4. *Electrometric Studies of the Precipitation of Hydroxides. Part VIII. Standardisation of Acid Solutions by Means of Mercuric Oxide.*

By H. T. S. Britton and Beatrice M. Wilson.

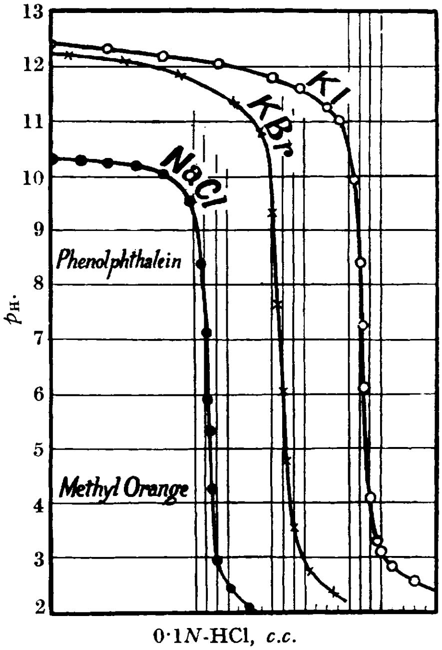
Rosenthaler and Abelmann (*Pharm. J.*, 1913, **91**, 144) and Incze (*Z. anal. Chem.*, 1917, **56**, 177; 1918, **57**, 176) have shown that mercuric oxide dissolves in concentrated potassium iodide solutions to form an exactly equivalent amount of alkali, which can be titrated by acids with methyl-orange, methyl-red, or phenolphthalein. It was shown in Part VII (J., 1932, 2553) that alkali had no effect on the HgI_4'' anion, and hence it would appear that the method depends upon the reaction $HgO + 4KI + H_2O \longrightarrow K_2HgI_4 + 2KOH$. Glass-electrode titration curves of such solutions have confirmed this view. We have also shown that owing to the formation of the complex anion $HgCl_4''$, the p_H of alkali precipitation from mercuric chloride depends on the amount of alkali chloride in the solution; in fact, if a sufficiently high proportion of alkali chloride is present, the p_H becomes very high and comparatively little precipitation ensues.

Mercuric bromide solutions suffer some precipitation with alkali at about p_H 10, but, by including some potassium bromide in the solution, it is possible entirely to prevent precipitation (cf. Bugarszky, *Z. physikal. Chem.*, 1893, **11**, 668; **12**, 223). It appeared probable, therefore, that concentrated solutions of either alkali chlorides or bromides would also dissolve mercuric oxide and yield equivalent amounts of alkali, which could be used to standardise acid solutions. With chlorides, saturated solutions are necessary, but with bromides, concentrations of 1—1·5*M* suffice.

A glass-electrode titration with 0·04*N*-NaOH of 100 c.c. of 0·005*M*-$HgBr_2$ + 0·25*M*-KBr gave no ppt., and the p_H values obtained were only slightly below (within 0·5 p_H unit) those which would have been produced if no alkali had reacted. With still larger proportions of KBr, practically no decomp. of the complex anion $HgBr_4''$ occurred.

In order to ascertain the precise nature of the reactions underlying such titrations, a series of glass-electrode titrations have been performed. Fig. 1 gives the final portions of three titration curves of 100 c.c. of solutions (1) 0·1*M*-KI + 0·4348 g. of HgO, (2) 1·5*M*-KBr + 0·4348 g. of HgO, (3) satd. NaCl + 0·2709 g. of HgO. The HCl solution employed was approx. 0·1*N* in each case. The HgO was dissolved by heating. The curves marked KI and KBr are very similar to those of the neutralisation of KOH with HCl, the difference being that the curves at the inflexion points are slightly more inclined than in the case of direct alkali–acid titration curves. The first section of the NaCl curve reveals that only a small portion of the NaOH was liberated in the solution, evidently owing to some alkali having entered into equilibrium with the $HgCl_4''$ anions, probably thus: $2NaOH + HgCl_4'' \rightleftharpoons Hg[(OH)_2Cl_2]'' + 2NaCl$.

FIG. 1.



On the progressive addition of HCl, the free alkali is neutralised and the complex anion, $HgCl_4''$, re-formed, for it happens that the amount of HCl required to bring the solution to the change-point of methyl-orange was exactly 2 equiv. A similar explanation would also account for the slopes of KI and KBr curves in the vicinity of the end-point. In each titration the end-point was correctly indicated by means of methyl-orange, though, as the curves show, phenolphthalein gave titres that were too low.

If KI is used, only a little more than is indicated by the equation is necessary. On dissolving 0·4 g. of HgO in 10 c.c. of KI solutions, containing amounts of KI ranging from 2 to 10 g., it was found on titration with 0·1*N*-HCl that phenolphthalein yielded results which were on the average 2·5% too low, whereas methyl-orange gave accurate results.

HgO also dissolves in KCN aq. with quantitative liberation of KOH: $HgO + 4KCN + H_2O \longrightarrow 2KOH + K_2Hg(CN)_4$. The validity of this reaction has been proved by glass-electrode titrations with HCl, but, owing to the excess of KCN present, and the fact that the replacement reaction of HCN by HCl takes place between p_H 11·3 and 7·3 (see Britton and Robinson, *Trans. Faraday Soc.*, **1932**, **28**, 531), the inflexion produced on the neutralisation of the liberated alkali is not sufficiently well-defined to permit of its accurate estimation by glass-electrode titration.

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