination of glass-electrode potentials by Stadie (*J. Biol. Chem.*, 1929, **83**, 477), Dubois (*ibid.*, 1930, **88**, 729), Partridge (*J. Amer. Chem. Soc.*, 1929, **51**, 1), Elder (*ibid.*, p. 3266), Fosbinder (*J. Physical Chem.*, 1930, **34**, 1299), Müller (*Z. Elektrochem.*, 1930, **36**, 923), Harrison (J., 1930, 1528), Greville and Maclagan (*Trans. Faraday Soc.*, 1931, **27**, 211), and Voegtlin, de Eds, and Kahler (*Amer. J. Physiol.*, 1929, **91**, 225).

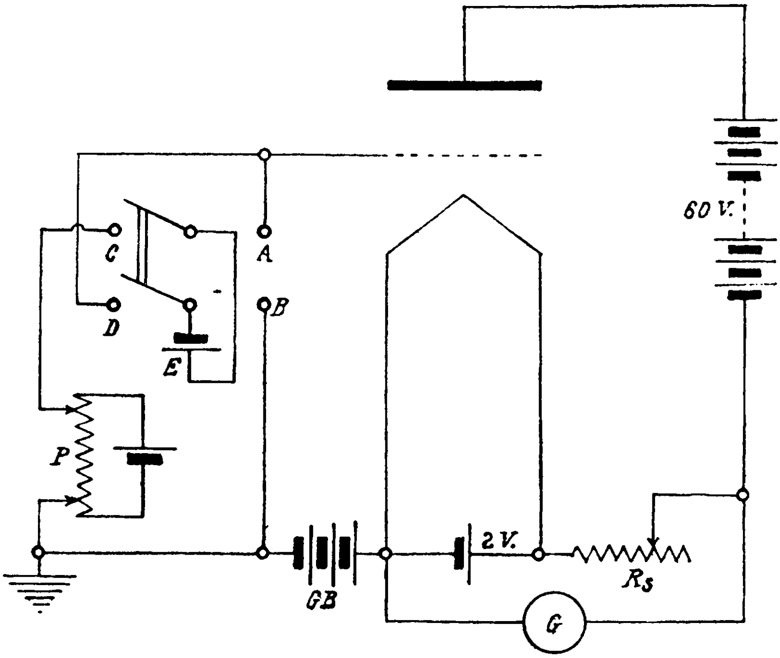
The method described in the present communication differs from those hitherto employed in that the sensitivity increases with the resistance of the cell, and becomes very great when the latter is equal and opposite to the internal grid impedance of the valve.

The sensitivity of a valve potentiometer may be defined as $\partial i_{ga}/\partial E$, *i.e.*, the change in the current through the galvanometer for unit change in applied potential. At a certain lower limit of ∂E, the zero drift becomes comparable with the deflexion due to the unbalanced *E.M.F.* applied to the grid, and increasing the sensitivity of the galvanometer does not further extend the range. With the majority of the valve potentiometers previously described, owing to the low grid sensitivity, the consistent attainment of an accuracy of $\pm$ 1 millivolt is a matter requiring some skill and patience, although occasional measurements may show an accuracy of a somewhat higher order. By taking full advantage of the relay action of the valve, the deflexion for an unbalanced *E.M.F.* of

$\pm$ 0·01 millivolt may be made large in comparison with the uncontrolled zero drift, and thus the accuracy may be increased. It is for this reason that, in the present work, consideration has been paid to the conditions under which high sensitivity may be obtained.

General Principles.—The electrical circuit is simple, and is shown in Fig. 1*a*. During the initial zero adjustment, the switch arms make contact at A and B, and the component of the anode current flowing through the galvanometer is balanced in the usual manner by varying R_s, which regulates the compensating current supplied

