CXCV.—*The Application of a New Type of Triode Valve to the Determination of Hydrogen-ion Concentration with Glass Electrodes.*

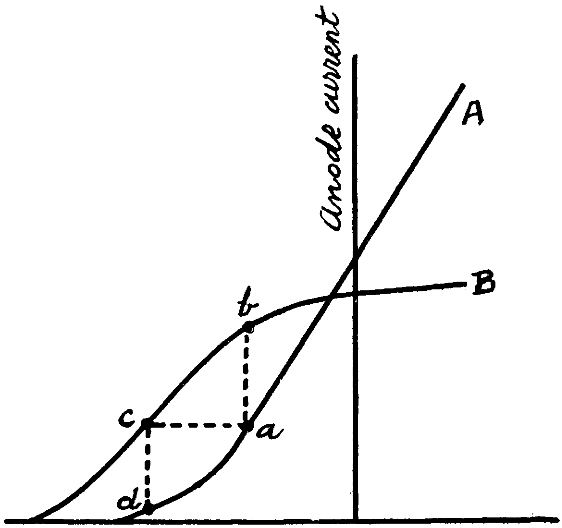
By Geoffrey B. Harrison.

Owing to the realisation of the increasing importance of p_H measurement and control during certain works' processes, there has arisen a demand for a glass electrode apparatus suitable for routine testing. The apparatus now described combines accuracy of the degree requisite for scientific research (*i.e.*, of less than 0·02 p_H unit) with ease of operation, strength, and trustworthiness.

The existing methods of measuring the *E.M.F.* across a glass membrane suffer from certain disadvantages. Since the resistance of the membrane may be from 10^6 to 10^8 ohms, the measurement of the *E.M.F.* requires the use of some form of high-resistance electrometer which is capable of detecting a potential difference of one millivolt. The instrument generally used is the Lindemann electrometer; this is certainly very efficient, but it has the disadvantage that it requires careful handling if the sensitivity is made sufficiently high to detect changes of one millivolt. Moreover, a microscope must be used in conjunction with it, and this is undesirable in routine work.

Several workers, notably Stadie (*J. Biol. Chem.*, 1929, **83**, 477), have successfully employed the ordinary triode valve; the important factor in the use of such valves for *E.M.F.* measurement is the grid

FIG. 1.



Grid potential.

characteristic, *i.e.*, the relation between grid potential and anode current with zero resistance in the grid circuit (see Fig. 1, Curve A). If a high resistance of the order of 10^8 ohms is placed in this circuit, a considerable change occurs in the characteristic, as shown in Fig. 1, Curve B, owing to the fact that the grid filament resistance of an ordinary valve is comparable with 10^8 ohms. Stadie's procedure is as follows. He selects some point, *a*, corresponding with a convenient anode current with the electrode out of circuit, *i.e.*, with the grid short-circuited to the filament through the grid-bias battery. The electrode and the potentiometer (reading zero) are then inserted in the grid circuit by opening the short-circuiting key. If the p_H inside and outside the glass bulb of the electrode is the same, there will be no *E.M.F.* across the bulb, but when the electrode is put in circuit, its resistance alone causes a change from point *a* to point *b* (Fig. 1), giving an increase of anode current corresponding with *a b*. By means of the potentiometer, he now puts on an additional potential corresponding with *a c*, to bring the anode current back to its original value. Let this potential difference be denoted by *V*; then, if the p_H to be measured gives an *E.M.F.* across the particular bulb equal to *e* millivolts, the potentiometer reading required to bring the anode current back to its value at *a* will be $V + e$. Thus, from every reading, this standard value *V* must be subtracted. Also, 20 minutes must be allowed for the valves to reach a steady state before this value can be obtained.

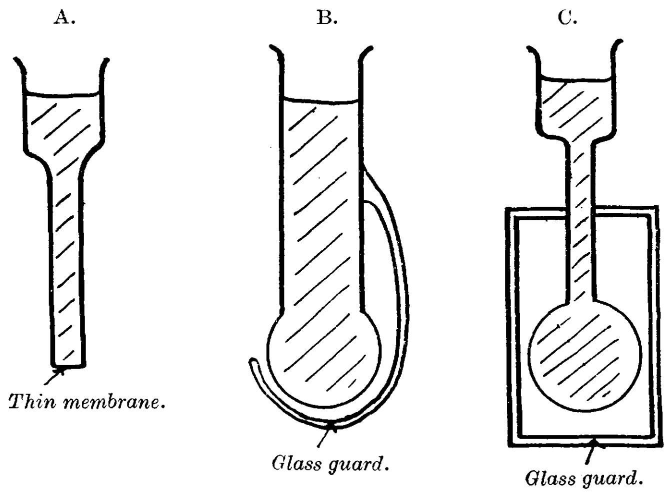
Stadie uses very low values of filament current and anode voltage, and balances two matched valves against each other in the form of a valve bridge. He claims for this method that it gives a high order of constancy of anode current and of potential difference *V*, but the obvious disadvantage of this apparatus is that, in order to find the value of *V*, it has to be standardised against a known p_H every time it is used; further, certain parts of it require very careful insulation.

