365. *The Automatic Control and Recording of Hydrogen-ion Concentration by Means of the Glass Electrode.*

By Charles Morton.

In many researches in which accurate p_H control is of importance, the use of automatic devices for regulating and recording the concentration of hydrogen ions is rendered difficult by the paucity of suitable indicating electrodes. Similar difficulties are encountered in technical applications of hydrogen-ion control, especially in the sugar, paper, leather, and photographic industries. Attempts have been made to use the oxygen or metal–metallic oxide electrodes for controlling purposes in large-scale operations: as, however, the electrode reactions are irreversible, the calibration is unstable and empirical, and the accuracy of a low order.

The instrument now described is designed for use with the glass electrode, and may be employed for recording (with an accuracy of $\pm$ 1 millivolt) potentials which are otherwise inaccessible. The regulator may be arranged to give warning, by means of electric bells or other devices, whenever a change of predetermined magnitude occurs; alternatively, limits may be set to the travel of the recording pen to provide for the automatic control of the conditions under investigation, and electric currents up to 10 amps. at 250 volts may be made or broken without the use of an intermediate relay. As no appreciable electrical load may be imposed upon the source of *E.M.F.*, thermionic valves are of necessity used for amplifying purposes: the design is such, however, that the calibration is permanent and independent of changes in the variable battery voltages and valve characteristics, and the instrument may be relied upon to function continuously for many months without attention. The recorder may be used also for controlling or recording photoelectric or other minute leakage currents, the current sensitivity being approximately 10^6 times that of the standard thread recorder.

General Principles.—The accuracy of a thermionic voltmeter or electrometer is determined ultimately by the stability of the zero. In general, the rate of zero displacement due to drift of anode current is such that, when a sensitive thread recorder is included in the anode circuit of a thermionic valve, the pointer traverses the scale completely in the course of some 12—18 hours. In a multi-stage *D.C.* amplifier the effect is cumulative, and cascade amplification does not lead to any real gain in available sensitivity. Clearly, in the design of a recording installation which is required to function over long periods without readjustment, provision must be made for the abolition of zero drift, and in a recent communication (J., 1931, 2977) the author suggested a means whereby this object may be achieved. In this arrangement, a ballistic galvanometer is connected, in series with a blocking condenser, across a resistance included in the anode circuit of the output valve, and the ballistic throws consequent upon the intermittent application of the source of *E.M.F.* to the grid of the input valve are noted or suitably recorded.

Fox and Groves (*J. Soc. Chem. Ind.*, 1932, **51**, 7T) have recently utilised this suggestion in the construction of a thermionic recording instrument. A deflexion method was used, the assumption being made that the throws are proportional in magnitude to the applied *E.M.F.* In considering the suitability of an instrument of this type for general use, it is important to differentiate between stability of zero and stability of calibration. The inclusion of a blocking condenser in series with the galvanometer prevents zero displacement due to drift of battery voltages; as, however, these slow changes in the battery potentials affect the sensitivity (and therefore the deflexion produced by a given applied potential) the calibration curve of a deflexion instrument varies from hour to hour. Appreciable error may result also from an imperfect adjustment of the interval between the initiation of the ballistic impulse and the operation of the recording mechanism. Moreover, an instrument of this type cannot be arranged to operate automatic regulating or alarm devices.*

For the object which Fox and Groves had in view, the errors due to these causes were of little or no consequence, since an empirical calibration scale—which was checked daily—was used, and a high order of accuracy was not required. It is clear, however, that for general purposes a deflexion instrument is unsuitable, and in the instrument now described these sources of error have been avoided by using a null ballistic method. In order to obtain adequate sensitivity, Fox and Groves used as the blocking condenser a capacity of 100 microfarads, and owing to the lengthy time constant of the resistance–condenser combination, were unable to record phenomena in which the conditions were changing somewhat rapidly. In the present design the speed of operation is independent of the electrical characteristics of the circuit, being governed solely by the mechanical inertia of the recording instrument. By the use of regeneration, the initial voltage impulse is built up to a value limited only by the available grid swing of the output valve, and high sensitivity is thus obtained. Resistance-capacity coupling is employed to link the various stages of the cascade amplifier; this makes it possible to use a common source of anode potential.

EXPERIMENTAL.

