64. *The Effect of Electrical Leakage on the Electromotive Behaviour of the Glass Electrode.*

By CHARLES MORTON.

MACINNES and DOLE (*J. Amer. Chem. Soc.*, 1930, **52**, 29) have given formulæ for preparing glass which is stated to yield electrodes of uniformly high efficiency, low *D.C.* resistance, and low and constant asymmetry potentials. Other workers, however, have not in all cases verified their claims; in particular, as Ingham and Morrison (J., 1933, 1200) have pointed out, the calibration graphs of Britton and Robinson (*Trans. Faraday Soc.*, 1932, **28**, 531), although obtained with electrodes of the composition recommended by MacInnes and Dole, appear to indicate considerable changes in efficiency. Kahler and de Eds (*J. Amer. Chem. Soc.*, 1931, **53**, 2998) have drawn attention to the fact that the types of glass which yield satisfactory results are almost invariably those of high electrical conductivity, and that for electrodes blown from glass of a given composition those of low *D.C.* resistance, *i.e.*, the thinnest membranes, always possess the highest efficiency and the lowest and most constant asymmetry potentials. Using thick-walled electrodes of high resistance, they found that the deviations from the theoretical *E.M.F.*-p_H relationship disappeared when exposed surfaces were coated with paraffin or other non-hygroscopic insulating media; on the other hand, when the coating consisted of an acid electrolytic solution the deviations increased.

It is well known that electrical leaks which shunt the glass cell seriously affect the measurements by producing polarisation (MacInnes and Belcher, *ibid.*, p. 3315); it is perhaps not generally appreciated, however, that even in the absence of significant polarisation, electrical leakage inevitably leads to distortion of the *E.M.F.*-p_H graph and to the creation of apparent asymmetry potentials of appreciable magnitude. The observed or experimentally determined *E.M.F.* of the glass electrode is not its true potential *E*, but a

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* Analyses by Warburg of spirographis hæmin agree well with those of oxorhodoporphyrin, but the compounds have different spectra.

lower potential e, the value of which depends on the relative magnitudes of the resistance R of the membrane and the " parallel leakage resistance " r of the system. The last term includes the input *D.C.* resistance of the potential-measuring instrument, the surface leakage of the electrode from the outer to the inner surface, and also any other stray leakages, *e.g.*, those over the surfaces of supporting clamps, which are electrically in parallel with R. The relationship between the true and observed *E.M.F.*'s is $E/e = (R + r)/r$ and the percentage error in the determination is $100(E - e)/E = 100R/(R + r)$. To obtain an accuracy of 0·1% we must have $r > 10^3R$, so for an electrode of average resistance (about 100 megohms) the parallel leakage resistance should be at least 10^{11} ohms. The slope of the experimental calibration graph, and the apparent efficiency, are $0{\cdot}0001983Tr/(R + r)$ and $100r/(R + r)$ respectively for an electrode having a true efficiency of 100%, from which it appears that if $R = r$ (to cite an extreme case) the slope of the curve will be halved, *i.e.*, the electrode will display an apparent efficiency of 50%. The experimentally determined asymmetry potential $E - e = RE/(R + r)$ is similarly affected by the parallel leakage resistance of the system. Any procedure, such as treatment of exposed surfaces with electrolytic solutions (as in the experiments of Kahler and de Eds), which tends to reduce the resistance of the leakage paths, increases these irregularities; on the other hand, if the insulation of the system be sufficiently improved by the application of non-hygroscopic and non-conducting media, the deviations disappear.

Under certain conditions the instrument used for measuring the potential may itself be responsible for distortion of the *E.M.F.*–p_H graph. Occasionally the input impedance of the potential-measuring device (*e.g.*, the insulation resistance of the condenser used in a ballistic system, or the grid-filament impedance of a valve potentiometer in which valves of the ordinary type are used) may be as low as 10,000 megohms; the error in the determination, for an electrode having a resistance of 100 megohms, is then of the order of 1%, and the slope factor is altered by a corresponding amount. The calibration graphs of Britton and Robinson (*loc. cit.*), which show diurnal rotation around the mid-point, undoubtedly owe their peculiar form to the system of measurement. The method (*J. Sci. Instr.*, 1930, **7**, 187) is a modified ballistic system in which, to obtain high sensitivity, advantage is taken of the fact that the charge of a condenser follows a logarithmic decrement law. By means of the exponential theorem it may be shown (J., 1932, 2469) that if a condenser of sufficiently large capacity be used, the average charging current for time t is $i = e/R$, and the accumulated charge is thus $Q = et/R = rt(K \pm 0{\cdot}0001983Tp_H)/R(R + r)$, where K is a constant. Hence the slope of the experimental calibration graphs of Britton and Robinson is

$$\partial d/\partial p_H = 0{\cdot}0001983T \, . \, ts/(R^2/r + 1),$$

where d is the observed deflexion and s the ballistic sensitivity of the galvanometer. As the denominator of this expression contains a term in R^2, it is clear that small daily variations in the resistance of the membrane, due to spontaneous changes or temperature fluctuations, will lead to considerable changes in slope. Moreover, the experimental graphs will tend to oscillate around the mid-point, since at the latter point the *E.M.F.* of the type of cell used by Britton and Robinson passes through zero and is unaffected by the changing values of R. By inducing artificial changes in R the writer has obtained a family of curves identical in form with those of Britton and Robinson. Although this modified ballistic system provides a convenient and accurate means of translating glass-electrode potentials into p_H values, very careful temperature control is necessary, and in this respect the system is inferior to a well-designed thermionic electrometer.

