

XXXVIII.—*Hydrogen Electrode Studies of the Reactions between Solutions of Salts of Weak Metallic Bases and the Acetate, Oxalate, and Tartrate of Sodium, with a Note on the Effect of Dextrose on Zirconium Chloride Solution.*

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It has been shown (this vol., p. 125) that in the reactions between certain metallic salts and the alkali-metal salts of very weak acids (chromic [second stage], boric, and carbonic), basic substances separate when the solutions attain the p_H at which the respective hydroxides are precipitated.

The present paper deals with the reactions of the sodium salts of moderately weak acids, weak at least in respect of one stage of ionisation, with solutions of salts of weak bases and of bases which form "soluble basic salts." Sodium tartrate was one of the salts selected, first because of the comparative weakness of the acid and secondly because it was thought that the titrations might give some insight into the nature of complex tartrate solutions. Titrations with the hydrogen electrode have also been made of zirconium chloride solutions containing dextrose and alkali, in order to study the function of the hydroxy-group in these complex solutions.

All the electrometric titrations now recorded were performed with the hydrogen and normal calomel electrodes described in J., 1924, **125**, 1576; 1925, **127**, 2111.

I. *Sodium Acetate Titrations.*

As acetic acid has a small dissociation constant, 1.8×10^{-5} , it was thought that the hydrion concentrations produced during some reactions would be so low that the p_H would not be attained at which the hydroxides are precipitated, and it was expected, therefore, that basic acetates would be obtained from solutions of salts of the weakest bases.

Zirconium.—A solution of zirconium oxychloride, $ZrOCl_2$, slowly yields a precipitate on treatment with sodium acetate, but no pre-

cipitate is produced if there has been added to the solution the quantity of hydrochloric acid corresponding with the formula $ZrCl_4$.

The solubility of freshly precipitated zirconium hydroxide in acetic acid is inconsiderable; and this is in accord with hydrogen-ion requirements, for zirconia is precipitated from chloride or sulphate solution (J., 1925, 127, 2135, 2138) before the hydron concentration has been reduced to 10^{-2} , which acetic acid can barely acquire even in concentrated solution. Also it is not surprising that the zirconium tetra-acetate prepared (Rosenheim and Hertzmann, *Ber.*, 1907, 40, 810) by dissolving anhydrous zirconium chloride in boiling anhydrous acetic acid hydrolyses completely and rapidly in water.

FIG. 1.

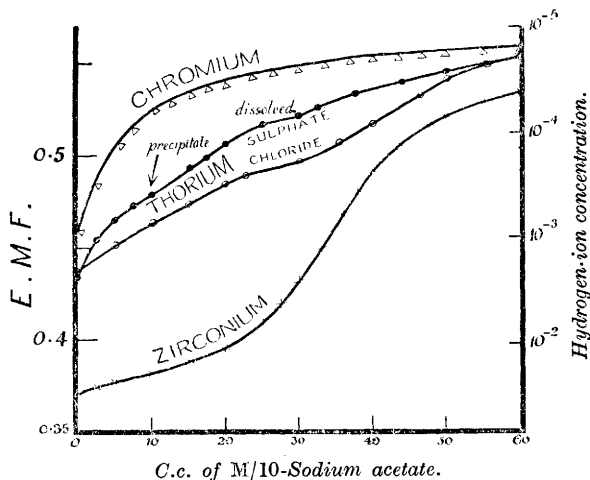


Fig. 1 shows the titration curve of 100 c.c. of $M/100$ -zirconium chloride and $N/10$ -sodium acetate at 18° . The solution remained clear throughout the titration. The extent to which the sodium acetate reacted with the zirconium chloride may be deduced from the hydrogen-ion concentrations of the solution when more than 40 c.c. (*i.e.*, 4 mols. of $NaAc$: 1 mol. of $ZrCl_4$) of sodium acetate had been added. These are in Table I, E being the $E.M.F.$ of the hydrogen electrode measured against a N -calomel electrode.

TABLE I.

C.c. of $N/10$ - $NaAc$.	E .	p_H .	p_H calc.
40	0.392	3.62	3.15
60	0.536	4.38	4.34
80	0.553	4.69	4.64
100	0.560	4.80	4.81

The values given in the last column were calculated on the assumption that no acetic acid had combined with the zirconium hydroxide, the reaction supposed to have taken place being $ZrCl_4 + 4NaAc + 4H_2O \rightarrow Zr(OH)_4 + 4HAc + 4NaCl$, and that the hydrogen-ion concentrations of the solution were due to the equilibria between these ions, the acetate ions from the sodium acetate (taken as 79% dissociated), and the acetic acid.

The agreement between the calculated and the observed values of p_H for additions of 60, 80, and 100 c.c. of sodium acetate seems to confirm the view that the solution, although quite clear, must have contained uncombined zirconium hydroxide. There is, however, no agreement between the values of p_H for the addition of 40 c.c. of sodium acetate; the higher, observed p_H is probably to be attributed to the presence of undecomposed sodium acetate, and not merely to the dissociation of all the acetic acid shown in the equation. It has been found from an acetic acid titration curve (see Prideaux, "Theory of Indicators," 1917, p. 226) that the observed value of p_H is 3.62 for an acetic acid solution which has been neutralised to the extent of 9% by sodium hydroxide. (In titrations of dilute solutions of weak acids the concentration of the solution has very little effect on the p_H ruling during the major part of the titration, the variations in p_H occurring at the beginning and the end.) In the zirconium titration, this proportion of acetic acid neutralised corresponds to 3.6 c.c. (*i.e.*, 9% of 40) of *N*/10-sodium acetate having remained unattacked, and therefore the reaction at this stage may be represented by the following scheme, 4 mols. of sodium acetate having been added to 1 mol. of zirconium chloride: $4NaAc + ZrCl_4 + 3.64H_2O \rightarrow ZrCl_{0.36}(OH)_{3.64} + 3.64HAc + 0.36NaAc$. A highly basic zirconium chloride was therefore present in the solution. Its composition happens to be similar to that of the basic zirconium chloride, $ZrCl_{0.5}(OH)_{3.5}$, present during the greater part of the alkali titration of zirconium chloride solution (J., 1925, 127, 2135).

The agreement of the observed with the calculated value of p_H obtained when an excess of sodium acetate had been added shows that the chloride which had earlier been attached to the zirconium hydroxide reacted with sodium acetate. It seems evident that the zirconium hydroxide was present in the solution in a colloidal state, although the solution was clear, probably owing to some slight solvent action of the acetic acid. Boiling brought about its slow decomposition.

The titrated solution was precipitable with alkalis, a precipitate first appearing when 1.2 equivalents of *N*/10-sodium hydroxide had been added.