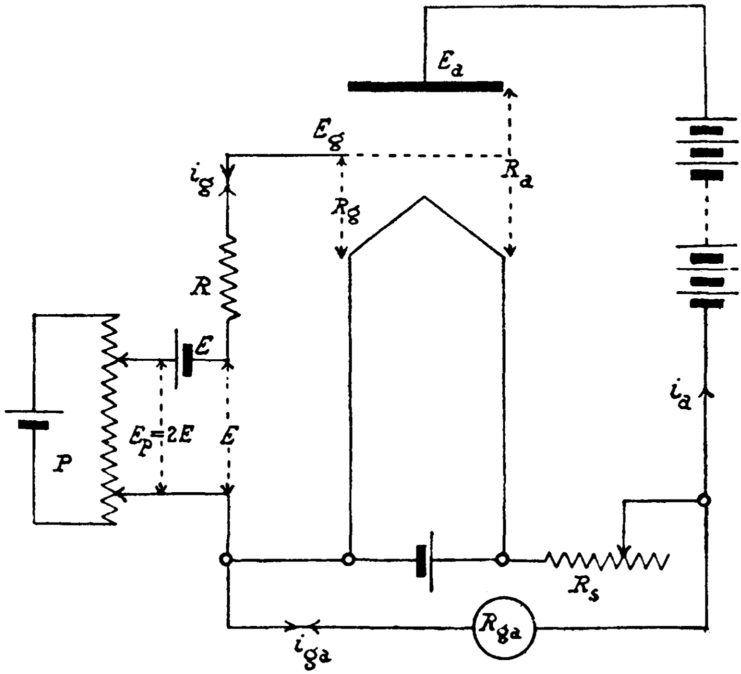
FIG. 1*a*.



by the filament accumulator. The switch is now thrown so that contact is established at C and D, and the system is balanced by adjustment of the potentiometer P. The effective grid potential is evidently equal to $(+E \pm i_gR - E_{gb})$ and $(-E + E_p \pm i_gR - E_{gb})$ at the completion of the first and the second adjustment respectively, i_g being the grid current, E_{gb} the nominal grid-bias potential, E_p the potentiometer reading, and E and R the *E.M.F.* and resistance of the cell. Hence $E = \frac{1}{2}E_p$, *i.e.*, the *E.M.F.* is equal to half the reading of the potentiometer dials. If desired, the latter may be re-graduated (the readings being halved) so as to give directly the *E.M.F.* of the cell.

The conditions at balance are represented in Fig. 1*b* : to simplify matters the nominal grid-bias potential E_{gb}, which serves merely to fix the mean grid potential at the operating point, has been omitted. At balance, let R_g and R_a be the internal grid and anode impedances respectively, E_g and E_a the effective grid and anode potentials, i_g and i_a the grid and anode currents, and $R_{ea} = R_s \,.\, R_{ga}/(R_s + R_{ga})$ the total external anode resistance. Since a null method is employed, only small displacements, *e.g.*, unbalanced potentials

FIG. 1*b*.



of the order of 0·1 millivolt, need be considered : under these conditions R_a and R_g are sensibly constant, and Ohm's law is applicable. Thus for a small change E_a in the anode potential, or of $\mu \,.\, \partial E_g$ in the effective grid potential (where μ is a constant, the "amplification factor" of the valve under operating conditions), the change in anode current is

$$\partial i_a = \frac{\partial E_a}{R_a + R_{ea}} = \frac{\mu \,.\, \partial E_g}{R_a + R_{ea}} \quad . \quad . \quad . \quad . \quad (1)$$

The effective grid potential at balance is $E_g = - E \pm i_g R +$

$E_{\mathrm{p}}(=2E) = E \pm i_{\mathrm{g}}R$. For a small displacement ∂E from the balance point $\partial E_{\mathrm{g}}/\partial E = R_{\mathrm{g}}/(R_{\mathrm{g}} + R)$

$$\frac{\partial i_{\mathrm{a}}}{\partial E} = \frac{\mu}{R_{\mathrm{a}} + R_{\mathrm{ea}}} \cdot \frac{R_{\mathrm{g}}}{R_{\mathrm{g}} + R} \quad . \quad . \quad . \quad . \quad (2)$$

An important characteristic of the valve for the present purpose is its mutual conductance G, which is defined as the slope of the anode characteristic curve, when R_{ea} and R are equal to zero. From (2) we have $G = \mu/R_{\mathrm{a}}$. The ratio

$$G' = \frac{\partial i_{\mathrm{a}}}{\partial E} = \frac{\mu}{R_{\mathrm{a}} + R_{\mathrm{ea}}} \cdot \frac{R_{\mathrm{g}}}{R_{\mathrm{g}} + R} = \frac{R_{\mathrm{a}}}{R_{\mathrm{a}} + R_{\mathrm{ea}}} \cdot \frac{R_{\mathrm{g}}}{R_{\mathrm{g}} + R} \cdot G \qquad (3)$$

