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STUDIES IN ELECTRODE POLARISATION.
PART IV.—THE AUTOMATIC CONTROL OF THE POTENTIAL OF A WORKING ELECTRODE.

BY A. HICKLING.

Received 16*th September*, 1941.

Although the electrode potential is considered to be the dominating factor governing many electrolytic processes, it is one of the variables least amenable to direct experimental control. In general it can only be indirectly changed or maintained during electrolysis by alteration of such factors as current density, temperature, electrode material and electrolyte composition. A device whereby the potential of a working electrode can be fixed at any desired arbitrary value would seem, therefore, to have many valuable applications in the exploration of electrolytic processes, and the present paper describes an electrical circuit by means of which this aim can be achieved.

Experimental.

The electrical circuit of the device, which will subsequently be referred to as a " potentiostat," is shown in Fig. 1. The method of working is as follows. Direct current from any suitable source (battery or rectifier) is fed to the electrolytic cell through the large triode valve V_1. A heavy negative bias is imposed on the grid of this valve by the battery B_1 so that initially no current will pass. The grid circuit, however, includes a large condenser C, which is gradually charged up through the resistance R, and the condenser voltage opposes the fixed negative bias on the valve. Thus the current through the electrolytic cell tends continually to increase, and, if no other factor intervened, would rise to the maximum value which V_1 can pass. The condenser, however, can discharge through the second valve V_2 which acts as a switch, its operation being controlled, *via* a thyratron circuit, by means of the potential difference between the electrode which is being studied and a suitable reference electrode. The

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thyratron T is supplied with alternating current, so that it is automatically set 50 times a second, and its grid is adjusted to the critical tripping voltage by means of the automatic biassing potentiometer r_1-r_2. Into the grid circuit of the thyratron is also introduced an external potentiometer P, connected so as to make the grid more negative, and, in opposition to this, the combination of the working electrode, either anode or cathode, and the reference electrode. It follows, therefore, that the thyratron will pass no current until the potential difference between the working and reference electrodes is equal to the e.m.f. derived from the external potentiometer P. The valve V_2 is ordinarily biassed by the battery B_2 so that it will pass no current, but when the thyratron trips, the voltage across r_2, which is included in the grid circuit of the valve, renders V_2 conducting and hence the condenser C can partially discharge and the main current through the electrolytic cell will drop. Hence on switching on the apparatus, the current will rise until the working electrode has a potential relative to the reference electrode equal to the voltage set upon

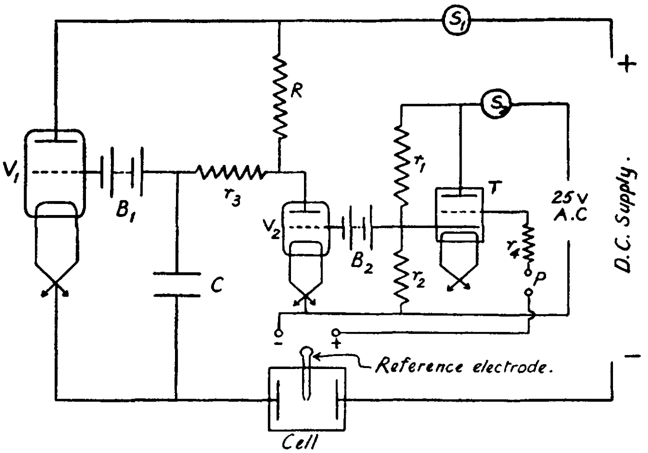

FIG. 1.—Potentiostat Circuit.

the potentiometer, and the current will then be automatically controlled so that this potential is indefinitely maintained. If no electrode process is possible at the arbitrarily fixed potential then the thyratron will operate continuously and the current through the cell will be zero. If, on the other hand, some electrolytic process is possible, then the limiting current for that process will pass.

