CXVII.—*The Use of the Tungsten Electrode in Potentiometric Titrations and p_H Measurements.*

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The exact determination of p_H values of alkaline solutions containing substances that render the hydrogen electrode useless is often a problem of some difficulty, particularly in the case of complex cyanide solutions which we are now investigating. We therefore undertook an examination of the possibilities of bare tungsten as an electrode, since this metal has not yet received comprehensive study, though it is the subject of a recent patent. It has, however, as the following record shows, been found to give satisfactory results in certain solutions. Baylis (*Ind. Eng. Chem.*, 1923, **15**, 852; see also Parker and Dannerth, *ibid.*, 1925, **17**, 637; U.S.P. 1,513,558/1924) used the tungsten filament of an electric lamp to measure the p_H values of river water over the range 6·5—8·6, but his data reveal the extraordinary difference of 0·09 volt for each p_H unit change; he has, however, recently patented this form of electrode (U.S.P. 1,727,094/1929).

Parker (*Ind. Eng. Chem.*, 1925, **17**, 737) studied tungsten electrodes, both bare and in intimate contact with various metal oxides, in four different buffer solutions of p_H values ranging from 4 to 9 and concluded that those coated with specially prepared manganic oxide were the most satisfactory.

Bare wire electrodes were considered by Holven (*ibid.*, 1929, **21**, 965) to be capable of yielding accurate p_H measurements of sugar liquors for periods of a day, after they had undergone immersion in a solution of normal sodium phosphate for two days, followed by a further two days in a solution of the substance which was subsequently to be tested. This possibility appeared worthy of further investigation in presence of substances of widely different types.

Preparation and Calibration of the Electrodes.—As in a previous communication (Britton and Robinson, this vol., p. 458), the calibration of the electrodes was based on the neutralisation with sodium hydroxide of the modified Prideaux–Ward universal buffer mixture. 100 C.c. of the latter were titrated with 0·2*N*-alkali, the liquid being mechanically stirred. Stirring was discontinued prior to the taking of each potentiometer reading, but had no appreciable effect on the value of the final *E.M.F.* reading. There was no indication of polarisation of the electrode, and a steady reading was usually obtained within 1—2 mins. of the addition of the alkali. From p_H 4 to p_H 2, 5-minute periods had to be allowed owing to slight initial drifts in the voltages. By means of the buffer titration it was possible to obtain a series of *E.M.F.* readings of the three electrodes at various p_H values between 2 and 12, and hence to construct calibration curves. The potentials of three different tungsten electrodes were measured against the normal calomel electrode, with respect to which they gave a negative *E.M.F.* A saturated solution of potassium nitrate was used as the "salt-bridge."

The tungsten used for the electrodes was in the form of a filament and of rods of various sizes, and was provided through the courtesy of Dr. C. J. Smithells of the General Electric Co. Research Laboratories, Wembley. In order to test any influence that the form of the tungsten might have upon the electrode potential, three electrodes (filament, 0·016 mm. in diameter; and two rods, 1 mm. and 5 mm. in diameter) were used simultaneously. The larger rod had been subjected to a process of recrystallisation by heating to 3000° Abs. in an atmosphere of hydrogen for 2 mins. and was therefore quite free from oxide, and the smaller one was covered with a film of oxide and graphite as a result of being drawn. Before use, both were well rubbed with emery paper, and each presented a clean, metallic surface. The filament was wound on a piece of glass rod, the ends being bound to a piece of copper foil fastened to the upper portion of the rod, through which was also made the connexion to the potentiometer circuit. The copper foil and contacts were coated with paraffin wax. The two rods were supported in such a way that the three electrodes were simultaneously immersed in the solution under investigation, and the *E.M.F.*'s were recorded after each addition.

