CCCCXIV.—*The Determination of Glass-electrode Potentials by Means of a Null Ballistic Valve Electrometer.*

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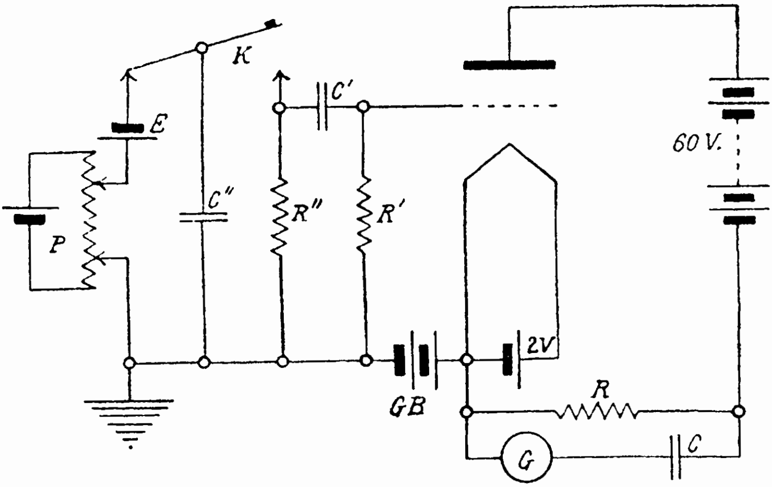
THE difficulties associated with the measurement of glass-electrode potentials by means of the quadrant electrometer have led to the development of the thermionic valve potentiometer (Morton, *Trans. Faraday Soc.*, 1928, **24**, 14) into an electrostatic instrument. The null ballistic valve electrometer now described is characterised by its complete zero stability and by the absence of variable resistances or other controls. The sensitivity is such that an *E.M.F.* of 0·01 millivolt operating through a resistance of 1000 megohms may be detected.

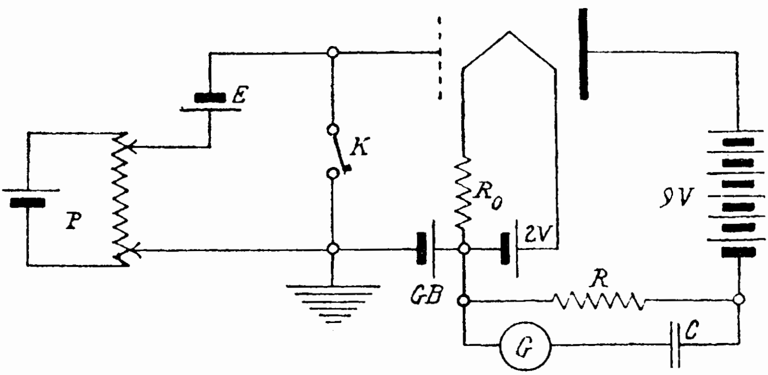
The most satisfactory form of thermionic electrometer previously described is that due to Harrison (J., 1930, 1528), in which the electrometer valve is used. The grid current of this valve is of the order of 10^{-16} amp., and the grid-filament capacity and insulation resistance are in the neighbourhood of 1·5 $\mu\mu$ farads and 10^9 megohms respectively. The instrument thus behaves as an electrometer of small capacity. Unfortunately, the limit of accuracy is $\pm$ 1 millivolt according to Harrison, the deflexions produced by potentials of a lower order of magnitude being comparable with the uncontrollable zero drift. Greville and Maclagan (*Trans. Faraday Soc.*, 1931, **27**, 211) sought to increase the accuracy of Harrison's method by employing a more sensitive galvanometer, and claimed an accuracy of $\pm$ 0·05 millivolt. It is noteworthy, however, that the maximum deflexion which they obtained for a potential of 0·05 millivolt was only 0·6 mm., whereas the zero drift amounted to 2 mm. per minute. Increasing the sensitivity of the galvanometer beyond a certain limit does not extend the range, since controlled and random deflexions are proportionately magnified. The limit of accuracy is thus determined by the steadiness of the zero.

FIG. 1*a*.



