Apparatus for Rapid Electrometric Titration.

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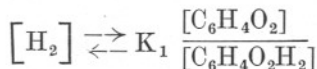
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I. INTRODUCTION.

THIS apparatus was assembled at Millport for the electrometric titration of solutions which, being highly coloured, cannot well be titrated with an indicator. It may be used also for highly dilute solutions, unless they are so slightly buffered that their pH value is appreciably changed by the addition of a small quantity of quinhydrone. Measurement of hydrogen-ion concentrations at the quinhydrone electrode has also been attempted with the apparatus. The apparatus is suitable for use at sea.

II. OUTLINE OF A TITRATION METHOD.

Biilmann (**1**) has described a method of measuring hydrogen-ion concentrations at what he terms the quinhydrone electrode. Quinhydrone may be considered as an equimolecular compound of quinone, $C_6H_4O_2$, and hydroquinone, $C_6H_4O_2H_2$. In acid aqueous solution there is an equilibrium which may be represented by :—

$$\left[H_2\right] \underset{\leftarrow}{\overset{\rightarrow}{=}} K_1 \frac{[C_6H_4O_2]}{[C_6H_4O_2H_2]}$$

(It is necessary to specify that the solution shall be acid, because in solutions with a pH value of 8·0 or more, weak acids are formed by oxidation.)

The square brackets denote molar concentrations ; and in this case of

an equimolecular compound, the concentrations of quinone and of hydro-
quinone must always be equal, so that there is, in the solution, a concentra-
tion of free hydrogen, equal to the constant, K_1. The half-cell formed by
the immersion of a gold or platinum electrode in the solution, alters its
potential with the hydrogen-ion concentration exactly as does the
" hydrogen electrode " half-cell, and may therefore be used for the

TABLE I.

Alkali added. (c.c.)	E.M.F. (m.v.)	Increment of E.M.F.	dE/dx.
0	−64		
		5	0·5
10·0	−59		
		7	1·4
15·0	−52		
		14	3·5
19·0	−38		
		19	6·3
22·0	−19		
		11	11
23·0	− 8		
		19	19
24·0	+11		
		16	40
24·4	+27		
		10	50
24·6	+37		
		6	60
24·7	+43		
		11	110
24·8	+54		
		15	150
24·9	+69		
		45	450
25·0	+114		
		134	**1340**
25·1	+248		
		62	620
25·2	+310		
		32	320
25·3	+342		
		14	140
25·4	+356		

measurement of hydrogen-ion concentrations. It is connected to a standard half-cell (usually a calomel half-cell) by an electrically conducting " bridge " of potassium chloride and agar-agar, and the E.M.F. of the complete cell is measured with a potentiometer.

Now the rapid change in hydrogen-ion concentration which occurs at the " end-point " of a titration may be detected by this method as a
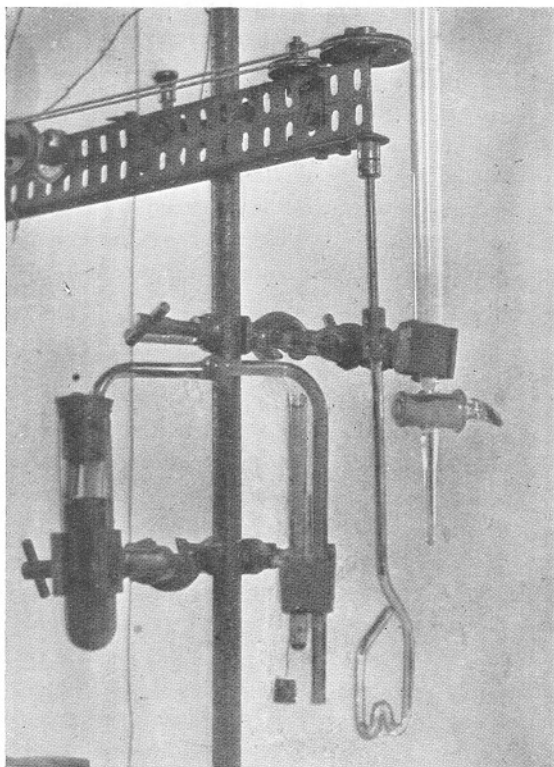

Fig. 1.—The electrodes, etc., the mechanical stirrer and the burette. The titration beaker, into which the stirrer and the exposed electrode dip, is placed in position and supported by a wooden block.

rapid change in potential. And that point in the titration where this change in potential is most rapid, is the end-point. This, the Potentiometric method of titration, has been discussed in detail by Kolthoff and Furman (2), and a number of practical applications of it are excellently summarised by Callan and Horrobin (3).