is the slope of the anode characteristic under operating conditions, and may be termed the effective mutual conductance. The ratio $\partial i_{\mathrm{ga}}/\partial i_{\mathrm{a}}$ of the galvanometer current to the total anode current is $\partial i_{\mathrm{ga}}/\partial i_{\mathrm{a}} = R_{\mathrm{s}}/(R_{\mathrm{s}} + R_{\mathrm{ga}})$. We thus obtain

$$\frac{\partial i_{\mathrm{ga}}}{\partial E} = \frac{\partial i_{\mathrm{ga}}}{\partial i_{\mathrm{a}}} \cdot \frac{\partial i_{\mathrm{a}}}{\partial E} = \frac{R_{\mathrm{s}}}{R_{\mathrm{s}} + R_{\mathrm{ga}}} \cdot \frac{R_{\mathrm{a}}}{R_{\mathrm{a}} + R_{\mathrm{ea}}} \cdot \frac{R_{\mathrm{g}}}{R_{\mathrm{g}} + R} \cdot G \qquad (4)$$

The conditions under which high sensitivity may be obtained are as follows :

(1) The sensitivity being directly proportional to the mutual conductance, a " power " or pentode valve should be employed.

(2) Of two galvanometers of equal sensitivity, that of lower resistance is the more suitable. If for any reason it is necessary to use a high-resistance galvanometer, it is advantageous to supply the compensating current, not from the filament accumulator, but from a separate battery of higher *E.M.F.* in order that R_{s} may be maintained at a high value. Under these conditions $R_{\mathrm{s}}/(R_{\mathrm{s}} + R_{\mathrm{ga}})$ is sensibly equal to unity.

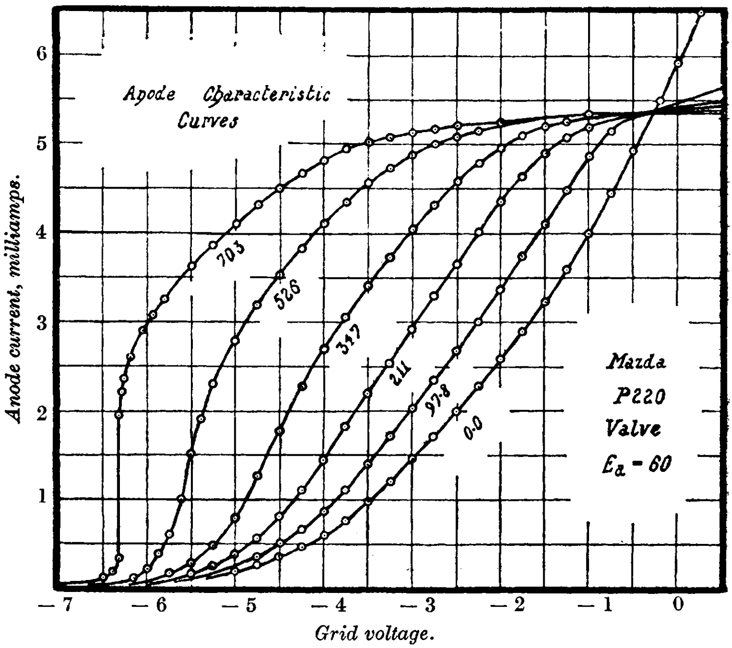
(3) Since R_{a} is always positive, the introduction of the load R_{ea} into the anode circuit must result in a loss of sensitivity. The loss is negligible if a low-resistance galvanometer (10—30 Ω) is employed, or a high-resistance galvanometer in conjunction with a pentode valve, which combines a high mutual conductance with a high value of R_{a}. If, in addition, the condition mentioned under (2) is satisfied, equation (4) reduces to

$$\partial i_{\mathrm{ga}}/\partial E = R_{\mathrm{g}}G/(R_{\mathrm{g}} + R) \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(4) When the resistance of the source of *E.M.F.* is low, equation (5) reduces further to $\partial i_{\mathrm{ga}}/\partial E = G$; the maximum sensitivity obtainable when low-resistance cells are employed is equal to the mutual conductance of the valve. When, however, the source of *E.M.F.* is a glass electrode, the degree of sensitivity ultimately depends on the slope b of the grid characteristic at the operating grid potential : since b may be positive, negative, or equal to zero,