As the behaviour of tungsten as an electrode is essentially that of the metal–metal oxide type, attempts were made to coat it with oxide films by anodic oxidation. The electrodes were placed in a 0·04*N*-solution of caustic soda, and a current of 7·5 milliamps. was passed for 30 minutes. This destroyed the filament, but a buffer titration with the two rod electrodes showed only a very small variation in *E.M.F.* over the whole p_H range 2—12. The electrodes appeared to have become passivated, and rubbing with emery-paper and repetition of the buffer titration with the bright electrodes enabled satisfactory variations in potential with change of p_H to be obtained.

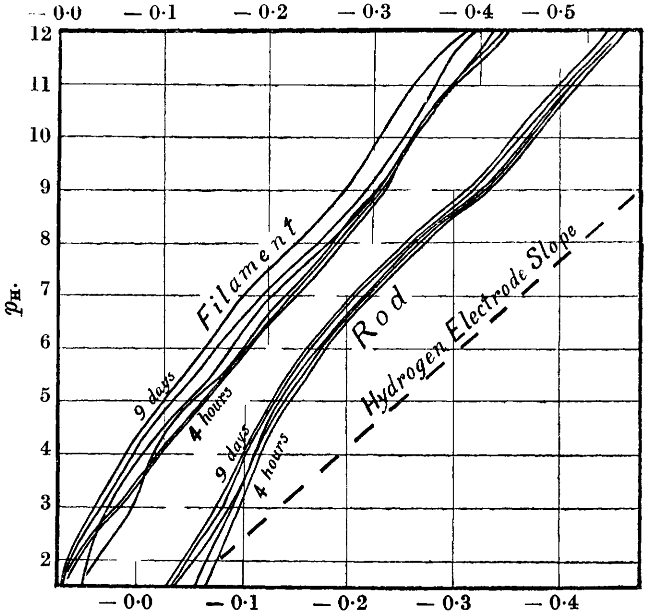
Since anodic oxidation failed to produce a sensitive oxide film, the three electrodes were kept immersed in a strongly alkaline buffer solution, with free access of air. By this means a very thin film of oxide was probably formed on the surface of the tungsten, though its presence was not visible. A series of potentiometric titrations of acids was carried out with the electrodes during a period of several days following the construction of the three calibration curves, and gave p_K values that became more discrepant as the electrodes aged.

This suggested that the observed *E.M.F.*'s were not in strict accordance with the original calibration curve, and this was confirmed on re-calibration. The buffer titration was repeated frequently for several days following, and a series of distinct calibration curves was obtained. Although their form usually remained about the same, these showed that the potential of the electrodes, whilst sometimes altering in the contrary sense, tended to become more positive on ageing. This gradual change in the electrode potential of the tungsten is possibly connected with the gradual formation of a very thin oxide film through oxidation by the air during the immersion of the electrodes in the alkaline buffer. The necessity for the latter treatment has been recognised by Parker (*loc. cit.*). Hence as the tungsten electrodes did not retain their calibration for a period of days, calibration curves were obtained immediately before performing a titration. The p_H values used to calculate p_K values were read off from the calibration curve of the particular electrode immediately preceding the titration.

Fig. 1 gives the calibration curves of the filament and thin rod at various times during 10 days. The effect of ageing of the two forms of electrode is seen to be somewhat different, the filament becoming much more positive than the thin rod. Judging from the smaller and also more uniform change of the potential of the rod it would appear that the tungsten in the massive form should be a more satisfactory electrode than the filament. Similar small variations were observed with a thicker rod.

FIG. 1.

E.M.F. of tungsten filament against N-calomel.



E.M.F. of tungsten rod against N-calomel.

If the tungsten–tungsten oxide electrode behaved simply as a hydrogen electrode, then the *E.M.F.* of the cell $\overset{+}{W}|\text{solution}|H_2$ should be constant whatever the p_H of the solution. This was not the case, and extrapolation shows that with, *e.g.*, the thin rod, after 4 hours in a solution at p_H 2, the *E.M.F.* was 0·322 volt; at p_H 6 it was 0·446; whilst at p_H 12 it was 0·510 volt. After nine days these values became respectively 0·354, 0·464, 0·523. Very different values were given by the filament. After the lapse of a period from 4 hours to 9 days at p_H 2 the *P.D.* increased from 0·361 to 0·389 volt; at p_H 6 from 0·451 to 0·487; and at p_H 12 from 0·543 to 0·581 volt. Parker (*loc. cit.*), using a tungsten filament, obtained *E.M.F.*'s ranging from 0·371 to 0·453 volt over a p_H range of 4 to 9.