The most usual method is to measure the E.M.F. by potentiometer and galvanometer, at intervals as the titration proceeds, and to express increment of E.M.F. as millivolts per c.c. of alkali added. This factor,

termed " dE/dx " by Callan and Horrobin, is greatest at the end-point. The increments of alkali are, of course, made progressively smaller as the end-point is approached. Table I represents the titration of 25 c.c. of N/10 HCl with N/10 NaOH.

The end-point is read from the table as 25·05 c.c.

Greater accuracy may be attained if the increments of alkali near the end-point are made still smaller. Indeed, the accuracy with which the burette can be read is probably the limiting factor. The end-point may therefore be read direct from the figures ; the plotting of a curve is superfluous.

The performance of a titration in this manner is a lengthy operation, but in practice it is not necessary to take more than five accurate readings of the potentiometer, as is shown later. Moreover, in the apparatus described below, the galvanometer is replaced by a pair of head telephones, with an interrupter in the circuit, a modification which causes a great saving in time. Actually, a complete titration occupies only three or four minutes.

III. DESCRIPTION OF THE APPARATUS.

The electrodes and their vessels (Fig. 1) are very simple. The standard half-cell used is not a calomel half-cell, but the standard quinhydrone half-cell of Veibel (**4**). It is a medium-sized tube, containing a buffer solution (pH 2·2) saturated with quinhydrone. The exact value of the buffer solution need not be known, as absolute measurements are not to be made ; a solution of pH 2·2 is found to give convenient readings on the potentiometer. The tube is stoppered with a rubber bung pierced by two holes. The electrode is a square centimetre of gold foil attached to a platinum wire which is fused into the bottom of a small glass tube. This tube passes through one of the holes in the bung, and contains mercury, with which contact with the external lead is made.

The twice-bent glass tube which contains the KCl-agar bridge passes through the other hole in the bung. A small bulb is blown in this tube to frustrate the tendency of the jelly to slip bodily out of the tube. The bridge is prepared as follows : 50 c.c. of distilled water is heated on the water-bath to near boiling-point, and 1·5 gm. of agar-agar is then added. Care should be taken to avoid air bubbles. After about five minutes, 20 gm. of pure KCl is added, and after a further five minutes, one end of the glass tube, which is previously heated in hot water, is inserted into the mixture, and enough sucked up to fill the tube, which is then cooled under the tap. It is well to slip a short length of rubber tubing over each end of the glass. Not only does this make filling easier, but when the rubber is removed after the jelly has set, the tube is left quite full ; if no rubber is used the jelly, contracting as it cools, withdraws a little up

the tube, so that proper cleaning between titrations is difficult. The jelly loses KCl when in use, and has to be replaced at intervals. It may last from three to fifteen days, but this does not seem to depend on the extent to which it has been used.

Titration is carried out in an ordinary beaker. The electrode in this is exactly like that in the other half-cell. Another rubber bung is slipped over the tube which holds the bridge, and the tube into which the platinum wire is fused is held in a second hole in this bung. As Figure 1 shows, the entire assembly is supported by an ordinary retort clamp.
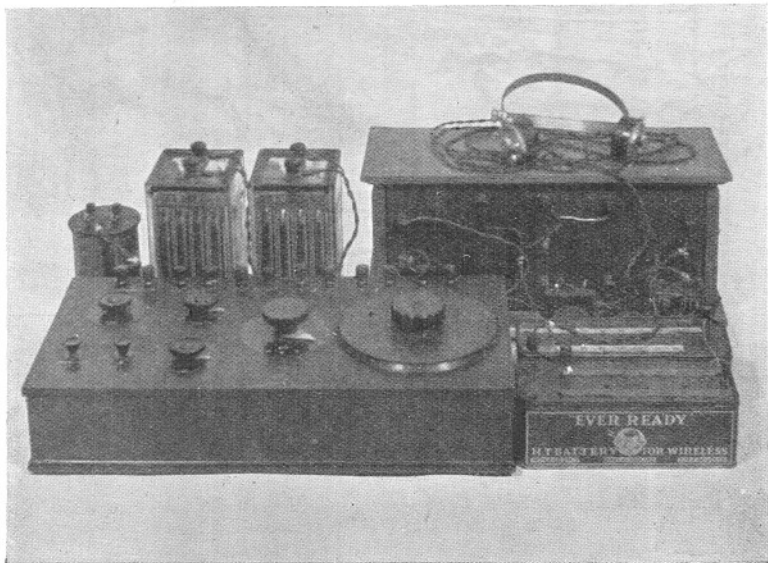

FIG. 2.—The potentiometer and amplifier, and their batteries. The interrupter is kept at the other end of the bench.