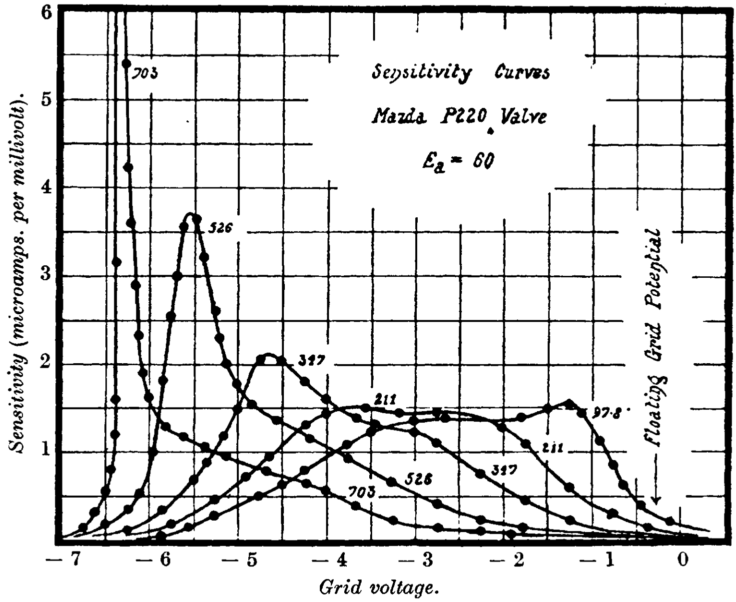
and $R_g = 1/b$, three cases arise: (4*a*) When R_g is positive, the introduction of the high-resistance cell into the grid circuit diminishes the sensitivity, and if R is large compared with R_g the sensitivity falls almost to zero. (4*b*) At the maximum of the grid characteristic, equation (5) reduces to $\partial i_{ga}/\partial E = G$; the sensitivity is equal to the mutual conductance, and is unaffected by the resistance of the glass electrode. (4*c*) When R_g is negative the sensitivity is enhanced by the introduction of the high-resistance cell into the grid circuit. When $R_g = -R$, the sensitivity is infinitely great.

FIG. 2*a*.



These results are illustrated by the curves of Fig. 2, which were obtained with the Mazda P 220 valve operated at normal filament temperature and with an anode potential of 60 volts. Fig. 2*a* shows graphically the effect, on the slope of the anode characteristic, of the introduction of a series resistance into the grid circuit. Each resistance consisted of a thin glass bulb (a glass electrode) filled with dilute acid saturated with quinhydrone, and immersed in a solution, also saturated with quinhydrone, such that no *P.D.* was set up between platinum wires dipping into the solutions on either side of the glass membrane. The curve for $R = 0$ is the normal anode characteristic. The remaining curves are convex with respect to the normal characteristic (*i.e.*, of steeper slope) when the grid is highly negative, and each attains a maximum slope at a point which may be termed the critical grid potential : as the negative grid bias is reduced the curves approach the normal characteristic, and intersect the latter at what is known as the "floating grid potential." This is the potential which the grid assumes when completely isolated, and is the point at which the grid current becomes zero and changes sign : in this region the slope is reduced almost to zero. The influence of the external grid resistance on the effective mutual conductance is strikingly shown

FIG. 2*b*.



by the curve for $R = 703$ MΩ. At the critical grid potential there is a break in the characteristic, and the sensitivity attains the remarkable value of 38 microamps. per millivolt.

The dependence of the sensitivity on the mean grid potential is illustrated by the sensitivity curves of Fig. 2*b*, which were obtained by plotting $\partial i_{ga}/\partial E$ against E, the mean grid potential. Each curve passes through a maximum at the critical grid potential and falls almost to zero on either side of this point. The maximum values of $\partial i_{ga}/\partial E$ are 1·55, 1·5, 2·1, 3·7, and 38 microamps. per millivolt for $R = 97{\cdot}8$, 211, 347, 526, and 703 megohms respectively, as compared with 0·05—0·25 at the floating grid potential (the method of Dubois; Fosbinder; Müller; and Voegtlin, de Eds, and

Kahler), and 0·03 for the electrometer valve used by Harrison and by Greville and Maclagan.

EXPERIMENTAL.

Methods of applying routine tests for the efficiency of insulation and shielding have been described by Greville and Maclagan and others, and will not be discussed. It may be remarked, however, that, since each pole of the cell in turn is connected to the grid, both poles are adequately shielded and insulated; the insulation of the switch contacts must also be of a high order. During the transit of the switch the grid is momentarily isolated, and tends to acquire a charge which is not readily dissipated subsequently through the high resistance leak to earth. This is avoided by employing a spring-loaded trigger release.