Thorium.—Under certain conditions, sodium acetate produces a precipitate from thorium sulphate solutions, but not from those of thorium chloride. Two hydrogen electrode titrations were carried out, one of 100 c.c. of 0.01*M*-thorium chloride and the other of 100 c.c. of 0.01*M*-thorium sulphate, with *N*/10-sodium acetate. The curves are given in Fig. 1. Precipitation from the sulphate solution began when 10 c.c. of sodium acetate had been added and p_H 3.4 attained (the precipitation value of p_H is 3.5 for thorium hydroxide) and appeared to be at a maximum when 25 c.c. had been added, but after the addition of 30 c.c. the precipitate, which was chiefly basic sulphate, dissolved and a clear solution was obtained. No trace of a precipitate formed in the thorium chloride solution under these conditions. The two titration curves converged at 60 c.c. and then became coincident, at least during the addition of the next 40 c.c. of sodium acetate.

The changes in hydrogen-ion concentration which occurred after 60 c.c. of sodium acetate had been added are indicated by the data : 80 c.c., p_H 4.97 ; 100 c.c., p_H 5.15, and were such as would be caused by the presence of acetic acid in amounts varying from 1.5 to 1.9 equivalents per one atom of thorium. It appears, therefore, that the thorium hydroxide present in these solutions was associated with at least 2 equivalents of acetate radical. The fact that the solutions were quite clear, although the precipitation value of p_H , 3.5, for the hydroxide had been exceeded, seems to indicate that the thorium-ion concentration had become considerably reduced by the change which had taken place in the solution, a change which might have been due to the formation of complex ions, or, perhaps more probably, to the formation of basic thorium acetate micelles which were capable of undergoing a different kind of ionisation.

The precipitate Haber obtained by boiling a thorium chloride solution with sodium acetate (*Monatsh.*, 1897, **18**, 687) is interesting, in that it contained 2 equivalents of acetate to one atom of thorium.

The precipitation of basic thorium sulphate from thorium sulphate solutions by sodium acetate seems to be accounted for by the tendency of sulphates of weak bases to form fairly stable basic sulphates in solution (compare zirconium sulphate, *J.*, 1925, **127**, 2140). The sodium acetate added to the 0.01*M*-thorium chloride solution had a continuous hydrolysing action, shown in the curve by the greater hydrogen-ion concentrations ruling during the early part of the reaction, whereas when it was added to the thorium sulphate solution hydrolysis was somewhat impeded, with the result that basic thorium sulphate was precipitated.

Acetic acid may have some solvent action on thorium hydroxide, for the hydrogen-ion concentrations of dilute solutions of the acid

are a little greater than that at which thorium hydroxide is normally precipitated (p_H 3.5). This solvent action may be responsible for the holding of thorium hydroxide in solution at a p_H greater than 3.5, by causing, through the formation of comparatively inert basic thorium acetate micelles, the concentration of thorium ions to be so reduced that the solubility product of thorium hydroxide is not exceeded.

Chromium.—Substances containing chromium and the acetate radical have been the subject of many investigations, chiefly by Weinland and his collaborators (see Weinland, "Einführung in der Chemie der Komplex-Verbindungen," Stuttgart, 1919). Their chief interest lies in the remarkable colour changes which they exhibit on becoming more and more basic; *e.g.*, the green solution of chromium acetate itself, on addition of alkali, may remain green or become red or reddish-violet according to conditions such as time of keeping or of boiling (compare Recoura, *Compt. rend.*, 1899, **129**, 158, 208). Weinland and Büttner (*Z. anorg. Chem.*, 1912, **75**, 293) claim that these colours are due to salts of one or more complex "acetato-chromium" bases, whose constitutions are supposed to be accounted for by the co-ordination theory. The fact that these so-called bases, although essentially basic substances, contain varying amounts of acetate, *viz.*, 2.67, 2.33, 2.17, 2, or 1.5 equivalents of acetate for each atom of chromium, suggests that the colours may be due to the basic acetates themselves, and this view is supported by the experiments now to be described.

The curve in Fig. 1 represents the titration of 100 c.c. of 0.01M-chrome alum with *N*/10-sodium acetate. The p_H , which was 4.80 when 60 c.c. of sodium acetate had been added, became, on addition of 100 c.c., 5.02, and only just fell short of the precipitation value (5.34) for the hydroxide. The failure of the sodium acetate to produce a higher p_H after the theoretical quantity (60 c.c.) had been added was due to the "buffering" effect of the liberated acetic acid. It was pointed out in previous papers that in salts of chromium with strong acids one equivalent of the acid radical is loosely bound and reacts with alkali-metal salts of weak acids as if it were free acid, liberating an equivalent quantity of weak acid. In the present titration, this would correspond to the setting free of 20 c.c. of *N*/10-acetic acid. An idea of the amount of acetic acid actually liberated may be obtained from the fact that the p_H produced on addition of 60 c.c. of sodium acetate was the same as that produced by neutralising 60% of the acid in *N*/10- or *N*/100-acetic acid with sodium hydroxide. It seems certain, therefore, that the solution, besides containing an appreciable amount of free acetic acid, contained also basic chromium acetate aggregates capable of supplying

acetate ions to the solution. The solution remained green throughout the titration and was precipitated by alkalis, but the precipitate redissolved on addition of less alkali than would have been necessary had the precipitate been obtained from a solution of a chromium salt of a strong acid.

Chromium combined with acetic acid sometimes resists precipitation by alkalis. This property depends on the treatment to which the solution has been subjected, as may be seen from the data in Table II: under *a* is the number of c.c. of *N*/10-sodium acetate that were added to 10 c.c. of *M*/10-chrome alum, and in the last two columns are the equivs. of *N*/10-sodium hydroxide (per 1 atom of chromium) that were required to produce (*b*) a precipitate and (*c*) neutrality to phenolphthalein.

TABLE II.

<i>a</i> .	Remarks.	Colour.	<i>b</i> .	<i>c</i> .
60	Violet chrome alum solution used, and mixed at room temperature.	Green.	0.64	2.81
„	Green chrome alum solution, mixed at room temperature.	„	1.18	2.67
„	Reactants mixed, boiled, and cooled to room temperature.	Purplish-green.	No ppte.	1.89
„	Alkali added to boiling reactants.	Green.	2.21	2.21 to 2.80
„	Reaction mixture on protracted boiling became completely precipitated as basic acetate.	Solution colourless.	—	2.51
„	Violet chrome alum; mixture kept for 24 hours.	Bluish-red.	1.76	2.38
120	„	Purple.	No ppte.; solution green.	2.11
„	Mixture boiled for 20 minutes and kept for 24 hours.	Green.	No ppte.	2.22