A flashlamp bulb in a small metal reflector, and a hand lens, are supported in a wire frame which slides up and down the burette, that it may be more accurately read.

Hand stirring was practised at first, but this proved inadequate, as additions of alkali were not distributed evenly for some time. A mechanical stirrer was therefore arranged, driven by a small electric motor. The power is transmitted by a belt working over a system of pulleys. Meccano components were used for this, as may be seen in Figure 1.

Figure 3 shows that the electrodes are directly connected to a reversing switch, the use of which is illustrated in Table I. Then they pass to the potentiometer and the interrupter respectively. The potentiometer (Fig. 2) used is the " Slide Wire Potentiometer (Modified Form) " of the

Cambridge Instrument Co., Ltd., which is a precision instrument, and was obtained with a view to making hydrogen-ion concentration measurements. But for titrations only, a much cheaper instrument would suffice, since absolute measurements of E.M.F. are not required. Good results could probably be obtained from an improvised potentiometer.

A two-valve amplifier is placed before the head telephones, as was done by Poole (5). This was constructed from the standard components sold for radio sets, and contains two transformers, one of which comes before the first valve. As an output transformer is placed between the
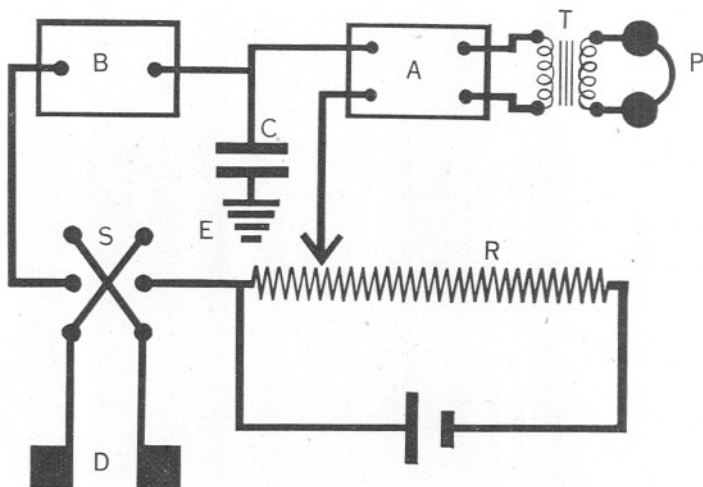

FIG. 3.—The circuit used. The internal circuits of the interrupter and of the amplifier are omitted, and the potentiometer circuit is reduced to its simplest form.

A, amplifier ; B, interrupter ; C, 2-microfarad condenser ; D, electrodes ; E, " earth " ; P, telephones ; R, potentiometer ; S, reversing switch ; T, output transformer.

second valve and the telephones (although not actually incorporated in the amplifier), the batteries of the amplifier are completely insulated from the remainder of the apparatus. The amplifier is built into a wooden case which is lined with copper sheet, to minimise " interference " from the motor which drives the interrupter. This copper sheet, and the negative terminals of the amplifier batteries, are connected to " earth." " Interference " is further reduced by a two-microfarad condenser between " earth " and the primary of the first transformer.

Several interrupters have been tried. A Meccano assembly, which seemed to be superior to the buzzer device of Poole (5) and to the Meccano assembly of Poole and Atkins (6) (both of which were tried), was used for some months. Two teeth out of every three were removed from a

heavy-toothed wheel, and the gaps were filled with sealing-wax. This composite wheel was rotated by an electric motor between two pieces of clock spring, pressed firmly against it by rubber buffers. Contact between the springs was made and broken ten times in each revolution. This was very satisfactory, except for the rapidity with which the sealing-wax wore away. When the apparatus had established itself as permanent, a new interrupter was designed, and was manufactured specially by the General Electric Company, Ltd. A motor, driven at 1800 r.p.m. by a 12-volt accumulator, bears on an extension of the armature shaft an extra commutator, carefully insulated from the
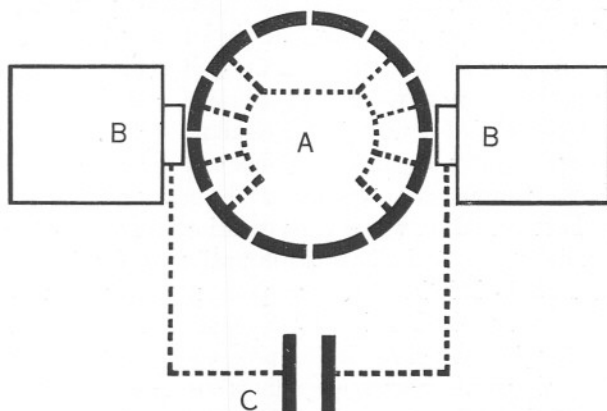

Fig. 4.—Diagrammatic view of the interrupter, showing the electrical connections as broken lines.