Circuit Arrangement and Mode of Operation.—The electrical circuit is given in Fig. 1. The recording installation consists of (*a*) a ballistic recording potentiometer and (*b*) a ballistic amplifier. The former is a modification of the standard recorder of the Cambridge Instrument Company, additions being made to the mechanism to adapt the instrument for ballistic operation.

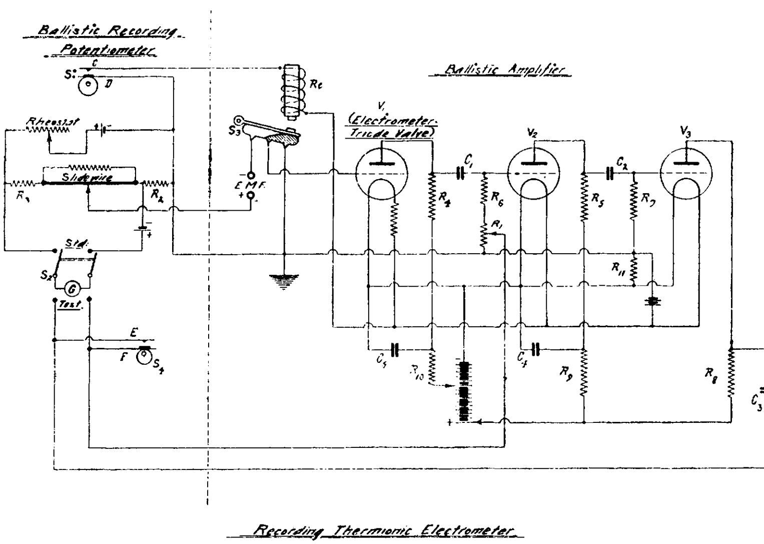
The circuit used in the standard recorder is similar to that employed in orthodox potentiometric practice. The pointer of the galvanometer (a double-pivoted instrument of the moving-coil type) has a cylindrical tip which swings between two horizontal rotatable discs mounted on a vertical spindle: this spindle carries also a slider moving over the horizontal semicircular slide wire. At intervals of approx. 10 secs. the cylindrical tip of the pointer is clamped between the two discs, and a cam-operated mechanism causes two scissor arms

* A deflexion recorder, subject to similar errors and limitations, has recently been described by Vickers, Sugden, and Bell (*J. Soc. Chem. Ind.*, 1932, **51**, 545).

to move the pointer (if deflected to right or left at the moment of clamping) back to the zero position, thus rotating the clamping discs by an amount corresponding with the galvanometer deflexion. The rotation of the discs is transmitted also to a recording pen which moves over a continuous paper chart driven by an electrically-wound clock. By suitable choice of values for the resistances R_2 and R_3 (Fig. 1), any desired voltage range may be covered.

In the modified recorder certain additions are made to this cycle of operations. Two additional cams (S_1 and S_4, Fig. 1) are mounted on the main driving shaft of the recorder : S_1 is arranged alternately to open and close the contacts C and D, and S_4 brings about a similar sequence of events in the contacts E and F. The galvanometer coil is specially wound for ballistic operation, and is undamped. The wiring of the recorder is rearranged, as shown in Fig. 1, in

FIG. 1.



such a manner that the galvanometer may be connected, by means of the standardising switch S_2, either (*a*) in series with a standard cell across the potential coils for the purpose of standardising the current through the slide wire, or (*b*) to the output terminals of the ballistic amplifier.

