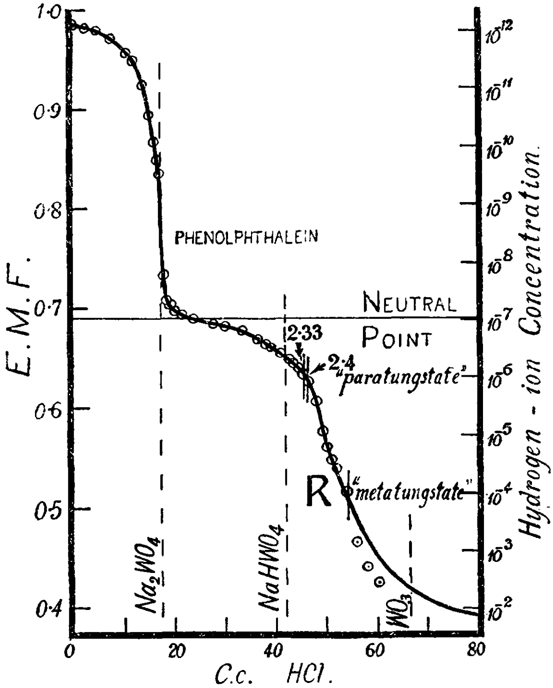
XXIV.—*An Electrometric Study of Tungstic Acid.*

By HUBERT THOMAS STANLEY BRITTON.

THE facts that tungstic oxide forms salts with the alkali metals, R_2WO_4, and that tungsten appears in the same group of the periodic system as sulphur have led to the impression that tungstic acid is an ordinary dibasic acid. An attempt was made to study the acidic nature of the oxide by following electrometrically the variation in hydrogen-ion concentration during the course of its neutralisation with sodium hydroxide; for this purpose, however it was found more convenient to back-titrate a solution of the oxide in sodium hydroxide with hydrochloric acid. The first portion of the titration curve, given in Fig. 1, was constructed from *E.M.F.* measurements at 20° made between a hydrogen electrode immersed in the solution and a normal calomel half-element, the junction liquid being a saturated solution of potassium chloride. The titration was performed as previously described (J., 1924, **125**, 1572) and the *P.D.*'s were found to be reproducible until 0·5 volt was reached ($[H^\cdot] = 10^{-4}$). At this stage, the hydrogen in the electrode began to reduce catalytically the sexavalent tungsten to the quinquevalent state, as indicated by the appearance of the characteristic blue coloration around the electrode. This position is denoted by R on the curve. The three points on the diagram obtained after reduction became obvious represent initial readings made before the effect of the reduction had become appreciable. To complete the titration curve, resort was made to the oxygen electrode, with which a similar titration was carried out using solutions of the same concentrations. Neither the hydrogen-electrode nor the oxygen-electrode curve showed that any abrupt changes in hydrogen-ion concentration occurred in solutions more acidic than p_H 4. The remaining portion of the curve in Fig. 1 was plotted from the oxygen-electrode curve, calibrated against the portion obtained with the hydrogen electrode, the accuracy of which is considered to be of the order of one-tenth of a p_H unit (compare J., 1924, **125**, 1572; 1925, **127**, 1896). The curve given in Fig. 1 represents the titration by 0·1020N-hydrochloric acid of 100 c.c. of a solution which was 0·0678N with respect to sodium hydroxide and 0·0250M with respect to tungstic acid (WO_3).

The curve shows that a sharp diminution in p_H took place with the amount of hydrochloric acid necessary to react with the alkali in excess of that required to form the normal sodium tungstate.

FIG. 1.



This explains why tungstic acid may be estimated volumetrically either by titrating a suspension of it directly with sodium hydroxide or by dissolving the oxide in alkali and titrating the excess of alkali with acid, using in each case phenolphthalein as indicator (Hundeshagen, *Chem.-Ztg.*, 1894, **18**, 547; Herting, *Z. angew. Chem.*, 1901, **14**, 165; Lind and Trueblood, *J. Amer. Chem. Soc.*, 1907, **29**, 477). The remaining part of the curve down to the dotted line indicating WO_3 represents, in effect, the reverse of the neutralisation of tungstic acid with sodium hydroxide. The large inflexion produced when the acid was about one-quarter neutralised is surprising in that it did not occur when the acid was half neutralised, as would have been the case had tungstic acid behaved as an ordinary dibasic acid with widely differing dissociation constants.

No precipitation of tungstic oxide occurred throughout the titration even although a large excess of hydrochloric acid had been added. The solution remained perfectly clear, suggesting that the oxide had passed into a sub-colloidal state and not into combination with the hydrochloric acid, which would have been indicated by the p_H readings. It is of course possible that the hydrochloric acid had some stabilising influence through being slightly adsorbed by or feebly combined with the tungstic oxide. Using more concentrated solutions, precipitation ensues (see van Liempt, *Z. anorg. Chem.*, 1923, **127**, 215; *Rec. trav. chim.*, 1924, **43**, 30).

The curve throws some light on the so-called "paratungstates" and "metatungstates." Sodium paratungstate is stated to have the composition $3Na_2O,7WO_3,21H_2O$ or $5Na_2O,12WO_3,28H_2O$, and thus it contains either 2·33 or 2·4 mols. of Na_2O to 1 mol. of WO_3. The points on the titration curve marked 2·33 and 2·4 indicate the hydrogen-ion concentrations of the solutions when the solutes were present in those ratios, the p_H being 6·1 and 6·0, respectively. Schmidt (*Amer. Chem. J.*, 1886, **8**, 16) found that a solution of the 2·4-salt was acidic to rosolic acid and alkaline to cochineal; consequently the p_H of his solution was in the neighbourhood of 6, and is thus in accord with the value indicated by the curve. The point marked "metatungstate" gives the hydrogen-ion concentration, 10^{-4}, of the solution when the alkali in combination with the tungstic acid was that required by $Na_2W_4O_{13}$, the formula for sodium metatungstate. Although the hydrogen-ion concentrations of the "para" and "meta" solutions show that some kind of union has taken place, it is difficult to picture the exact nature of that union. It appears from the curve that the paratungstate solution is the same as that of a solution of sodium tungstate saturated with tungstic oxide such that the change in hydrogen-ion concentration undergone is very small, whereas the metatungstate solution corresponds to a still greater saturation, but one which involves a considerable variation in hydrogen-ion concentration. These are the conditions which underlie the preparation of these salts. Seeing that tungstic acid cannot be considered as an ordinary dibasic acid, it is not apparent what kind of compounds these are, unless it be supposed that they contain tungstic acid either in a polymerised form or in a semi-colloidal form, which on dissolution in water gives rise to a micellar ionisation.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
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