Some experiments done in this laboratory on the same lines failed from an entirely different cause. Although the *E.M.F.* is set up across the glass membrane when a p_H difference exists across it, very little current can be drawn from it; if, therefore, the resistance of the grid-filament circuit of the valve is of the same order as that of the glass electrode, the charge producing the *E.M.F.* across the glass membrane would be expected to leak away nearly as fast as it is produced, with the result that a certain time would elapse before equilibrium is established, and very probably when this had taken place, the value of the *E.M.F.* obtained would not be its true value. This is actually what took place: as much as 10 minutes were required to reach equilibrium in some cases, and even then the results were not trustworthy.

It was obvious that if the resistances of the electrodes could be reduced sufficiently, this difficulty might be overcome. The bulbs actually used for the experiments had resistances of 4×10^8 ohms or more, which was very high compared with those of other workers, although Stadie claims to be able to work with electrodes of 6×10^8 ohms resistance. An attempt to reduce this resistance by making the membrane thinner was based on the method of McInnes and Dole [*Ind. Eng. Chem.* (*Anal.*), 1929, **1**, 57]: a very thin glass bulb is blown with a special glass so that interference colours can be seen, and a glass tube about 4 mm. in diameter is heated at the end to a low red heat and placed against the thin bulb; the thin glass fuses round the sides and should form a water-tight joint (Fig. 2, A), and this electrode is then used in the usual way. Great difficulty was experienced at first in making the membranes hold liquid, and many of those that were satisfactory in this respect were found to have a very small hole, which gave direct connexion between the inside and outside, making them useless : this was only detectable by measuring their resistances. Even when, after considerable practice, this type of electrode could be made, a slight jar would break the membrane, so the design was unsuitable for works' use.

At this stage a new glass was obtained from Messrs. Dixon, of Devonshire St., W.C.1. It is made according to the formula of Mr. C. Morton, of Chelsea Polytechnic, who has kindly allowed the author to state that the mixture used for the fusion is : Silica, 60% ;

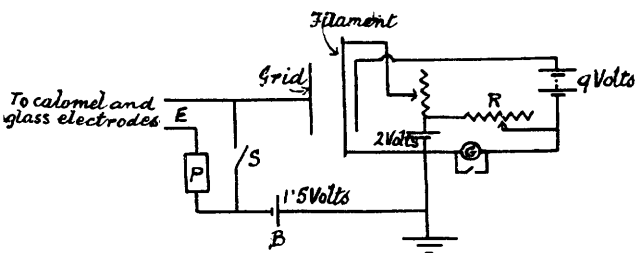
FIG. 2.



sodium carbonate, 30% ; calcium carbonate, 10%. With this glass, instead of the bulbs being blown on a large-diameter tube, as shown in Fig. 2, B, they could be made of narrow tubing, as in Fig. 2, C, and so were thin but of convenient dimensions. The combined effect of the new glass and the thinner bulbs was to reduce the resistances from 400 to less than 100 megohms, but this reduction was still quite insufficient for the purpose if ordinary valves were used. By the substitution of a special design of triode valve, however, an apparatus has been constructed which is ready for use 3 minutes after being turned on, needs no standardisation, and requires careful insulation of one terminal only.