The consequences of the simple electrical theory discussed above have been confirmed by experiment. It is not, of course, suggested that all irregularities in the electromotive behaviour of the glass electrode may be accounted for in this way, or that the composition of the glass is unimportant except in so far as it affects the resistance of the membrane. It is well known that mere traces of certain metallic impurities may exert a significant influence on the electrode potential and conductivity, and the unsatisfactory results occasionally obtained with glass of the composition recommended by MacInnes and Dole may in some instances be due to accidental contamination during manufacture. In the experience of the writer the high-conductivity glass now commercially obtainable is not always above suspicion in this respect, since electrodes blown from different samples of the commercial material differ appreciably in their electromotive behaviour.

EXPERIMENTAL.

The cell used was of the type

$$\text{Pt}\ \left|\ \begin{array}{c}\text{Reference solution}\\ \text{Quinhydrone}\end{array}\ \right|\ \text{Glass}\ \left|\ \begin{array}{c}\text{Test}\\ \text{solution}\end{array}\ \right|\ \begin{array}{c}\text{Saturated}\\ \text{KCl–HgCl}\end{array}\ \Big|\ \text{Hg}$$

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

$$\text{Pt}\ \left|\ \begin{array}{c}\text{Test solution}\\ \text{Quinhydrone}\end{array}\ \right|\ \begin{array}{c}\text{Saturated}\\ \text{KCl–HgCl}\end{array}\ \Big|\ \text{Hg.}$$

The electrode, of the bulb type, was blown from glass of the composition recommended by MacInnes and Dole. In making this glass the author prefers to remove the melt from the furnace before all carbon dioxide bubbles have been expelled : when bulb electrodes are blown from glass containing minute bubbles, the latter expand into circular or oval areas which appear as iridescent patches (showing interference colours) in the relatively thick wall of the bulb. The *D.C.* resistance is then frequently as low as 5 megohms, and the electrode invariably has an efficiency of over 99% ; however, for the present purpose electrodes of higher resistance were deliberately selected. The stem of the electrode was approximately 0·5 m. long (ensuring a high ratio r/R) and was supported, at its base only, by an orca-insulated clamp.

To investigate the cause of the anomalous results of Britton and Robinson, a family of curves was obtained, at temperatures ranging from 18° to 25°, by the modified ballistic method used by these authors. The capacity of the condenser was 1·5 microfarads and the charging period 15 seconds. Two solutions were used for purposes of calibration, *viz.*, $M/20$-solutions of (*a*) potassium hydrogen phthalate, and (*b*) borax.* At the same time direct measurements of the *E.M.F.* of the system were made by means of a thermionic electrometer (*J. Sci. Instr.*, 1932, **9**, 289). The data obtained by the two methods are recorded in Table I.

TABLE I.

Temp.	18°	19°	20°	22°	25°
Deflexion, mm. : Solution (*a*)	62	68	72	81	114
,, ,, ,, (*b*)	−23	−25	−27	−31	−44
E.M.F., mV. : Solution (*a*)	219	218	216	212	208
,, ,, ,, (*b*)	−83	−85	−88	−92	−97
$\partial d/\partial p_H$	16·1	17·7	18·8	21·2	30·0
$\partial E/\partial p_H$	57·3	57·5	57·8	58·0	58·4
Theoretical slope factor (mV/p_H)	57·7	57·9	58·1	58·5	59·1

The ballistic calibration graphs, like those of Britton and Robinson, exhibit rotation around the mid-point, the angle of rotation increasing rapidly with rise of temperature. From Table I it will be seen that, whereas the slope $\partial d/\partial p_H$ of the calibration graphs obtained by the ballistic method increases by 86% for a temperature rise of 7°, the corresponding change in the slope of the true *E.M.F.*–p_H graph is only 2%, and is, moreover, in good agreement with the theoretical value for the hydrogen electrode. It is clear that no reliable conclusions can be drawn as to the constancy or otherwise of the electrode efficiency from the results of ballistic measurements unless the temperature control be accurate to about ± 0·01°.