The potentiostat was constructed as a compact unit working from the A.C. mains, with terminals for external connection to the D.C. source, the potentiometer and the electrolytic cell. The maximum current which the potentiostat can control is limited only by the anode current which the valve V_1 can pass; in the present case two Osram PX25 valves were used in parallel, and with a 200 v. main battery, currents up to 0·3 amp. were possible. R was a 5 megohm resistance, B_1 a 60 v. dry battery, and C an 8 μF. electrolytic condenser; r_3, which serves to retard the discharge of C, was a 100,000 Ω resistance. The choice of the valve V_2 is not in any way critical, and almost any thermionic valve which requires only a small negative bias to stop the anode current completely will serve; in the present instance a screened grid valve, Osram MS4B, which happened to be available, was used with anode and screen connected together. B_2 was a 6 v. dry battery. T was an Osram GT1C thyratron, and it was supplied with 25 v. A.C. from a mains transformer, separate

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4 v. windings of which also supplied the heaters of the thyratron and valves. r_1 was a 5000 Ω fixed resistance, and r_2 a 300 Ω theostat. To give an audible indication when the thyratron was tripping, a high resistance telephone was connected across r_1, and the thyratron was initially set by adjusting r_2 until an intermittent buzzing was obtained when the external terminals of the controller circuit were connected together. Once adjusted, the thyratron should need no further attention provided the A.C. mains voltage is reasonably steady, and the whole of the present work was carried out with one initial setting;[1] r_4 was a 10,000 Ω resistance which served to limit grid current in the thyratron circuit. This current varies with the rate at which the thyratron is tripping but is in general of the order of 50μa; since it passes through the reference electrode, the latter should be relatively unpolarisable. Switches S_1 and S_2 were included in the D.C. and A.C. supplies in the positions shown.

A saturated calomel half-cell was used as reference electrode in the study of anodic processes. For cathodic reactions it is desirable to have a reference electrode of potential more positive than any which it may be required to maintain, and a platinum wire coated with PbO_2 and immersed in N. H_2SO_4 was used; this had a very steady and reproducible potential of 1·60 v. on the hydrogen scale. Connection with the working electrode under investigation was made by means of a Luggin capillary. P was a potentiometer-voltmeter reading to 0·01 v. In use it is only necessary to set the desired potential upon the potentiometer, and the potentiostat automatically adjusts the current to give this potential at the electrode. The current which passes is actually fluctuating slightly about a mean value, since it is tending continually to rise and being repeatedly prevented from doing so by the controller circuit, but these operations take place so rapidly that an ammeter in the circuit usually shows a perfectly steady reading. The time lag in the response of the potentiostat to an alteration of potentiometer reading was found to be very brief; for an increase of potentiometer voltage it amounted to a few seconds, and for a decrease of voltage only to a fraction of a second.

Results and Applications.

The applications of the potentiostat in electrochemical investigations would appear to be very numerous, and it is only desired here to outline and illustrate some of the main uses which show the characteristic properties of the instrument.

Current-potential Curves.—The potentiostat is admirably suited for the plotting of current-potential curves and the detection thereby of the various possible electrode reactions. It is only necessary to set various voltages upon the potentiometer and to read off from a milliammeter the corresponding currents which flow, and a complete curve can be obtained in less than 5 minutes. In Fig. 2 is shown the curve for a typical anodic process,—the deposition of iodine from an acid iodide solution. A smooth Pt wire anode of 1 sq. cm. area (10·6 cm. length of 0·03 cm. diameter wire, coiled spirally and mounted vertically) was used with 300 c.c. of 0·1 N. KI in N. H_2SO_4 as electrolyte, the solution being unstirred and maintained at 20°; a Pt wire cathode contained in a compartment separated from the main electrolyte by a filter paper plug completed the cell. A saturated calomel electrode was used as reference electrode, and all potentials are given on the hydrogen scale. The broken curve is that obtained for N. H_2SO_4 as electrolyte alone. It will be seen that no current passes until a potential of approximately + 0·5 v.

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[1] New thyratrons are occasionally liable to sudden shifts in the critical grid voltage, but these invariably disappear after the thyratron has been run for some time.

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is attained, which is slightly lower than the standard potential for a saturated iodine solution. The current then rises rapidly to a steady value of 5·5 m.a., which represents the limiting rate at which iodine can be deposited under the experimental conditions. The current remains entirely steady as the anode potential is increased until a value of about + 1·8 v., in the region of oxygen evolution, is reached when a sudden increase takes place as some other electrode reaction occurs, this then passing smoothly into oxygen evolution with corresponding very large increase of current.