It will be noticed that in one case prolonged boiling caused basic chromium acetate to be precipitated completely; 2.51 equivs. of acetic acid remained in the solution, and therefore the composition of the precipitate was $\text{CrAc}_{0.49}(\text{OH})_{2.51}, x\text{H}_2\text{O}$. In three instances, solutions were obtained which were non-precipitable with sodium hydroxide; one of these, which contained a larger proportion of sodium acetate, was purple and had been rendered non-precipitable merely by keeping, the other two had been rendered so by initial boiling. The amounts of alkali required to make the three solutions alkaline to phenolphthalein, being approximately 2 equivalents to one atom of chromium, suggest that about 1 equivalent of acetate radical was linked to the chromium hydroxide in an inert manner,

probably in a colloidal complex. The reaction which took place while the chromium solution was thus changed by boiling may perhaps be represented by the following equation: $\text{Cr}_2(\text{SO}_4)_3 + 6\text{NaAc} + 2x\text{H}_2\text{O} = 2\text{CrAc}_{(3-x)}(\text{OH})_x + 2x\text{HAc} + 3\text{Na}_2\text{SO}_4$. The data in the table show that the value of x in the basic complex, after any acid this may have set free by hydrolysis had been neutralised, varied from 1.89 to 2.22.

A further electrometric titration was carried out to ascertain whether the acid liberated in the formation of the basic complex was a complex acid or merely acetic acid. A mixture of 120 c.c. of $N/10$ -sodium acetate with 10 c.c. of $M/10$ -chrome alum was rendered non-precipitable by boiling for 5 minutes, and the reddish-violet solution cooled to 18° . The *E.M.F.* of the hydrogen electrode, compared with the N -calomel electrode, was 0.551 volt, and therefore p_{H} was 4.64. The first section of the curve representing the titration with $N/10$ -sodium hydroxide was similar to that of acetic acid, and the free acid became neutralised when 46.8 c.c. of alkali had been added. The solution remained violet throughout the titration, but the violet solution to which 60 c.c. of $N/10$ -sodium hydroxide had been added appeared colloidal after 24 hours, and was precipitated on continued boiling. If the basic acetate complex did not undergo any hydrolysis during the titration, the free acid was equivalent to 46.8 c.c. of $N/10$ -acid and the excess of sodium acetate to 60 c.c. of $N/10$, 13.2 c.c. of $N/10$ -sodium acetate having been decomposed. The sodium acetate being assumed to be 79% ionised, and the free acid to be acetic ($K = 1.8 \times 10^{-5}$), the hydrogen-ion concentration of the solution should have been $10^{-4.74}$, which is in fair agreement with the observed value. The experiment seems, therefore, to confirm the view expressed by the equation.

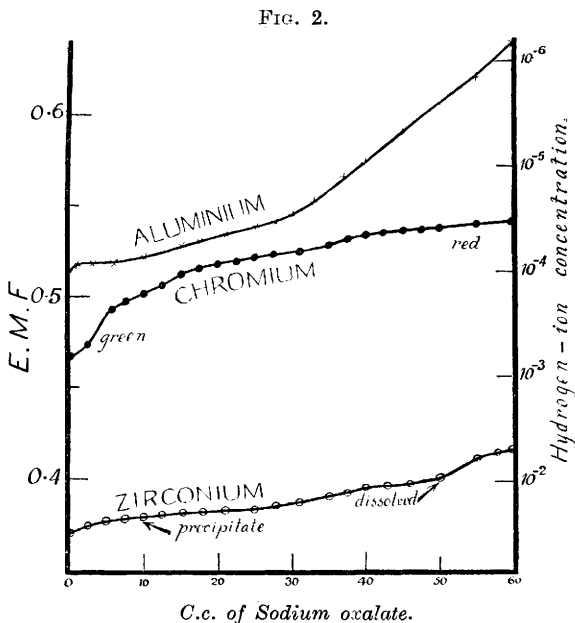
When the solution is rendered inert to alkalis merely by keeping, the hydrolysis is not so marked, and probably much of the acetic acid is in a state of loose combination. The change that renders the basic chromium acetate complex inert is probably similar to that which chromium hydroxide undergoes slowly on keeping, and rapidly on boiling, in contact with its mother-liquor. The hydroxide becomes considerably less reactive and requires an appreciable time for dissolution in acids. If the basic chromium acetate complexes are colloidal, they may undergo some ageing or stabilising process and their size may have some effect on the absorptive power for light which modifies the colour of the solution.

II. Sodium Oxalate Titrations.

Oxalic acid is a strong acid in regard to its first stage of ionisation, but fairly weak in respect to its second stage, K_2 being 1.3×10^{-4}

(J., 1925, 127, 1905). The titrations described in this section were therefore carried out to see if the latter had any influence on the reactions between sodium oxalate and salts of weak bases. It is significant that the hydroxides which are generally supposed to enter into complex formation with oxalates are weak bases, all of which are precipitated by alkalis from solutions whose hydron concentrations are greater than 10^{-7} (compare Schäfer and Abegg, *Z. anorg. Chem.*, 1906, 14, 293).

Zirconium.—As zirconium hydroxide is ordinarily precipitated from solutions whose hydrogen-ion concentrations are greater than



10^{-2} , it was considered that the hydrogen-ions arising from the second dissociation of oxalic acid would be too few to affect the dissolution of the hydroxide.

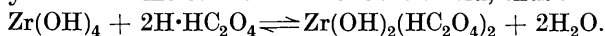
The reaction between 100 c.c. of $M/100$ -zirconium chloride and $N/10$ -sodium oxalate was studied by means of the hydrogen electrode. The variation in hydrogen-ion concentration is given in Fig. 2. A gelatinous precipitate appeared when 10 c.c. of sodium oxalate had been added, and precipitation was at a maximum with 40 c.c., after which the precipitate began to dissolve; the solution became quite clear again on addition of 50 c.c. The precipitate obtained when 20 c.c. of sodium oxalate had been added had the composition $Zr(OH)_{2.69}(C_2O_4)_{0.69} \cdot xH_2O$. The precipitates obtained by Venable

and Baskerville (*J. Amer. Chem. Soc.*, 1897, **19**, 11) on treating zirconium chloride solutions with a saturated solution of oxalic acid had the compositions $\text{Zr}(\text{OH})_{2.67}(\text{C}_2\text{O}_4)_{0.67}$ and $\text{Zr}(\text{OH})_{2.4}(\text{C}_2\text{O}_4)_{0.8}$.

The complex formed on re-solution of the basic zirconium oxalate was not readily precipitated with alkalis: *e.g.*, the acid liberated by the interaction of 100 c.c. of *M*/100-zirconium tetrachloride and 100 c.c. of *N*/10-sodium oxalate was neutralised (phenolphthalein) by 35.3 c.c. of *N*/10-sodium hydroxide without a precipitate forming, and indeed only a slight opalescence was produced when sufficient alkali had been added to convert all the zirconium salt into the hydroxide and the solution boiled (40 c.c.).