The valve employed throughout this work, *viz.*, the Electrometer Triode, is supplied by Philips Lamps, Ltd. : others of similar design are on the market. The chief characteristic of this valve, which makes it so suitable for *E.M.F.* measurements across high resistances, is that the grid current, when the grid potential is — 2 volts, is less than 10^{-14} amp. The result of this is that, whatever the resistance in the grid circuit, there is no change in anode current due to the introduction of resistance alone, as there is in an ordinary valve (see Fig. 1, A and B). This extremely low value of grid current is brought about by the disposition of the electrodes: unlike that in the ordinary valve, the grid is *not* situated between the filament and the plate, hence the electrons passing from the filament to the plate and constituting the anode current do not pass through, or indeed anywhere near, the grid. The characteristic curve of this valve when the grid is negative is similar in shape to that of an ordinary triode, but has a slope of only about 0·03 milliamp. per volt. This slope is, of course, considerably less than that of an ordinary triode valve, but is sufficient for the purpose. The other features of this valve are the

FIG. 3.



low values of anode voltage and filament current required, which are respectively 4—9 volts and 0·7 amp. from a 2-volt accumulator.

The valve is used in the circuit shown in Fig. 3. The electrode *E* and potentiometer *P* are in the grid circuit together with the 1·5-volt grid-bias battery *B*. The electrode and potentiometer can be short-circuited by means of the switch *S*. The anode current (of the order of 200 microamps.) passes through the galvanometer together with the compensating current drawn from the filament accumulator, the variable resistance *R* being used for adjustment. The galvanometer is provided with a short-circuiting key, which must be closed when the instrument is turned on; if this is not done, the compensating current, which starts to flow instantaneously, is not at first balanced by the anode current, which gradually increases as the filament becomes heated, so the galvanometer may be damaged. The valve filament has an exceptionally large heat capacity and requires over 10 seconds to reach its final temperature.

The working procedure is as follows: The electrode, having been calibrated, is placed in the liquid of which the p_H is required. The switch S is closed, and the galvanometer needle brought to a convenient position on the scale by means of the variable rheostat in the compensating current circuit. The position of the needle is accurately noted, and the switch S opened. The *E.M.F.* across the glass membrane due to the p_H difference between the inside and outside of the bulb causes a change in anode current, with consequent movement of the needle. This electrode *E.M.F.* is counteracted by means of the potentiometer P until the needle resumes its original position. The switch S may be closed and opened several times to ensure that balance has been obtained. The reading of P then gives the *E.M.F.* across the membrane, and comparison with the calibration graph gives the p_H of the liquid.

The essential feature of this design is that when the switch S is opened *there is no change of anode current due to any change of characteristic curve brought about by the high resistance of the electrode*; that is to say, if the potentiometer P were reading zero and the electrode were giving no *E.M.F.* (*i.e.*, the same p_H on each side of the glass membrane), then on opening and closing the switch S, no change of anode current would occur. This is because there is no change of characteristic, as there would be in an ordinary valve (see Fig. 1), the reason being that the grid current is negligible compared with the current which can pass through the electrode.

The galvanometer is a matter of choice, but a double-pivoted pointer instrument, supplied by Messrs. Turner of High Wycombe, and having an angular deflexion of 1·1° per microamp., has proved satisfactory: its sensitivity is only just sufficient, but it has the advantage of being an ideal instrument for works' use, since it is almost dead-beat in action; it can be built in the instrument itself and requires no levelling.

In the experimental model of this apparatus, constructed in these laboratories, the amplifier, including the high-tension battery (a 9-volt grid-bias battery), is made up in a cabinet, the galvanometer being mounted in the lid. Three pairs of terminals only are required, *viz.*, those for the potentiometer, filament accumulator, and calomel electrodes. Ebonite is a sufficiently good insulator for all parts of the circuit, except that a collar of amberoid is used for mounting the terminal connecting the grid of the valve to the calomel half-element of the glass electrode. The switch S (Fig. 3) consists of an amalgamated copper wire dipping into a mercury cup, which is entirely supported by a stout wire fixed to the insulated terminal.

A series of readings with this apparatus and a Cambridge potentiometer will show a maximum variation of 1 millivolt (*i.e.*, less than 0·02 p_H unit), so that a single reading may be regarded as accurate within this limit; it is doubtful whether the accuracy is increased by taking the mean of a series of readings, for the small errors in individual readings are probably due to changes in the *E.M.F.* set up across the glass membrane rather than to errors in the measurement.

Experience has already shown that the apparatus can be worked very successfully by those who are quite unskilled in this kind of measurement, and that they can quickly read to an accuracy of 0·02 unit over a p_H range of 1—12.

The author wishes to express his thanks to Dr. T. Slater Price, F.R.S., Director of Research of the British Photographic Research Association, and to his colleagues, Dr. F. C. Toy and Dr. S. O. Rawling, for their helpful criticism and advice throughout this work.

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30 Russell Square, W.C. 1. [*Received, May* 13*th*, 1930.]