Had the tungsten electrode been sensitive to p_H changes in a reversible manner, and therefore such that the *E.M.F.* of the cell W|solution|*N*-calomel = *E.M.F.* of W|solution|H_2 – 0·058 p_H, the slope of the calibration curve would have been that of the broken line in Fig. 1, which would have been that of the calibration of thin rod taken after a period of 4 hours.

Potentiometric Titrations.—A number of acids were titrated against the tungsten electrode to ascertain the extent to which the latter could be used in the determination of titration end-points and the calculation of dissociation constants. The three acids acetic, boric, and phosphoric, to which the hydrogen electrode can be applied, on titration gave the normal type of titration curve, the end-points being plainly and correctly indicated. Though a distinct curve was obtained for each of the three varieties of tungsten electrode employed, the contour of each was similar and all three coincided at the end-points. The p_K values obtained are shown in Table I, and are the mean of seven values calculated from points on the curve corresponding to successive one-eighths in the degree of neutralisation. Comparison of these values with the published values shows that on the whole there is a remarkably good agreement irrespective of the form of the electrode employed.

The p_{K_1} values for phosphoric acid are not trustworthy, since the curve is here situated in the region of p_H 2, in which the behaviour of the tungsten electrodes is rather erratic. Similar objections apply to the extreme end of the titration (p_H 12—13) affecting p_{K_3}.

TABLE I.

Acids to which the hydrogen electrode is applicable: 100 c.c. of 0·05*N*-acid titrated with 0·2*N*-NaOH.

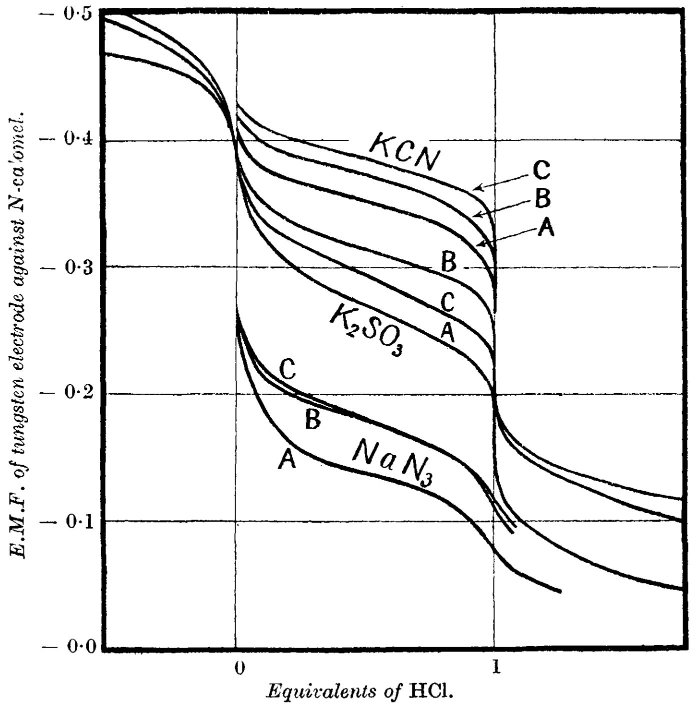
				Previous values.		
Acid.	Electrode.	Mean p_K.	p_K range.	p_K.	Method.	Reference.
$CH_3·CO_2H$	*a*	4·76	4·60— 5·00	4·74	Conductivity	Ostwald (*Z. physikal. Chem.*, 1889, **3**, 170, 241, 369).
	b	4·53	4·35— 4·60	4·74	,,	Kendall (J., 1912, **101**, 1283).
	c	4·67	4·44— 4·80			
HBO_2	*a*	9·19	9·10— 9·23	9·26	Hydrolysis	Lundén (*J. Chim. physique*, 1907, **5**, 574).
	b	8·82	8·70— 8·90	9·20	,,	Lundberg (*Z. physikal. Chem.*, 1909, **69**, 442).
	c	9·10	9·00— 9·25			
H_3PO_4 p_{K_1}.	*a*	1·98	1·95— 2·00	2·03	*E.M.F.*	Britton (J., 1927, 614).
	b	2·03	1·95— 2·15			
	c	1·98	1·95— 2·00			
H_3PO_4 p_{K_2}.	*a*	7·09	6·99— 7·13	6·85	,,	,,
	b	7·14	7·04— 7·19			
	c	7·10	7·01— 7·16			
H_3PO_4 p_{K_3}	*a*	11·79	11·68—11·90	11·57	,,	
	b	11·71	11·41—11·89			
	c	11·70	11·51—11·86			