The titration curve shows that a large concentration of hydrogen ions persisted throughout the whole reaction, p_{H} being 2.32 at 60 c.c., 3.10 at 80 c.c., and 3.64 at 100 c.c. There occurred a small inflexion just after 50 c.c. of sodium oxalate had been added, which indicated the stage at which oxalate ions had been added in an amount just sufficient to combine with the hydrogen ions from the first stage of dissociation to form $\text{HC}_2\text{O}_4'$ ions (compare oxalic acid titration curve, *loc. cit.*). Thereafter the hydrogen-ion concentration arose from the ionic equilibrium $\text{HC}_2\text{O}_4' \rightleftharpoons \text{H}^+ + \text{C}_2\text{O}_4''$.

The zirconium hydroxide is present in the oxalate solution probably in the colloidal state, having been rendered so by combination with or adsorption of oxalate ions through the interplay of slight chemical forces. As the first stage of the ionisation of oxalic acid is that of a strong acid, there is reason to believe that this acid would, like hydrochloric or nitric acid, be capable of maintaining zirconium hydroxide in solution. Two molecules of oxalic acid, which on valency grounds should react with zirconium hydroxide to form the unknown zirconium oxalate, $\text{Zr}(\text{C}_2\text{O}_4)_2$, are only capable of reacting as if they were two molecules of a monobasic acid, thus:



The basic zirconium hydro-oxalate, by analogy with the chloride (*q.v.*), would be strongly hydrolysed in solution, giving highly basic hydro-oxalate aggregates which would tend to remain in colloidal solution by virtue of the tendency which they may have to react with the hydrogen ions from the $\text{HC}_2\text{O}_4'$ ions. The fact that sodium hydroxide does not readily precipitate zirconium hydroxide from oxalate solutions seems to show that zirconium ions are absent, or nearly so, from the solutions.

Sodium oxalate when added to a zirconium sulphate solution did not give a precipitate. An attempt was made to follow the changes in hydrion concentration during the addition of sodium oxalate by means of the hydrogen electrode, but the entry of a little potassium chloride, used in the junction liquid, into the zirconium sulphate

solution immediately rendered it precipitable. $M/100$ -Zirconium sulphate (100 c.c.) was titrated and precipitation due to the potassium chloride began, but the precipitate did not redissolve until 85 c.c. of the oxalate solution had been added.

The clear solution obtained by adding sodium oxalate in not too great an excess to a zirconium sulphate solution gave a precipitate on addition of a little electrolyte, *e.g.*, the chloride or nitrate of sodium or potassium.

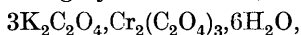
Chromium.—The curve in Fig. 2 is that of the titration of 100 c.c. of $M/100$ -chrome alum with $M/10$ -sodium oxalate. The solution was green initially, but became red towards the end of the titration. The diagram shows a very slight inflexion just after 30 c.c. of sodium oxalate had been added, *i.e.*, 3 mols. $\text{Na}_2\text{C}_2\text{O}_4$ to 1 mol. $\text{Cr}_2(\text{SO}_4)_3$, but the curve does not thereafter assume the upward course which it would take had simple double decomposition taken place. The very gradual diminution in hydrion concentration caused by the addition of sodium oxalate was due to the "buffering" action of the hydro-oxalate ions which had failed to react. The hydrogen-ion concentration at the end of the titration was $10^{-4.4}$, which was greater than the precipitation value, $10^{-5.3}$, for the hydroxide, but gradually approached it when larger quantities of sodium oxalate were employed. The solution to which 60 c.c. of $M/10$ -sodium oxalate had been added was afterwards titrated with $N/10$ -sodium hydroxide by means of the hydrogen electrode. Precipitation began when 1.85 equivalents had been added (p_{H} 5.4); thereafter the alkali caused only a partial precipitation and the graph of the change in p_{H} plotted against the amount of alkali added was rectilinear instead of curved, as is usually the case for precipitation by alkali. The slow change in hydrion concentration appears to have been caused by slight decomposition of the basic complex.

Some experiments were made to ascertain the conditions which rendered the solutions non-precipitable by alkalis. A mixture of $M/10$ -chrome alum (1 mol.) and $M/10$ -sodium oxalate (3 or 6 mols.) at room temperature gave a precipitate on treatment with $N/10$ -sodium hydroxide; but if it had been first boiled and then cooled, no precipitate was obtained. Non-precipitable solutions were also produced by keeping. For example, two solutions, each 250 c.c., containing 30 and 60 c.c., respectively, of $M/10$ -sodium oxalate and 10 c.c. of $M/10$ -chrome alum, were kept over-night; the one containing the larger quantity of oxalate failed to give a precipitate with alkali.

An interesting gradation in colour was observed in a series of solutions, of the same concentration with respect to chrome alum but containing different quantities of sodium oxalate, the smallest

being 3 mols. (to 1 mol. of the sulphate), which had been boiled for the same length of time (a few minutes) and then kept over-night. They were all red in transmitted light, but had a green tinge in reflected light; the redness increased in intensity with increasing molar proportion of sodium oxalate. This may have been due to the effect of the diminishing hydrogen-ion concentration on the basic chromium oxalate complexes, produced by the increasing amounts of sodium oxalate. The solutions gave no precipitate in the cold on treatment with alkali, but a precipitate slowly formed on boiling. If the alkali was added in amounts just sufficient to convert the chromium salt into chromium hydroxide, precipitation took place after about a day. These alkaline solutions were also coagulated by the addition of 2 or 3 c.c. of saturated potassium chloride solution. Solutions which had been rendered non-precipitable by keeping only were very slightly more hydrolysed than the others.

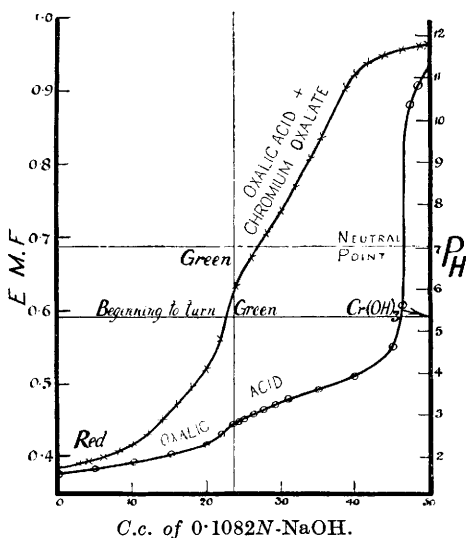
An oxalic acid solution of chromium hydroxide was prepared by boiling a chromic acid solution with oxalic acid until reduction was complete. The solution so obtained was claret-red and was not immediately precipitable by alkalis; on evaporation, it gave a green mass and oxalic acid crystals. From such a solution another was prepared which contained oxalic acid and chromium hydroxide in the proportions required by Werner's hypothetical tribasic chromi-oxalic acid, $H_3[Cr(C_2O_4)_3]$ (*Ber.*, 1912, 45, 3061). The molar ratio may therefore be represented as $3H_2C_2O_4 : Cr_2(C_2O_4)_3$. The quantity of free and combined oxalic acid in 100 c.c. of the solution was equivalent to 51 c.c. of $N/10$ -alkali, and on the latter method of representing the formula one-half of this, 25.5 c.c., may be regarded as combined with the chromium. This solution was titrated with $0.1082N$ -sodium hydroxide at 18° by means of the hydrogen electrode. The titration curve is given in Fig. 3. (The lower curve represents the titration, with the same alkali, of 51 c.c. of $N/10$ -oxalic acid diluted to 100 c.c.) In reply to the objection that such a solution cannot possibly supply any information concerning Werner's hypothetical acid, it may be mentioned that the acid solution has the peculiar properties of Gregory's double salt,