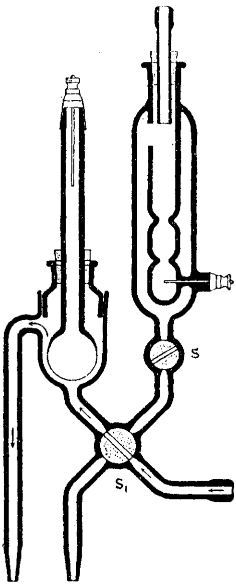
The sequence of events is as follows. The recording mechanism having been switched on, the potentiometer current is standardised in the usual manner and the switch thrown to the " test " position. At intervals of approx. 10 secs., the contacts C and D close, and the relay *Re* is energised. The armature carrying the mercury switch S_3 is attracted, and the source of *E.M.F.*, in series with the opposing potential derived from the potentiometer slide wire, charges the grid of the input valve. Amplified impulses are thus impressed on the grids of the amplifying valves V_2 and V_3. A transient charging current flows through the galvanometer, producing a ballistic throw to left or right. The interval between the closing of the contacts C and D and the operation of the recording mechanism is adjusted so that clamping occurs at the instant when the pointer has attained zero velocity. Immediately afterwards, the contacts E and F close, short-circuiting the galvanometer. As has been explained, by the movements of the scissor arms and clamping discs the pointer is moved back to the zero position and the contact on the slide wire is moved in such a direction as to restore balance to the circuit. When this automatic balancing adjustment is completed, the potential impressed by the potentiometer on the grid of the input valve is equal and opposite to that due to the source of *E.M.F.*, and this potential is simultaneously recorded graphically on the chart. In the meantime the contacts C and D open, and the grid of the detector valve is thus earthed in readiness for the reception of the succeeding impulse. The earthing of the grid causes a reverse or discharge current to flow along the galvanometer leads, but since the galvanometer is short-circuited throughout this period, the reverse surge is ineffective. At the conclusion of the automatic balancing and recording operation, the contacts E and F open, leaving the galvanometer undamped, and shortly afterwards the contacts C and D close. The sequence of events is then repeated, the period occupied by each cycle being approx. 10 secs. The ballistic sensitivity of the modified recorder is such that a discharge of 3·77 microcoulombs through the galvanometer coil causes the slider to move through a distance equal to 0·01 of the length of the slide wire. From the above description it is clear that slow changes in the battery voltages and valve characteristics are without effect on the calibration, and further, that the only effect of an inexact adjustment of the interval between the initiation of the ballistic impulse and the operation of the clamping mechanism is to reduce the sensitivity to some extent.

For simplicity, the mode of application of the regenerative principle has been omitted in the preceding description. Again referring to Fig. 1, it is clear that if the polarity of the unbalanced *E.M.F.* is such as to increase the negative grid bias of the detector valve, the grid of V_2 will receive a positive, and that of V_3 a negative, potential surge, whilst the output surge flowing through the galvanometer will be of positive sign. By means of the back-coupling resistance R_1, this potential surge is applied to the grid of V_2, where it reinforces the effect of the initial impulse: the effect being cumulative, the voltage impulse is built up to a value limited only by the available grid swing of the output valve. As the regenerative control is advanced, the sensitivity increases very greatly, until ultimately a point is reached at which rhythmic oscillations of the galvanometer pointer are observed. For normal operation, the regenerative coupling is reduced a little below this point of instability.

When it is desired to record or control photoelectric or other minute leakage currents, a high resistance, through which the current is led, is connected across the input terminals, and a record is obtained of the potentials developed across the resistance: assuming the latter to be of known value, the recorder may be calibrated directly in micro-microamperes.

Practical Details.—Oscillographs show that on the application of the unbalanced *E.M.F.* to the grid of the first valve, the galvanometer current rises sharply, passes through a well-defined maximum, and again falls to zero: the initial unidirectional impulse is followed by a few damped oscillations of small amplitude which are apparently without effect on the galvanometer. The earthing of the grid during the second stage in the cycle of operations produces an impulse of similar wave-form but of opposite sign: this is rendered ineffective as already explained. The wave-form and duration of the ballistic impulse are considerably affected both by the electrical constants of the circuit and by the regenerative effect. Reducing the time constants of the various resistance-capacity combinations has the effect of shortening the period of the discharge, but the sensitivity is also reduced somewhat. Increasing the tightness of the reaction coupling greatly increases the peak value of the impulse; at the same time, the oscillatory character of the discharge becomes more and more marked, until ultimately a point of instability is reached at which continuous oscillations are generated. The mechanical inertia of the recorder being such as to necessitate comparatively slow-speed operation, no trouble due to "grid choking" is experienced, and the time constants may be made large in order to increase the sensitivity; in the experimental apparatus used by the author, the time constant for the first stage (which determines that of the amplifier as a whole) is 0·5 sec.

FIG. 2.