a = Filament electrode; *b* = thin rod electrode; *c* = thick rod electrode.

Solutions of acids in which the hydrogen electrode cannot be used were next titrated, to see whether the electrode possessed any particular advantages. Fairly consistent values were obtained for the dissociation constants, which are compared in Table II with the values obtained previously by other workers.

The titration curves of hydrocyanic, hydrazoic, and sulphurous acids, as obtained by the back-titration of their salts, are shown in Fig. 2. The curves given by the three different electrodes are not coincident, although the p_K values calculated from them are in fair agreement. This is due to each electrode possessing its own calibration curve.

FIG. 2.



Equivalents of HCl.

For hydrocyanic acid, 100 c.c. of a solution of 0·05M-potassium cyanide were back-titrated with 0·24N-hydrochloric acid : the p_K values obtained from the curves were consistently higher than those usually accepted. A similar procedure was adopted in the case of hydrazoic acid, 100 c.c. of 0·046M-sodium azide being back-titrated with the same acid. The almost identical values given by the two rod electrodes are in better agreement than the filament value with those determined by previous workers.

In the case of sulphurous acid, a solution of potassium sulphite containing an equivalent of sodium hydroxide was titrated with hydrochloric acid. It was only possible to calculate p_{K_2} values; the mean values obtained were considerably higher than that of Kolthoff.

For telluric acid, 100 c.c of 0·025M-acid (as dihydrate) were titrated with 0·2N-sodium hydroxide. Consistent values for p_{K_1} were obtained, but the second half of the curve gave p_H values of the order of 12, and it was not considered justifiable to calculate values for p_{K_2}; the curve, however, plainly indicated the dibasic nature of this acid.

Although Britton and Robinson (*loc. cit.*) have found $p_{K_1} = 7·84$ for telluric acid, no determination of this dissociation constant has been made by the standard methods, and consequently one was made colorimetrically in a series of partially neutralised telluric acid solutions. The value so determined, *viz.*, 7·68, shows that the tungsten electrode functions satisfactorily in these solutions :

Fraction neutralised	0·125	0·25	0·375	0·50	0·625	0·75	0·875
p_H	6·75	7·20	7·52	7·75	7·85	8·20	8·50
p_{K_1}	7·60	7·68	7·74	7·75	7·63	7·72	7·65

Mean value for $p_{K_1} = 7·68$.

In the case of tellurous acid, 100 c.c. of 0·03M-potassium tellurite were back-titrated with 0·24N-hydrochloric acid; the solution remained clear until 1 equiv. of acid had been added, after which a white precipitate, probably of hydrated tellurium dioxide was formed, precipitation being complete when 2 equivs. of acid had been added. The course of the titration followed the characteristic curve of a dibasic acid, except at the extreme end, where the *E.M.F.* of the tungsten electrodes suddenly assumed a positive value, corresponding to an impossible p_H value. An attempt to calculate p_{K_2} from the first half of the curve gave values ranging from 10·00 to 11·50. These values are of the correct order, being similar to that, *viz.*, 10·22, which we have determined colorimetrically. Conductometric titrations by Blanc (*J. Chim. physique*, 1920, **18**, 8) gave the values $p_{K_1} = 2·52$ and $p_{K_2} = 7·70$ for this acid, the latter value being obviously in error.