In Fig. 3 is shown a typical cathodic process,—the deposition of copper from an acid solution of a copper salt. The general experimental arrangement was the same as above, but the 1 sq. cm. Pt electrode was used as a cathode and the electrolyte was 0·1 M. $CuSO_4$ in N. H_2SO_4; the PbO_2/N. H_2SO_4 electrode was used for reference purposes. The broken curve is that obtained with N. H_2SO_4 alone as electrolyte. It will be noted that at a potential of + 0·3 v., slightly more negative than the standard potential for copper, current begins to pass and rapidly reaches a limiting value of 25 m.a. at which it remains steady until the cathode potential reaches —0·5 v. when hydrogen evolution commences.

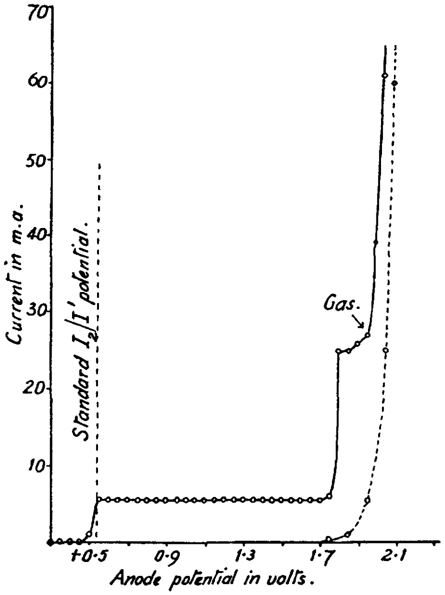

FIG. 2.

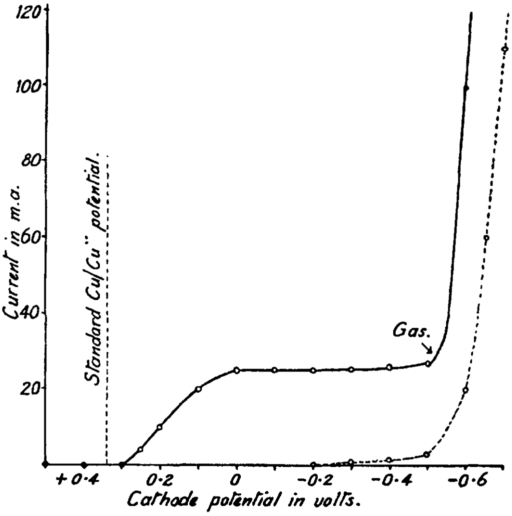

FIG. 3.

A more complicated current-potential curve is shown in Fig. 4 for the cathodic polarisation of the Pt electrode in an electrolyte consisting of 0·1 M. $Hg_2(NO_3)_2$ + 0·1 M. $Cu(NO_3)_2$ + 0·1 M. $Pb(NO_3)_2$ + N. HNO_3 Here four cathodic processes are possible,—the deposition of Hg, Cu, and Pb, and the evolution of H_2. It will be seen that each of the metal depositions occurs in turn, at a slightly more negative potential than the standard value for the metal in question, and each process is accompanied by its own limiting current contribution to the total current passing; hydrogen evolution sets in at about —0·55 v.

The current-potential curves obtained by the potentiostat are very similar to the polarograms given by the Heyrovsky-Shikata method with the dropping mercury cathode, and it should be possible to utilise them

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in the same way in analytical work. The present method has the advantage that the apparatus involved is relatively simple and manipulation is extremely easy.