Complete "decoupling" is necessary to prevent self-oscillation due to the impedance of the common source of anode potential. Suitable values for the various resistances and condensers are as follows: $R_{4,5}$, 100,000 ohms; R_6, 0·5$M\Omega$; R_2, 10,000 ohms (arranged as a potential divider with sliding contact); R_7, 2$M\Omega$; $R_{8,9,10}$, 20,000—40,000 ohms; $C_{1,2}$, 1 microfarad; $C_{3,4,5}$, 2—4 microfarads. $R_{4,5,8,9,10}$ should be wire-wound in a non-inductive manner. Mica-dielectric condensers should be used for $C_{1,2}$.

When the instrument is to be used for recording potentials upon which no electrical load may be imposed, the input valve should be of the "electrometer triode" type with a grid-filament insulation resistance of 10^{15} ohms and average grid current of about 10^{-15} amp. The second valve should possess a high amplification factor, and for the final stage a "power" or "super-power" valve of high mutual conductance is selected. Filament, grid, and anode potentials are adjusted in accordance with the instructions of the manufacturer.* The contact of the Hg switch should be highly insulated, and the volume of Hg should be so adjusted that, during the transit of the switch, the second path is made before the first is broken.

The Recording Cell.—A simple form of recording cell, suitable for use with continuously-flowing solutions, is illustrated in Fig. 2. The glass electrode is of the type previously described by the author (*J. Sci. Inst.*, 1930, **7**, 187). The bulb and tube are filled with an acid solution saturated with quinhydrone, and a terminal carrying a Pt wire which dips into the solution is fitted over the upper end of the tube. This type of half-cell has several advantages over the more usual form in which a calomel electrode is used to establish electrical connexion with the reference solution contained within the bulb. The troublesome liquid junction is eliminated, and the potential is independent of

* In the installation used by the writer, V_1 is an electrometer valve supplied by the General Electric Co., Ltd., and V_2 and V_3 are Mazda P220 valves. Grid bias for V_1, V_2, and V_3 is supplied by the voltage drop across R_{11}.

the [H˙] of the reference solution, thus permitting of a wide choice of suitable buffer solutions, the p_H values of which need not be known. The quinhydrone reference half-cell is more readily reproduced than those previously used, and the problem of providing adequate insulation is simplified. The terminal borne at the upper end of the high-resistance stem is highly insulated : a calomel electrode, on the other hand, is bulky and electrically leaky, and requires an independent highly-insulated support.

The course of the flowing solution is indicated in Fig. 2 by means of arrows. The complete cell is of the type

$$\mathrm{Pt}\left|\begin{matrix}\text{Reference solution}\\ \text{Quinhydrone}\end{matrix}\right|\text{Glass}\left|\begin{matrix}\text{Test solution}\\ (p_{H_x})\end{matrix}\right|\begin{matrix}\text{Satd. KCl}\\ \text{HgCl}\end{matrix}\Big|\,\mathrm{Hg}$$

the *E.M.F.* (disregarding the asymmetry potential) being identical with that of the cell

$$\mathrm{Pt}\left|\begin{matrix}\text{Test solution } (p_{H_x})\\ \text{Quinhydrone}\end{matrix}\right|\begin{matrix}\text{Satd. KCl}\\ \text{HgCl}\end{matrix}\Big|\,\mathrm{Hg}$$

viz., $0{\cdot}454 - 0{\cdot}058\, p_{H_x}$ at 18°. Normally the stopcock S is closed, the additional resistance thus introduced into the system being small compared with that due to the glass membrane. On opening S and turning S_1 through 90°, contaminated KCl aq. is discharged from the calomel electrode and connecting tube. The lead connecting the glass-electrode terminal with the contact of the Hg switch should be air-supported or otherwise highly insulated.

Summary.

A potentiometric regulator for automatic p_H recording or control in conjunction with the glass electrode is described. Powerful oxidising and reducing agents, suspended precipitates or colloidally-dispersed substances, and electrode "poisons" in general are without effect on the accuracy, which is of the order of $\pm$ 1 millivolt. Electric currents up to 10 amps. at 250 volts—sufficient for the operation of electromagnetic controlling valves in large-scale operations—may be made or broken without the use of an intermediate relay. The calibration is permanent and unaffected by changes in the battery voltages and valve characteristics. Photoelectric or other minute direct currents may also be recorded and controlled, the current sensitivity being approximately 10^6 times that of the standard thread recorder.

A description is given of a recording cell suitable for use with the glass electrode in continuously-flowing solutions.

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