

ELECTROMETRIC TITRATIONS WITH OXYGEN ELECTRODES.

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Received 28th June, 1933.

A number of attempts have been made to use oxygen electrodes in acid-alkali titrations,¹ but it has generally been found that the potentials are liable to fluctuate erratically and the titration curves are not very reliable. We have found that if a platinum electrode is polarised anodically for a short time and then given a very short cathodic polarisation, concordant potentials are observed which vary with the p_H of the solution. In certain cases excellent titration curves may be obtained with electrodes which have been treated in this way.

When a platinum electrode is polarised anodically in a solution in which oxygen is the anodic product, it has been shown² that a layer of adsorbed oxygen is formed at potentials considerably less positive than that required for the continuous evolution of oxygen. When the current is stopped the oxygen overvoltage which has been established decays

very slowly, and after several hours a nearly constant potential is reached which is a function of the p_H of the solution. This potential has some of the characteristics of reversibility, but it cannot at present be identified with certainty with the reversible oxygen potential. It can be reached much more rapidly by giving the electrode a very short cathodic polarisation, which takes the potential in a short time (a fraction of a second) to the same value, at which it then remains.

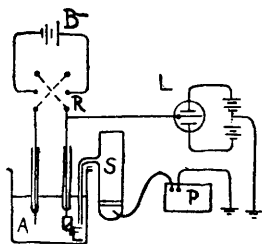


FIG. 1.—Apparatus.

The function of the anodic polarisation is thus to establish an adsorbed layer of oxygen on the electrode surface. The subsequent cathodic polarisation destroys the slowly decaying oxygen overvoltage and brings the electrode into a reproducible state in which its potential responds to changes of the p_H of the solution.

The apparatus used in the electrometric titrations is shown in Fig. 1. The bright platinum electrode E and an auxiliary platinum electrode A were connected with a 4-volt battery B through a reversing switch R. The potential difference between the electrode E and a standard half-cell S was measured by means of the potentiometer P and the Lindemann electrometer L. The electrode E was polarised for 10 seconds, and then cathodically polarised for a short time by momentarily closing the reversing switch in the opposite direction. During the titration air or oxygen was sometimes bubbled through the solution, but except as a means of stirring

¹ E.g. J. Furman, *J. Amer. Chem. Soc.*, **44**, 2685, 1922; J. Britton, *Trans. Far. Soc.*, **19**, 740, 1924. Goard and Rideal have used platinum electrodes which have been treated with oxidising agents such as HNO_3 , KMnO_4 for titrations (*J. Chem. Soc.*).

² Butler and Armstrong, *Proc. Roy. Soc.*, **137A**, 604, 1932.

this proved to be unnecessary. Mechanical stirring without any passage of gas was equally effective.

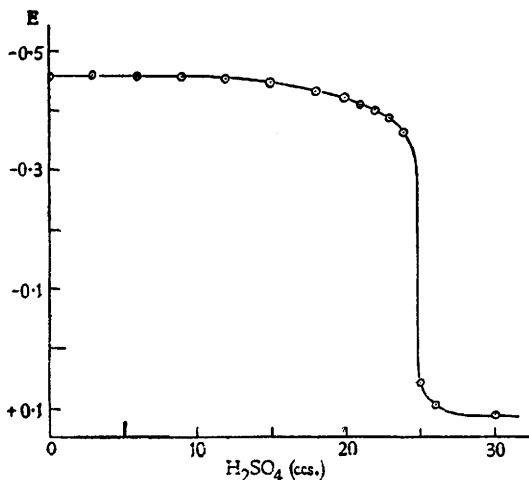
The following table shows the observations made during the titration of 25 c.c. of NaOH (*N*) with H_2SO_4 . The end point of the titration using phenolphthalein as indicator was at 24.8 c.c.

TABLE I.

H_2SO_4 (c.c.).	(1).	(2).	H_2SO_4 (c.c.).	(1).	(2).
0	-0.476	-0.457	20	-0.427	-0.421
3	-0.456	-0.461	22	-0.402	-0.400
6	-0.459	-0.459	23	-0.388	-0.388
9	-0.458	-0.458	24	-0.364	-0.364
12	-0.455	-0.454	25	+0.054	+0.06
15	-0.451	-0.448	26	+0.073	+0.097
18	-0.443	-0.432	30	+0.096	+0.114

Under column (1) are given the electromotive forces measured immediately after each addition of acid, and under (2) the values after the + - polarisations as described above (against the mercurous sulphate electrode). The final values are plotted in Fig. 2. It is not essential to carry out the + - polarisation after each addition of acid, but it is better to do so, for after a time the electrode ceases to respond well to the changes of p_{H} , if untreated. If the cathodic current is left on too long the potential of the test electrode may rise to the point at which hydrogen is liberated. This does not cause any interference for after a few seconds it returns again at open circuit to the characteristic oxygen potential.

When the electromotive force is measured by the ordinary potentiometric

FIG. 2.—Electrometric titration of NaOH with H_2SO_4 .

arrangement, the values obtained are not so well defined on account of the polarisation of the electrode by the small currents which pass during the determination. Good titration curves have been obtained in this laboratory by students who have had no previous experience of such methods, using a valve potentiometer for observing the electromotive force. Successful titrations have been obtained with nitric and acetic acids. The method fails with hydrochloric acid (owing to interference by chlorine), with easily oxidisable organic acids which may act as oxygen depolarisers, and for some reason phosphoric acid gave rather erratic values.

Summary.

Bright platinum electrodes which have been polarised anodically for a short time, followed by a momentary cathodic polarisation, exhibit a reproducible potential which responds well to the p_{H} of the solution, and may, in the absence of depolarisers, be used for electrometric titrations.