Isolation of Electrode Processes.—By utilising the appropriate potential, it should be possible, with the aid of the potentiostat, to carry any one electrolytic process to completion with the exclusion of all other processes occurring at a more positive potential, in the case of an anode, or a more negative potential in the case of a cathode. To test this, 25 c.c. of 0·1 M. $CuSO_4$ in N. H_2SO_4 was electrolysed with the cathode potential fixed at + 0·1 v. At this potential practically all the copper should deposit, but no hydrogen liberation should occur. To increase the limiting current and so shorten the time of electrolysis a 50 sq. cm. copper cathode was used; a hydrogen coulometer was placed in series with the cell. On first switching on the apparatus, a current of 0·15 amp. passed, but this decreased, rapidly at first and then more slowly as shown in Fig. 5, until after 3½ hours electrolysis had practically stopped, the current then being less than 0·002 amp. The volume of hydrogen evolved in the coulometer when corrected to N.T.P. was 56·2 c.c., while the calculated amount corresponding to the amount of copper initially taken was 56·0 c.c. The agreement is very satisfactory.

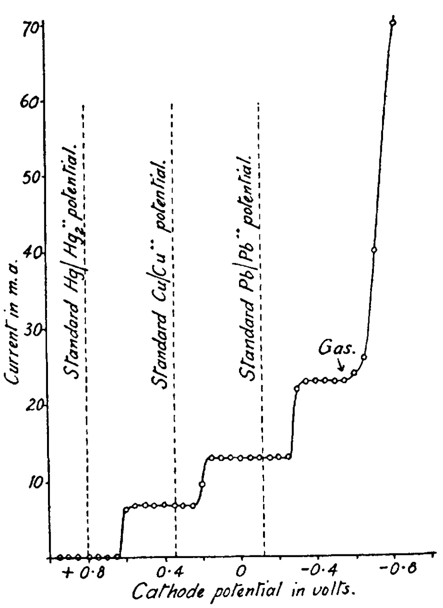

FIG. 4.

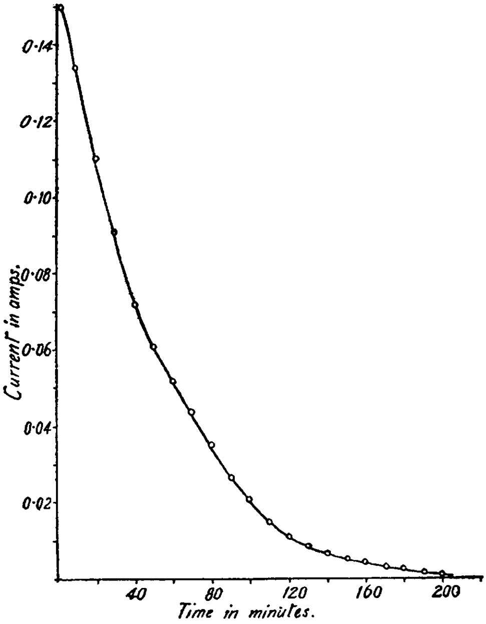

FIG. 5.—Electrolysis of copper sulphate solution at constant potential.

A similar experiment was carried out for the anodic deposition of iodine from acid iodide solution. 0·0025 equivalent of KI was added to 300 c.c. of N. H_2SO_4 and electrolysed with a 20 sq. cm. platinised Pt anode at 50°, the solution being mechanically stirred. The anode potential was set at + 0·75 v. A current of 0·07 amp. passed initially, but this decreased as electrolysis proceeded until after 3½ hours it was only 0·0005 amp. and electrolysis had practically stopped. The volume of hydrogen evolved in the coulometer was 27·7 c.c. as against a theoretical volume of 28·0 c.c.

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It is apparent that the potentiostat should find considerable application in a similar way to the control of electrode potential in electrolytic oxidation and reduction processes, and the investigation of the influence of this factor upon the nature and amounts of the products obtained.

Limiting Currents.—As has been pointed out above, the current which flows through the cell for any given potential setting is the limiting current at which the particular electrode process taking place can occur. This is in most cases controlled by the rate at which the particular ionic species can diffuse up to the electrode,[2] and hence the potentiostat is excellently adapted for studying the diffusion of substances in solution and the effect of such factors as concentration, temperature, stirring, etc. All that is necessary is to select an appropriate potential for the particular process being studied by inspection of the current-potential curve, and then to note the current which flows at this potential under various experimental conditions. As an illustration of this procedure, the effect of concentration on the limiting current for the anodic oxidation of ferrous chloride was studied. As electrolyte, 2N. HCl containing various amounts of ferrous chloride was used, and the solution was unstirred and maintained at 20° ; the 1 sq. cm. Pt wire anode previously used was employed. As a preliminary, the current-potential curve for M. $FeCl_2$ in 2N. HCl was obtained and is shown in Fig. 6*a*. By inspection of this, + 1·00 v. was selected as a suitable fixed anode potential, and the currents passing at this potential for various strengths of $FeCl_2$ were read. The results are shown below, and graphed in Fig. 6*b*.