which Werner regarded as a salt, $K_3[Cr(C_2O_4)_3]$, of his complex hypothetical acid and named potassium trioxalochromiate. The titration curve gives no evidence of the existence of a tribasic acid, but is composed of two distinct sections. Although no precipitate formed, it is significant that the claret-red solution began to turn green just when the hydron concentration had become that at which chromium hydroxide is normally precipitated. This suggests that the colour is in some way related to the hydroxide itself.

The fact that the first half of the reaction terminated with an inflexion in the curve and a change in colour seems to be connected with the great difference between the two stages of ionisation of oxalic acid. The simplest explanation is to regard the chromium in the original solution as combined almost entirely with HC_2O_4 radicals, thus: $\text{Cr}(\text{OH})_2 + 3\text{H}\cdot\text{HC}_2\text{O}_4 \rightarrow \text{Cr}(\text{HC}_2\text{O}_4)_3 + 3\text{H}_2\text{O}$. The relatively large hydron concentration could then be accounted for by slight hydrolysis having taken place owing to some little reaction with the hydrons from the hydro-oxalate ions. The first half of the titration would therefore be mainly that of the hydrogen ions from the large amount of HC_2O_4 ions with the added hydroxyl ions, and

FIG. 3.



therefore the range of hydron concentration covered would be approximately that covered in the second half of the oxalic acid titration. The high initial concentrations in the chromium titration being excluded, it will be seen that the two ranges are comparable. When exactly half the theoretical amount of sodium hydroxide had been added, the reaction $3\text{NaOH} + \text{Cr}(\text{HC}_2\text{O}_4)_3 \rightleftharpoons 3\text{H}_2\text{O} + \text{Cr}(\text{NaC}_2\text{O}_4)_3$ may be considered to have taken place, and the second half of the sodium hydroxide would therefore have to react with the double sodium chromium oxalate to form a basic oxalate, probably associated with some sodium. The second portion of the chromium curve shows that only a part of the theoretical amount of the alkali had reacted, for the solution became alkaline on addition of considerably less sodium hydroxide than in the case of the oxalic acid

titration. Therefore, if x be the fraction of sodium hydroxide which had reacted, the reaction may be represented by the equation :
$$\text{Cr}(\text{NaC}_2\text{O}_4)_3 + 3x\text{NaOH} \rightleftharpoons \text{Cr}(\text{OH})_{3x}(\text{NaC}_2\text{O}_4)_{3-3x} + 3x\text{Na}_2\text{C}_2\text{O}_4.$$

The basic chromium oxalate complex is probably capable of ionising, but not so much so that it would produce in the solution the concentration of chromium ions requisite for precipitation. From the titrated solution to which 60 c.c. of 0.1082*N*-sodium hydroxide had been added, *i.e.*, 12.9 c.c. in excess of that required for the complete decomposition of the chromium oxalate, the chromium was completely precipitated after 24 hours, and, like the previous solutions, those which had been rendered just alkaline were also immediately coagulable on addition of a few c.c. of saturated potassium chloride solution and shaking. These observations seem to point to the colloidal nature of the basic oxalate complexes.

The absorption spectra of solutions representing different stages of the titration were examined. The solutions corresponding to the first half of the reaction absorbed light in the red, yellowish-green, and extreme blue regions. The absorption in the blue region was fairly uniform throughout the titration, whereas the absorption band in the green became considerably reduced in the second half. The chief change in absorption appeared suddenly in the red region almost immediately after the middle point of the titration had been passed ; for the solution corresponding to the end of the titration, the band extended over the whole red field and partly into the orange. These absorptions were probably due to the size of the semi-colloidal particles. Lapraik's researches on the absorption spectra of chromium solutions (*J. pr. Chem.*, 1892, **47**, 305) included that of a colloidal solution of chromium hydroxide prepared by dialysing chromium chloride for some months, and also of chromium hydroxide suspended in water. He stated that the close resemblance between the absorption spectra of solutions of chromium hydroxide in several organic acids, including oxalic and some hydroxy-acids, despite the great difference in the molecular complexity of the acids used as solvents, suggested the probability of the absorption spectra being due mainly to the chromium hydroxide or oxide, and not to its compounds with the solvents. This constitutes strong support for the view that solutions of chromium salts of weak acids are essentially colloidal.

E. A. Werner (*J.*, 1904, **85**, 1438) made the interesting observation that chromium hydroxide dissolves in hot oxalic acid solution to the extent required by the formula $\text{Cr}_2(\text{C}_2\text{O}_4)_3$. This, however, is no evidence for the existence of chromium oxalate in the solution, for solutions of the chromium salts of strong acids may be rendered basic beyond the point corresponding with the formula $\text{Cr}(\text{OH})\text{R}_2$,

before any precipitation takes place. Hence in Werner's solution probably little more than the ions from the first stage of the dissociation of the oxalic acid combined with the chromium hydroxide, and this was present largely as a basic chromium hydro-oxalate; a small proportion of the second-stage hydrogen ions may have entered into reaction. Such an explanation would account for the anomalous conductivity data obtained by Rosenheim (*Z. anorg. Chem.*, 1896, **11**, 225) for a solution containing chromium oxide and oxalic acid in the proportion 1 : 3; he could obtain from the data no conclusive evidence that the substance in solution was either a free complex acid or a chromium salt of a complex chromioxalic acid.