The diminished slopes of the graphs obtained at the lower temperatures by the ballistic method are due to the decreasing conductivity of the membrane, which acts as a limiting factor to the charge received by the condenser. The resistance (determined by the method of MacInnes and Dole, *loc. cit.*) of the electrode used in these experiments decreased from 166 megohms at 18° to 0·26 megohm at 95°. The resistance–temperature curve (see fig.) attains its maximum slope at temperatures in the neighbourhood of 18°, and in this approximately linear region the resistance diminishes by about 6% of its value at 18° for 1° rise in temperature. At lower temperatures the conductance approaches zero; for this reason the ballistic method has been found to be useless in the investigation of problems connected with refrigeration. It

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* These solutions have the advantage over other standards that the ratio of acid to base is fixed by the composition of the crystals and not by adjustment of the ratio of the components. Walbum (*Biochem. Z.*, 1920, **107**, 219) has determined the p_H values for $M/20$-borax solution over the temperature range 10—70°; that for the phthalate solution was assumed to be constant over the range 18—25°.

is essential in work of this nature to use a quadrant or valve electrometer as null-point indicator, and exceptional precautions must be taken to guard against leakage and electrostatic disturbances. On the other hand, in metallurgical and other researches at elevated temperatures it has been found possible to simplify the technique of glass-electrode measurements by substituting a reflecting galvanometer of moderate current sensitivity for the thermionic or quadrant electrometer.

Finally, a few experiments were carried out to determine the influence of leakage on the apparent efficiency of the glass electrode. Solutions (*a*) and (*b*) (above) were used, and the potential of the cell—the resistance of which was 86 megohms at 18°—was measured by means of a thermionic electrometer having an input impedance of the order of 10^{14} ohms. The effect of leakage on the slope of the *E.M.F.*-p_H graph is illustrated by the data of Table II, which were obtained by shunting the electrode system with resistances varying from 164 to 7400 megohms. These resistances (the approximate values of which were determined by connecting each in turn in series with a battery of known *E.M.F.* and a galvanometer of known current sensitivity) were glass electrodes of zero *E.M.F.* In general, the potential of the shunted electrode tended to decrease slowly with time, apparently owing to polarisation; the potentials given in the table are those which were established immediately after the shunt had been switched across the glass cell. In measuring the resistances of the shunts, the switch (the contacts of which were insulated by substantial pillars of orca) was left in circuit, and the recorded values thus include the leakage across the switch contacts. The value of 99% obtained for the apparent efficiency of the unshunted electrode is probably a close approximation to the true efficiency, since the insulation of the system was of a high order. Shunt resistances of 7400 and 164 megohms reduced the apparent efficiency to 98% and 64·8% respectively. Calculated and experimental values for the apparent efficiency, $100r/(R + r)$ and $100\partial e/57{\cdot}7\partial p_H$ respectively, are in fair agreement.

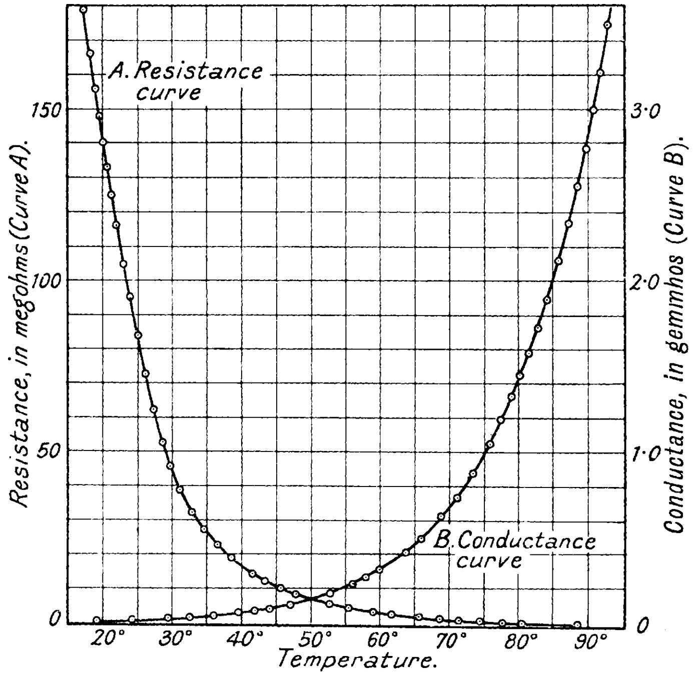

TABLE II.

Shunt resistance, r ($M\Omega$)	164	287	435	737	1580	7400	∞
E.M.F., Solution (*a*)	145	171	185	203	210	221	223
,, ,, (*b*)	−52	−61	−66	−69	−73	−77	−78
Apparent slope, $\partial e/\partial p_H$	37·4	44·1	47·6	51·6	53·7	56·5	57·1
,, efficiency (exptl.), %	64·8	76·3	82·5	89·4	93·1	98·0	99
,, ,, (calc.), %	65·6	76·9	83·5	89·3	94·8	98·9	100

It is clear from these experiments that, in fundamental investigations of the properties of the glass electrode, the only systems of measurement which can be relied upon to give true indications of the electromotive behaviour are those in which either the quadrant electrometer or the electrometer triode valve is used: other instruments distort the *E.M.F.*–p_H graph to a greater or less extent depending on their input impedances, but may be made to yield satisfactory results in routine work provided that the conditions obtaining during calibration be maintained constant by suitable control of temperature and humidity.

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