Concentration of $FeCl_2$ (M)	1·0	0·8	0·6	0·4	0·2	0·1	0·05	0·02
Limiting current (in m.a.)	51·0	43·0	34·0	22·4	10·7	5·1	2·2	0·7

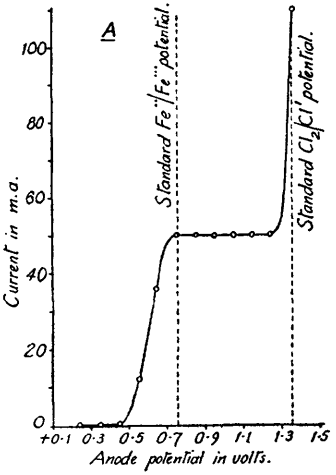

FIG. 6*a*.

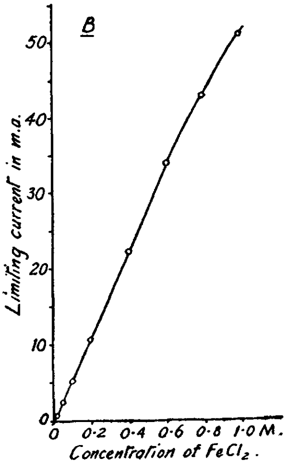

FIG. 6*b*.

It will be noted that, in accordance with diffusion theory, the limiting current is approximately proportional to the concentration of ferrous chloride ; slight deviations occur in the most concentrated solutions.

Current Stabilisation.—A minor but interesting application of the potentiostat is to the problem of maintaining a current in an electrical

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[2] See Glasstone and Hickling, *Electrolytic Oxidation and Reduction*, chap. III, for a general account of diffusion phenomena in electrolysis.

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circuit constant independent of changes in resistance and supply voltage. Much ingenuity has been expended upon this problem,[3] but most of the devices hitherto described are not true stabilisers but merely reduce variations from constant current. The potentiostat, however, can act as a true stabiliser since if the electrolytic cell in Fig. 1 is replaced by a resistance, the ends of which are connected to the controller circuit, such a current must flow indefinitely as will balance the voltage set upon the potentiometer. To illustrate this, the potentiometer voltage was fixed at 4·0 v., and resistances of 4000, 400, and 80 Ω substituted in turn for the electrolytic cell. In each case the D.C. input voltage to the potentiostat was varied from 100 to 350 v. and the corresponding currents noted. According to Ohm's Law the currents passing should have been 1, 10, and 50 m.a. The actual results are given below:—

Input voltage in volts—											
	100	125	150	175	200	225	250	275	300	325	350
Current in m.a.—											
4000 ω	0·85	0·90	0·93	0·96	1·00	1·01	1·04	1·06	1·08	1·10	1·11
400 ω	9·85	9·90	9·95	9·98	10·0	10·0	10·0	10·1	10·2	10·4	10·5
80 ω	50·0	50·0	50·0	50·0	50·0	50·1	50·1	50·2	50·4	50·8	51·6

It is to be noted that a very remarkable degree of constancy in the currents is attained.

Summary.

An electrical circuit is described whereby the potential of a working electrode is automatically maintained at any desired arbitrary value. Some of the main applications of the device, which is termed a potentiostat, to electrochemical problems are given and typical examples illustrated.

The author is indebted to Dr. S. Glasstone for first bringing the problem of the automatic control of electrode potential to his notice.

University College,
Leicester.

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[3] See Bruce and Hickling, *J. Scientific Instruments*, 1937, **14**, 367, for references and full discussion.