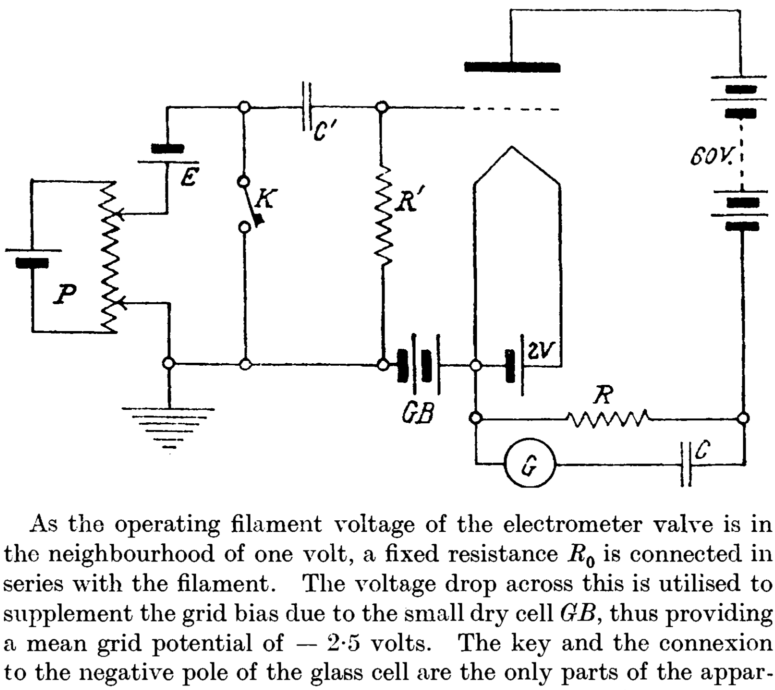
The electrical circuit of the ballistic electrometer is given in Fig. 1*b*, *E* being the glass cell and *P* the opposing potentiometer. When the tapping key *K* is opened and closed, the unbalanced

FIG. 1*b*.



E.M.F. is alternately applied to the grid and short-circuited. The consequent increase or decrease in the anode current leads to a corresponding change in the potential drop across *R*, and therefore to a readjustment of the charge on the condenser *C*, the capacity of which may be 1—4 microfarads. The transient charging current flows through the galvanometer and a ballistic throw results. Balancing is carried out by the usual potentiometric method of adjusting the potentiometer dials so that there is no deflexion to left or right at make or break: the *E.M.F.* of the cell is then equal to the potentiometer reading. Since the galvanometer is isolated from the high-potential circuit and the anode current does not pass through its coils, a sensitive reflecting galvanometer may be used with safety, and no current-compensating adjustment is required. The galvanometer is unaffected by the anode current "creep" which is the cause of the zero drift in the earlier forms of valve electrometer, and provided the apparatus is shielded from external electromagnetic disturbances, the zero remains stable for an indefinite period.

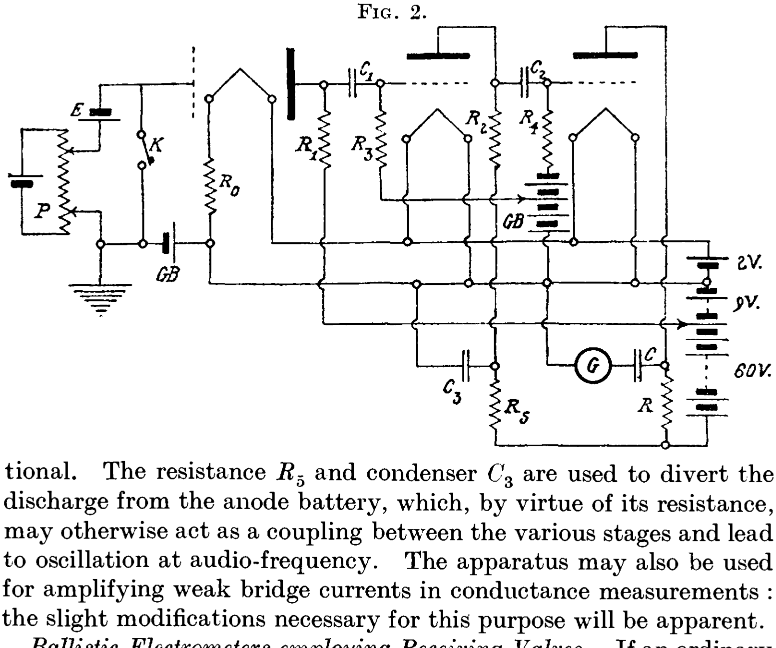
FIG. 1c.