The formula of the hypothetical tribasic chromioxalic acid is based on Rosenheim's measurements (*Z. anorg. Chem.*, 1896, **11**, 196, 225; 1899, **21**, 8) of the conductivity of solutions of double oxalates having the formula $3R_2C_2O_4 \cdot Cr_2(C_2O_4)_3 \cdot xH_2O$, where R is K, Na, or NH_4 . Regarding these as complex salts, $R_3[Cr(C_2O_4)_3]$, he found that the difference between Λ_{1024} and Λ_{32} (where Λ is the conductivity of $1/3R_3[Cr(C_2O_4)_3]$)

varied from 32.4 to 35.8 for the three salts, and thence deduced the tribasicity of the complex acid, $H_3[Cr(C_2O_4)_3]$. It may be pointed out that there is no accord between Rosenheim's data for the potassium salt solutions and the earlier values of Kistiakovsky (*Z. physikal. Chem.*, 1890, **6**, 98). Rosenheim's figures also show that the ammonium salt is much more ionised than the potassium salt. The conductivities of the sodium and ammonium salts measured by Burrows and Walker (J., 1923, **123**, 2738) are somewhat lower than those of Rosenheim, but the differences $\Lambda_{1024} - \Lambda_{32}$ are 29.3 and 32.9, respectively. By means of their cryoscopic and conductivity measurements these authors were able to show that in those solutions which were more dilute than 1/16-molar the number of ions into which each molecule of the salt dissociated was greater than 4. They concluded that it is only in comparatively concentrated solutions, greater than $M/10$, that the salt $R_3[Cr_2(C_2O_4)_3]$ dissociates into $3R^+$ and $[Cr(C_2O_4)_3]^{3-}$, and that at higher dilutions either the salt hydrolyses, giving ROH and $H_3[Cr(C_2O_4)_3]$, or the complex anion dissociates still further. The evidence for the existence of the complex tribasic chromioxalic acid is therefore inconclusive.

Some experiments have been carried out on Gregory's salt, $3K_2C_2O_4 \cdot Cr_2(C_2O_4)_3 \cdot 6H_2O$ (*vide* Graham, "Chemical and Physical Researches," Edinburgh, 1876, p. 369). It was obtained in deep blue needles by allowing to crystallise a solution, containing chromic anhydride, potassium oxalate, and an excess of oxalic acid, which had been boiled until the anhydride was completely reduced

[Found : Cr, 10.7; C_2O_4 , estimated by Burrows and Walker's method (*loc. cit.*), 54.1. Calc. : Cr, 10.7; C_2O_4 , 54.2%].

On addition of $N/10$ -sodium hydroxide to an $M/120$ -solution of the salt there was no immediate reaction, as shown by hydrogen electrode measurements, but the red solution on becoming alkaline turned green, and when sufficient alkali had been added to convert the chromium oxalate into chromium hydroxide and the solution kept for 12 hours, it became opalescent and addition of a little potassium chloride caused precipitation. Addition of potassium chloride to a solution rendered just alkaline produced opalescence within a few minutes and the chromium was completely precipitated as the hydroxide in the course of 2 hours.

Werner made use of Gregory's salt in the development of his theory of "mirror-image isomerism." He suggested that the substance, regarded as the salt of a complex acid, should show a type of molecular asymmetry and be resolvable into optically active isomerides. The six molecules of water were regarded as water of crystallisation, and not of constitution as in the case of the hexahydrated chromium chloride. He achieved a fugitive resolution, by means of strychnine, in which water must have played an important part, for the optical activity disappeared much more quickly in aqueous than in acetone solutions. Jaeger (*Rec. trav. chim.*, 1919, **38**, 245) obtained much larger rotations. Rideal and Thomas (*J.*, 1922, **121**, 196) found that the resolved salt on dissolution left a small, insoluble residue. This is surprising in view of the great ease with which the double oxalate dissolves. Their suggestion that the speedy loss in optical activity is due to decomposition of the complex anion into a less complex one seems to be confirmed by the *E.M.F.* measurements of Thomas and Fraser (*J.*, 1923, **123**, 2973).

As water appeared to be the important factor in those optical rotation experiments, measurements have been made with the hydrogen electrode to ascertain if any parallel hydrolytic change occurs. The *P.D.* between a hydrogen electrode immersed in 100 c.c. of water at 18° and the normal calomel electrode, with saturated potassium chloride solution as junction liquid, was measured; 0.8123 g. of Gregory's salt was then rapidly dissolved in the water, and the *E.M.F.* observed every few minutes over a period of several hours. The results, which are in Table III, showed that

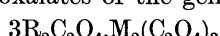
TABLE III.

Mins.	0	5	15	29	41	52
p_H	6.67	7.03	7.05	6.22	5.69	5.64
	(water)					
Mins.	70	93	105	138	180	20 hrs.
p_H	5.56	5.49	5.39	5.36	5.32	5.33

immediately following dissolution the hydrion concentration gradually increased until the p_{H} had become 5.49 (93 minutes); thereafter the change was much slower and the p_{H} became constant (5.33) after 12 hours and remained so during the next 20 hours. This p_{H} happens to be that at which chromium hydroxide is ordinarily precipitated. If the chromium oxalate in the salt were in a condition similar to that of the chromium salts of strong acids, a considerably higher hydrogen-ion concentration would have been produced. On referring to Fig. 3, it will be seen that the p_{H} (6.0) attained when the quantity of sodium hydroxide added was that required to form $3\text{Na}_2\text{C}_2\text{O}_4, \text{Cr}_2(\text{C}_2\text{O}_4)_3$ (indicated by the vertical line through the mid-point) was a little higher than the precipitation p_{H} of chromium hydroxide, probably owing to some decomposition of the oxalate complex having taken place. It therefore seems likely that the existence of the double salt may be due to the two different degrees of reactivity of oxalic acid, and that the change in hydrion concentration that occurs on its passing into solution may be due to the formation of basic complexes as suggested by the solution reaching the precipitation p_{H} of the hydroxide.

The concentration of oxalate ions in these complex salt solutions is small, for calcium chloride fails to give an immediate precipitate. Instead of being due to a complex anion, this may be equally well accounted for by the view now put forward, that the greater part of the oxalate ions is, in effect, removed from the solution in the form of colloidal complexes.

The fact that double oxalates of the general formula



exist, where M may be trivalent iron, chromium, or aluminium, seems to be attributable to the nature of oxalic acid. The bases of these elements are so weak that it is exceedingly doubtful whether they are capable of entering into reaction to form normal oxalates, and yet in conjunction with the alkali metals they form well-defined compounds. There seems to be little doubt that the weak bases enter into combination with the HC_2O_4 -ions, leaving the C_2O_4 ions to the alkali metals.