Batteries of dry cells are convenient as sources of anode and grid-bias potentials; that used in the grid circuit is variable in steps of 1·5 volts. The adjustment of the mean grid potential for high sensitivity is not critical unless cells of very high resistance are employed, but if desired, a potential divider connected across the filament accumulator may be used as a fine adjustment. The grid potential at which high sensitivity is attained is determined, for a given valve and glass electrode, from a sensitivity curve of the type given in Fig. 2*b*, or more simply, by trial.

The grid current of modern "hard" receiving valves at the critical grid potential is of the order of 10^{-10} or 10^{-9} amp., and extended tests have shown that it is insufficient to lead to significant polarisation. Operation at the floating grid potential does not, as has been supposed, confer immunity from polarisation effects. At this point the grid characteristic has a steep positive slope, and the slightest displacement from the balance point is sufficient to bring about a relatively heavy flow of grid current. Owing to the hardness of modern valves, leakage currents flowing from the grid battery through the valve base and holder are comparable with, and frequently exceed, the current due to ionisation within the valve, and profoundly affect the form of the grid characteristic. The sensitivity curves of Fig. 2*b* were obtained after isolating the grid by making saw-cuts through the base around the grid pin and removing the latter together with a portion of the bakelite base connexion was then made directly to the isolated grid lead Uncapped valves may be obtained from many British manufacturers

The zero variations of valve potentiometers are of two types:

(1) A drift of zero is caused by variations in the electronic emission of the filament: the drift usually takes place at a fairly steady rate and in the same direction. Wynne-Williams (*Proc. Camb*

Phil. Soc., 1927, **23**, 811; *Phil. Mag.*, 1928, **6**, 325) has shown that, provided certain stringent conditions be satisfied, it is possible partially to compensate the system for variations in battery voltages and thus reduce the rate of drift. The method described in the present communication renders such compensation unnecessary. The zero drift which takes place during the time necessary to take a reading is small in comparison with the deflexion produced by an unbalanced *E.M.F.* of $\pm$ 0·01 millivolt. In general, it will be found convenient to employ a somewhat insensitive pointer galvanometer giving a deflexion of, say, one division per microamp.: the zero drift is then imperceptible during the period required to take some 5—10 readings.

(2) Random excursions of the galvanometer result from electromagnetic disturbances or body capacity effects. Owing to the fact that the grid-filament impedance is reduced by the flow of grid current, the valve potentiometer described in the present communication is comparatively insensitive to potential surges impressed on the grid, and for most purposes electrostatic shielding is unnecessary. If the apparatus is to be used with cells of very high resistance, however, it is advisable to enclose it in an earthed metal box.

Differential Potentiometric Titration by Means of the Glass Electrode.—The valve potentiometer is especially valuable for use in differential potentiometric titration in conjunction with glass electrodes. Not only is the use of special forms of titration cell rendered unnecessary, but also, by taking advantage of the relay action of the valve, a higher order of accuracy is obtained. Moreover, the neutralisation curve may be determined simultaneously with the differential curve.

The titrant is added in successive equal increments, and the system balanced at each stage as already described, thus yielding data for constructing the neutralisation curve. At each step, after balancing, a small increment ΔV (one drop) of the reactant is added, and the resulting deflexion of the galvanometer is noted before the addition of the next larger increment. This deflexion is evidently proportional to $\Delta E/\Delta V$, and by plotting the deflexions against the total volume V of titrant added, the differential curve is obtained. Owing to the amplifying properties of the valve, a very slight increase in the value of $\Delta E/\Delta V$ may be detected, and the method gives excellent results in the titration of weak acids or bases at high dilutions. For many purposes it is unnecessary to plot the differential curve, the end-point being located merely by noting the value of V corresponding to maximum galvanometer deflexion.

Summary.

(1) A thermionic valve potentiometer for the measurement of glass-electrode potentials is described. The instrument differs from those of earlier design in that the sensitivity increases with the resistance of the source of *E.M.F.* A sensitivity of 38 microamps. per millivolt has been obtained.

(2) The application of the valve potentiometer to differential potentiometric titration with glass electrodes is discussed. The accuracy is of a higher order than is otherwise obtainable, and the use of special forms of titration apparatus is rendered unnecessary.

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