Maleic and cinnamic acids were chosen for titration because they are unsaturated and render the hydrogen electrode inapplicable. The former gave a good curve, from which it was possible to calculate values for both p_{K_1} and p_{K_2}. Comparison of these with the published values show that they are approximately correct, although, since it relates to the region p_H 1—2, the first constant is not considered trustworthy.

The titration of cinnamic acid followed an altogether abnormal curve, but the end-point was correctly indicated by the usual sudden inflexion.

TABLE II.

Acids to which the hydrogen electrode is inapplicable.

				Previous values.		
Acid.	Electrode.	Mean p_K.	p_K range.	p_K.	Method.	Reference.
HCN	*a*	10·38	10·05—10·48	9·35	Indicator	Britton and Robinson (this vol., p. 469)
	b	10·00	9·75—10·14	9·60	*E.M.F.*	,,
	c	10·22	9·91—10·54	9·41	Vapour pressure	Harman and Worley (*Trans. Faraday Soc.*, 1924, **20**, 502)
HN_3	*a*	5·35	5·01— 5·55	4·74	Conductivity	West (J., 1900, **77**, 705)
	b	5·10	4·97— 5·23	4·59	Glass electrode	Hughes (J., 1928, 491)
	c	5·08	5·04— 5·10	4·92 5·05 5·10	Conductivity	Oliveri-Mandalà (*Gazzetta*, 1916, **46**, ii, 137, 298)
H_2SO_3 p_{K_2}	*a*	8·74	8·48— 9·35	7·00	Indicator	Kolthoff (*Z. anorg. Chem.*, 1920, **109**, 69)
	b	9·17	9·03— 9·39	7·74	*E.M.F.*	Britton and Robinson (*loc. cit.*)
	c	8·82	8·71— 8·94			
H_2TeO_4 p_{K_1}	*a*	7·55	7·51— 7·60	7·84	,,	,,
	b	7·06	7·00— 7·10			
	c	7·43	7·35— 7·50			
Maleic acid p_{K_1}	*a*	2·01	1·75— 2·42	1·34	,,	Mizutani (*Z. physikal. Chem.*, 1925, **118**, 318)
	b	1·98	1·81— 2·13			
	c	2·15	1·97— 2·31			
Maleic acid p_{K_2}	*a*	6·47	6·34— 6·62	6·94	,,	Mizutani (*loc. cit.*)
	b	6·44	6·30— 6·52	6·29	,,	Larsson (*Z. anorg. Chem.*, 1924, **140**, 292)
	c	6·04	5·92— 6·10			

Britton and Robinson (J., 1930, 1261; this vol., p. 458) attempted the titration of sodium orthovanadate with hydrochloric acid, using the hydrogen, oxygen, and antimony electrodes, but were unable to obtain satisfactory results. The tungsten electrode also proved useless.

It has been found that no p_H values could be extrapolated from the oxygen electrode titration curve of silver nitrate with caustic soda (Britton, J., 1925, **127**, 2148). With the tungsten electrode the inflexions were also clearly defined, but the *E.M.F.*'s too were out of harmony with the calibration curve. The behaviour of the antimony electrode was similar. The foregoing observations together with the data in Table II reveal that solutions containing readily oxidisable or reducible substances may seriously interfere with the electrodic reaction and so lead to *E.M.F.*'s that are not in accord with the calibration curve determined in the manner here adopted. As the p_K values corresponding to each titration are fairly consistent, it would appear possible that the tungsten electrode might be calibrated for the particular solution in which it is to be used, but this point has not been pursued.

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[*Received, January* 21*st*, 1931.]