Aluminium.—The curve in Fig. 2 represents the hydrogen electrode titration of 100 c.c. of 0.005*M*-aluminium sulphate with 0.05*M*-sodium oxalate. No precipitate appeared, although the precipitation p_{H} of aluminium hydroxide was soon exceeded. The curve was only slightly inclined during the addition of the first 30 c.c. of sodium oxalate [*i.e.*, 3 mols. $\text{Na}_2\text{C}_2\text{O}_4$ to 1 mol. $\text{Al}_2(\text{SO}_4)_3$] and the corresponding p_{H} 's differed but slightly from the precipitation p_{H} (4.14) of aluminium hydroxide, which was attained when 10 c.c. of sodium oxalate had been added. This suggests that aluminium

hydroxide, although it was not precipitated, existed in the solution in a more or less nascent state. Also the fact that the sodium oxalate in excess of 30 c.c. produced a gradual change in hydron concentration, instead of an almost instantaneous fall to a concentration of the order produced by free sodium oxalate, shows that equilibria were being set up between the hydro-oxalate ions, which had failed to react with the aluminium hydroxide, and the oxalate ions from the added sodium oxalate. After the addition of 100 c.c. of *N*/10-sodium oxalate, the solution was titrated with *N*/10-sodium hydroxide; it became alkaline to phenolphthalein when 2.13 equivalents of sodium hydroxide (to one atom of aluminium) had been added, but no precipitate formed. Three equivalents of alkali, which were sufficient to convert all the aluminium salt into hydroxide, were then added; a precipitate appeared only after some time.

III. Sodium Tartrate Titrations.

Tartaric acid is comparatively weak in its first stage of ionisation, $K_1 = 1.27 \times 10^{-3}$, and much weaker in its second stage, $K_2 = 9.65 \times 10^{-5}$ at 18° (J., 1925, **127**, 1905). Of the metallic bases studied in these investigations, the only two that give basic tartrates on treatment with sodium tartrate are the very weak bases thoria and zirconia; these also dissolve in excess of the precipitant to give complex solutions which are not precipitable by alkalis. The reactions between zirconium, thorium, aluminium, beryllium, chromium, zinc, and lanthanum salts and *N*/10-sodium tartrate have been followed with the hydrogen and the normal calomel electrode. The titration curves of 100 c.c. of each of the solutions at 18° are in Fig. 4.

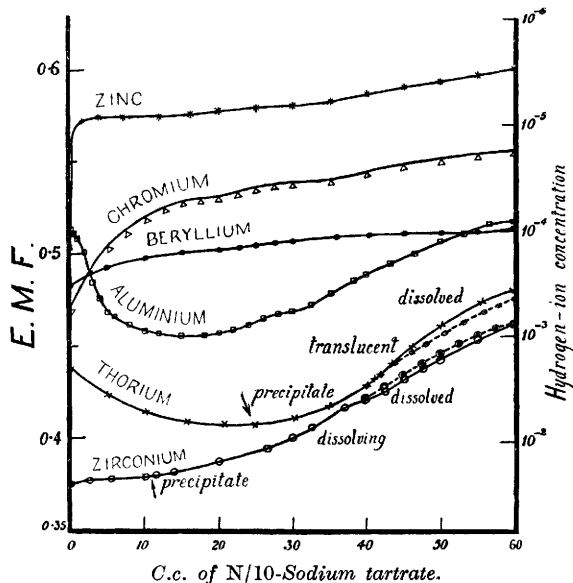
Zirconium.—The curve (Fig. 4) shows the changes in hydron concentration that occurred during the addition of *N*/10-sodium tartrate to 100 c.c. of *M*/100-zirconium chloride. A gelatinous basic tartrate began to be precipitated when 10 c.c. of sodium tartrate had been added (p_H 1.66), but it began to redissolve on addition of 30 c.c. With 40 c.c., the solution was translucent, but became clear with 42.5 c.c.

The precipitate corresponding with the addition of 20 c.c. of *N*/10-sodium tartrate was produced by mixing large volumes of the reactants, the supernatant liquor being poured off, and the precipitate washed by decantation. It passed entirely into a translucent colloidal solution. The precipitate had therefore to be freed from the adhering liquor as completely as possible by pressing between filter-paper; some sodium tartrate, however, remained [Found in the air-dried precipitate: ZrO_2 , 39.7; C (by "wet" combustion with chromic acid), 7.1%]. If the water content is neglected,

the composition of the precipitate may be expressed by the formula $ZrT_{0.45}(OH)_{3.1}$.*

In order to get some idea of the amount of titratable acid in these zirconium tartrate solutions, various quantities of $N/10$ -sodium tartrate were added to 100 c.c. of $M/100$ -zirconium chloride, and the resulting solutions titrated with $N/10$ -sodium hydroxide. The results are in Table IV: a = c.c. of tartrate added, and b and c

FIG. 4.



= c.c. of $N/10$ -alkali required to produce neutrality to phenolphthalein at 18° and 100° , respectively.

TABLE IV.

a	10	20	30	40	60	80
b	33.2	33.1	33.0	33.1	33.2	33.2
c	34.9	34.6	35.0	34.3	34.1	34.2

The alkali produced a precipitate, which did not redissolve, from the solution to which 10 c.c. of sodium tartrate had been added, but the precipitates that formed initially in the 20 c.c.- and 30 c.c.- solutions redissolved when 25 c.c and 14 c.c., respectively, of the alkali had been added. If no hydrolysis of the complex tartrate occurred, the table shows that, no matter how much sodium tartrate

* Throughout this paper T denotes $C_4H_4O_6$.

had been added, the quantity of free acid in the solution at 18° was equivalent to about 33.1 c.c. of *N*/10-sodium hydroxide, or 3.31 equivs. to 1 atom of zirconium. Under these conditions, the simplest formula for the basic complex in these solutions is $\text{ZrT}_{0.35}(\text{OH})_{3.3}$, which is in fair agreement with that obtained for the imperfectly washed, basic precipitate, *viz.*, $\text{ZrT}_{0.45}(\text{OH})_{3.1}$.

To confirm the existence of this complex in solution, and to show that the free acid was tartaric, the following titration was made. The change in hydrion concentration which occurred after 40 c.c. of *N*/10-sodium tartrate had been added was what would be expected to occur on addition of sodium tartrate to a solution containing free tartaric acid only. A solution (140 c.c.) was therefore prepared containing 33.1 c.c. of *N*/10-tartaric acid, which appears to be the amount of acid liberated on addition of the first 40 c.c. of sodium tartrate in the zirconium titration. The *E.M.F.* of the solution, measured with the hydrogen electrode against the normal calomel electrode, was 0.422 volt (the *E.M.F.* for the corresponding stage of the zirconium titration was 0.421 volt). Increasing quantities of *N*/10-sodium tartrate were now added; the voltages obtained are shown in the diagram by the broken line just above the zirconium curve. During the addition of the first 20 c.c. of *N*/10-sodium tartrate, *i.e.*, corresponding to 60 c.c. in the zirconium titration, the broken curve lay at a distance representing 3 millivolts at most from the zirconium curve, but during the addition of the next 40 c.c. (*i.e.*, corresponding with 60 to 100 c.c. in the zirconium titration) the two curves became coincident.