A, end view of extra commutator on the armature shaft of the motor; B, sprung carbon brushes, between which contact is made and broken; C, 0·5 microfarad condenser.

armature. Figure 4 shows how contact is made and broken between the two carbon brushes. A 0·05 microfarad condenser is connected across the brushes, and almost abolishes " interference." There is very little mechanical noise.

IV. Procedure in Titration.

The acid solution is placed in the beaker. When the solution to be titrated is alkaline, it must first be made acid by addition of a known amount of acid. If this is not practicable, e.g. when a precipitate would form in acid solution, the titration cannot be performed.

Quinhydrone is added to the solution in the beaker. Its small solubility causes a small quantity to saturate the solution, and this is usually done. But the result does not seem to be affected if the quinhydrone does not saturate.

The acid solution is usually diluted to a " standard volume," suited

to the type of titration. Thus, at Millport, it was necessary to make numerous titrations in which the acid solution was 25 c.c. of 0·1N HCl, partially neutralised by alkali distilled into it, and already diluted to about 190 c.c. The " standard volume " was therefore fixed as 200 c.c., and all the acid solutions in this series of titrations were diluted to this volume. If the titration does not belong to such a series, this dilution is not made. The " standard volume " for any series is made as small as possible, for if a relatively large volume of water be added, the CO_2 dissolved in it may appreciably alter the pH value of the whole.

When, in every titration in such a series, the acid solution has the same volume, the same E.M.F. marks the end-points, provided, of course, that the pH of the buffer solution in the standard half-cell remains constant. Actually this does not remain quite constant, because this solution takes up KCl from the KCl-agar bridge, and is, on this account, periodically renewed. Also, the amount of alkali added, during titrations, naturally varies slightly, so that the volumes at the end-points are not quite the same throughout a series. It is not, therefore, possible to use the Pinkhof method, in which the potentiometer would be set to the known end-point value, and alkali run in until no noise is audible in the telephones. But the E.M.F. at the end-point may be predicted within a few millivolts, so that the E.M.F. at any stage is an excellent indication of the extent to which the titration has proceeded.

In practice, therefore, accurate readings are not taken until within about 1 c.c. of the end point. The interrupter-telephone combination, being completely " damped," allows a rough reading to be taken in a few seconds, and the four or five accurate readings which are necessary, may be taken in two or three minutes. Between each addition of alkali from the burette the liquid in the beaker is very thoroughly stirred, and then the E.M.F. is read. The results are tabulated as in Table I, and the end-point is read direct from this.

The electrodes are subject to polarisation, so that the potentiometer switch should not be held down continuously while a reading is being taken.

If the end-point is overshot, the titration may usually be " brought back " by addition of acid, without serious error.

As there is no galvanometer, and as all the apparatus has sufficient mechanical strength, the whole assembly may be taken to sea, and there worked. It was for this reason that the interrupter was designed to run from an accumulator.

The apparatus is quite independent of colour and turbidity in the liquid. It has been in regular use at Millport for several months, and has been found quite reliable. The accuracy obtainable varies with the strength of the solutions titrated. Successive titrations of 0·01 HCl

against 0·01 NaOH tally within 0·02 c.c. This, of course, does not necessarily imply that the absolute accuracy is as high as this, but relative results have been adequate for the purposes for which the apparatus has been intensively employed.

V. pH MEASUREMENTS.

The apparatus is perfectly suited to the measurement of hydrogen-ion concentrations. Smaller electrode vessels are then used, and the standard half-cell is either a calomel half-cell or a quinhydrone half-cell containing a buffer solution of accurately known pH. A single E.M.F. is determined, and then a simple calculation should then give the pH of the liquid under test, as is described by Biilmann (1) and Clark (7). Unfortunately this has been a complete failure, the results being extremely erratic, owing, doubtless, to some fault in detail, at present undiscovered.

I have to thank Mr. H. B. Moore for considerable help in the designing and in the construction of the stirring apparatus and the various inter-rupters which have been tried.

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