As the operating filament voltage of the electrometer valve is in the neighbourhood of one volt, a fixed resistance R_0 is connected in series with the filament. The voltage drop across this is utilised to supplement the grid bias due to the small dry cell *GB*, thus providing a mean grid potential of $-$ 2·5 volts. The key and the connexion to the negative pole of the glass cell are the only parts of the apparatus which require exceptional care in insulation. The resistance *R* should be large in comparison with the combined series impedance of the galvanometer coils and the condenser *C*; a value of 10,000—20,000 ohms is satisfactory. *C* may be a paper-dielectric condenser having a capacity of 1—4 microfarads; good quality Mansbridge condensers of the type used in radio receiving sets are suitable.

As an alternative to the use of a reflecting galvanometer, it is both economical and convenient to employ a valve amplifier in conjunction with an inexpensive pointer galvanometer. Such an arrangement is shown in Fig. 2. Suitable values are R_1 and R_2, 0·1—0·5 megohm; R_3 and R_4, 2—5 megohms; R and R_5, 20,000 ohms; C_1 and C_2, 0·1 microfarad; C_3 and C, 2 microfarads. The first valve is the electrometer triode, the second a receiving valve of high amplification factor, and the third a "power" valve of high mutual conductance. The resistances and condensers may be of the inexpensive types used in receiving sets, the use of wire-wound resistances and mica-dielectric condensers being unnecessary. Transformer or choke coupling may, of course, be used, but these methods of coupling are costly and have no special advantage. Moreover, when inductances are present the impulse is not unidirec-

FIG. 2.



tional. The resistance R_5 and condenser C_3 are used to divert the discharge from the anode battery, which, by virtue of its resistance, may otherwise act as a coupling between the various stages and lead to oscillation at audio-frequency. The apparatus may also be used for amplifying weak bridge currents in conductance measurements: the slight modifications necessary for this purpose will be apparent.

Ballistic Electrometers employing Receiving Valves.—If an ordinary receiving valve is substituted for the electrometer triode valve in the arrangement of Fig. 1*b*, the potentiometer reading at balance is equal, not to E, but to $E \pm i_g R$, where i_g is the grid current and E and R are the $E.M.F.$ and resistance of the glass cell. Experimental calibration by means of buffer solutions is therefore necessary. Moreover, the method is no longer electrostatic, since the grid current of receiving valves amounts to 10^{-10} or 10^{-9} amp. Experimental calibration may be avoided by adopting the null ballistic method of Fig. 1*a*. The unbalanced *E.M.F.* charges the condenser C''. On depression of the Morse key, the condenser is discharged through the resistance R'' and the impulse is communicated, *via* the condenser C', to the grid. Balancing is carried out by adjusting the potentiometer dials so that there is no deflexion to left or right on depressing the key. At first sight it would appear to be permissible to omit the condenser C' and resistance R'', and to pass the discharge directly through R'. When this is done, however, the null point is reached, not when the unbalanced *E.M.F.* is zero, but when it is equal to the voltage drop across R' due to grid current.

Owing to the length of time necessary to charge the condenser. the process of balancing is somewhat tedious, and the method of Fig. 1*c* is preferable. C' is a condenser of about 0·2 microfarad capacity, which serves to prevent the flow of grid current through the high-resistance cell. Its insulation resistance must be high compared with the resistance R', and, as R' should have a value of at least 100 megohms, only high-grade mica-dielectric condensers are suitable. C' is virtually in series with the grid-filament capacity, and the combined capacity is exceedingly small. The method thus differs from that of Fig. 1*a*, and resembles that of Fig. 1*b*, in that, on depression of the key, the grid is charged instantly to practically the full value of the unbalanced *E.M.F.*, and the amount of energy withdrawn from the cell is vanishingly small. The resistance of the glass cell is in parallel with R'. Evidently, therefore, if the former is very high, the rate at which the charge on the grid leaks away through R' will be comparable with that at which it is supplied by the high-resistance cell. The author has not succeeded in obtaining satisfactory results with cells having a resistance greatly in excess of 20 megohms. The electrometer-valve method, on the other hand, is applicable to all determinations in which the resistance of the source of *E.M.F.* does not exceed 1000 megohms.

Other Ballistic Methods.—The opportunity is taken of correcting a misconception which appears to have arisen in regard to the ballistic system recently described by the writer (*J. Sci. Inst.*, 1930, **7**, 187). The system is especially suitable for use by laboratory assistants and others unacquainted with potentiometric technique, and provides a rapid and simple method of determining hydrogen-ion concentration by means of glass electrodes with an accuracy of $\pm$ 0·01 p_H unit. The apparatus consists essentially of a mica-dielectric condenser of large capacity and a charge-discharge key, and is used in conjunction with a ballistic galvanometer having a sensitivity of 3430 mm. per microcoulomb. The technique is extremely simple : the glass cell is allowed to charge the condenser for an accurately-timed period of 30 seconds, after which the condenser is discharged through the galvanometer coils. The p_H value corresponding to the observed deflexion is read directly from a calibration chart connecting the two. This chart, which is approximately linear over the p_H range 1—10, is prepared by standardising the apparatus by means of buffer solutions under precisely similar experimental conditions; for this purpose the universal buffer mixture recently described by Britton and Robinson (this vol., p. 1456) is convenient. The experimental calibration serves, not only to standardise the electrode, but also to compensate for asymmetry of the galvanometer field, irregularities in the graduation of the scale, etc. Electrostatic screening is unnecessary.

The method differs from earlier ballistic systems in that, by taking advantage of the fact that the charging rate follows a logarithmic decrement law, the time required to take a reading is shortened without loss of sensitivity. If E and R be respectively the $E.M.F.$ and resistance of the glass cell, and K the capacity of the condenser, the charge Q accumulated at time t is given by the well-known equation $Q = KE(1 - e^{-t/KR})$, and the average charging current for time t is $I = Q/t = KE(1 - e^{-t/KR})/t$. Evidently, the greater the value of K, the greater will be the charge accumulated in a given period of time. In the limit, if a condenser of sufficiently large capacity is used, so that t/KR is small enough for its square to be neglected, we have by the exponential theorem $I = KE(1 - 1 + t/KR)/t = E/R$; that is, the cell is virtually short-circuited during the time t, and a maximum charging current flows into the condenser. In practice, when high-conductivity cells—which are now commercially obtainable—are used, full-scale deflexion may be obtained by employing a condenser of 1—2 microfarads capacity with a charging period of 30 seconds; in fact, if an automatic time switch is used to ensure accurate timing, the period occupied by each reading may be reduced to 15 seconds. The statement of Greville and Maclagan (*loc. cit.*) that "although this method has proved to be sound, an almost prohibitive amount of time has to be spent over each reading" is apparently due to confusion with earlier methods. In comparative measurements of this kind, the fact that the $P.D.$ between the condenser plates at the moment of discharge is less than the $E.M.F.$ of the cell is of no consequence, since K, t, and R are constants and $Q \propto E$. The apparatus, which is manufactured by the Cambridge Instrument Company, has been employed in commercial practice, and has been found to be convenient and trustworthy.

Summary.

A null ballistic valve electrometer is described. The instrument is distinguished from earlier valve electrometers by its complete zero

stability and high sensitivity. The mode of operation differs in no respect from orthodox potentiometric technique, and involves no additional adjustments. The sensitivity, which may be increased to any desired degree by standard methods of audio-frequency amplification, is such that an *E.M.F.* of 0·01 millivolt operating through a resistance of 1000 megohms may be detected.

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