Tartaric acid also precipitates a basic tartrate from zirconium chloride solutions, but a considerably larger excess is required to effect its re-resolution than in the case of sodium tartrate. For example, the precipitate formed when *N*/10-sodium tartrate was added to 100 c.c. of *M*/100-zirconium chloride solution required just over 40 c.c. for both precipitation and dissolution, whereas, when *N*/10-tartaric acid was used, re-resolution did not occur until about 150 c.c. had been added. The precipitate so formed dissolved readily in alkali, and the composition of the soluble complex thereby produced appeared to be the same as that in the sodium tartrate solutions. It may be that re-resolution was actually due to the sodium tartrate which was formed, as may be seen from the following experiment. The heavy, gelatinous precipitate produced by adding *N*/10-sodium hydroxide to a mixture of 100 c.c. of *M*/100-zirconium chloride and 40 c.c. of *N*/10-tartaric acid dissolved when about 45 c.c. had been added, and the solution became alkaline to phenolphthalein with 73.2 c.c., which shows that the composition of the complex must have been $\text{ZrT}_{0.34}(\text{OH})_{3.32}$.

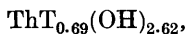
The last column of Table IV shows that the complexes underwent very little decomposition in boiling alkaline solution.

The solubility of the basic zirconium tartrate precipitates in sodium hydrogen tartrate is less than that in the neutral tartrate, but greater than that in the free acid. The limiting amount of sodium tartrate to be added to a zirconium chloride solution to render it non-precipitable by alkali appears to be about 1 molecular proportion. With this proportion, a precipitate is obtained, but it dissolves on the addition of alkali; at a stage, however, before the solution becomes alkaline.

Thorium.—The curve (Fig. 4) represents the titration of 100 c.c. of $M/100$ -thorium chloride with $N/10$ -sodium tartrate. It is remarkable in that it shows that the addition of a normal tartrate rendered the solution more acid and then produced a precipitate. The p_H of the original solution was 2.68, but had fallen to 2.15 on addition of 25 c.c. of sodium tartrate, when precipitation began. By analogy with the formation of other basic precipitates—chromates, borates, and carbonates (Britton, this vol., p. 125)—it would have been expected that the precipitation of a basic tartrate would not have taken place until the precipitation p_H of the hydroxide had been attained, *viz.*, 3.5. A basic tartrate of thorium may also be precipitated by free tartaric acid; precipitation began at p_H 1.75 when 27.5 c.c. of 0.112*N*-tartaric acid were added to 100 c.c. of $M/100$ -thorium tartrate, the large hydron concentration being no doubt due to hydrochloric acid produced by hydrolysis.

The precipitates were flocculent and were not of definite composition. Haber's analyses (*Monatsh.*, 1897, **18**, 687) of precipitates obtained with tartaric acid, the water contents being disregarded, lay between those required for $\text{ThT}(\text{OH})_2$ and $\text{ThT}_{1.33}(\text{OH})_{1.33}$. The basic tartrate produced above from sodium tartrate and thorium chloride contained still less tartrate. The precipitate obtained on addition of 30 c.c. of sodium tartrate was, when air-dried, amorphous and contained 45.51% ThO_2 and 5.69% C (found by "wet" combustion), corresponding to the formula $\text{ThO}_2 \cdot 0.69\text{T} \cdot 11.91\text{H}_2\text{O}$, or, the water content being disregarded, $\text{ThT}_{0.69}(\text{OH})_{2.62}$.

Like basic zirconium tartrate, basic thorium tartrate redissolved when a little more than 40 c.c. of $N/10$ -sodium tartrate had been added, *i.e.*, when the proportion was $2\text{Na}_2\text{T} : \text{ThCl}_4$. The acid liberated in the solution was equivalent to 26.2 c.c. of $N/10$ -sodium hydroxide. Therefore, of the acid initially present as thorium chloride (= 40 c.c., expressed in terms of $N/10$ -acid), 26.2 c.c. had been replaced by hydroxide and 13.8 c.c. by tartrate, and consequently the simplest formula of the basic thorium complex in the solution is



which happens to be also that of the precipitated basic tartrate. If it be assumed that 26.2 c.c. of $N/10$ -tartaric acid were liberated during the interaction of 40 c.c. of $N/10$ -sodium tartrate and 100 c.c. of $M/100$ -thorium chloride, the concentration of the tartaric acid in the 140 c.c. of solution was 9.33×10^{-3} , and K_1 of tartaric acid being taken as 1×10^{-3} (the effect of K_2 is negligible—see J., 1925, 127, 1899), the p_H was 2.51. A solution (140 c.c.) of tartaric acid of this concentration was found, by means of the hydrogen electrode, to have exactly this p_H . The solution was titrated electrometrically with $N/10$ -sodium tartrate; the titration curve, beginning at 40 c.c., is represented by the broken line lying a little below the thorium curve (Fig. 4). The differences in hydrogen-ion concentration shown in the two curves may be due to some interaction between the basic tartrate and the tartaric acid while the former is dissolving.

These solutions did not yield precipitates when treated with alkalis. Non-precipitable solutions could also be prepared by using less sodium tartrate. From the solutions employed in the titrations alkalis produced complete precipitation if 1 mol. or less of either tartaric acid or sodium tartrate had been added for each mol. of thorium chloride. Although $1\frac{1}{3}$ mols. of sodium tartrate produced a precipitate, this dissolved on addition of alkali and the solution became non-precipitable. Basic thorium tartrate, as was the case with the zirconium precipitate, required a considerable excess of tartaric acid to redissolve it, and the basic complex in the acid solution appeared to be the same as that in the sodium tartrate solution.

Rosenheim, Sammter, and Davidsohn (*Z. anorg. Chem.*, 1903, 35, 424), in their investigation on complex thorium tartrates, isolated what they regarded as two series of salts containing the thorium in the anion, *viz.*, $R_2[ThOT_2]$ and $R_2[ThO_2T]$, where $R = K, Na,$ or NH_4 . Some of the products are described as "crusts." They attempted to ascertain which of these two salts existed in solution by determining the proportions of thorium nitrate, tartaric acid, and alkali which produced the maximum optical activity. These were stated to be $Th(NO_3)_4 : 2H_2T : 6ROH$, and therefore the authors concluded that the salt $R_2[ThOT_2]$ was indicated. On recalculation, however, these proportions are found to be in error, approximately 1 mol. of tartaric acid having been required instead of the 2 mols. stated, and the amount of alkali ranging from 5 to 7 mols. These are roughly the proportions required in the formation of 1 mol. of thorium hydroxide and 1 mol. of alkali-metal tartrate (compare the series $R_2[ThO_2T]$, *i.e.*, R_2T and ThO_2). The data of those authors show that such a solution was on the point of precipitation, for when the amount of thorium nitrate was increased in the ratio 8 : 7,

a precipitate appeared. As stated above, solutions of thorium chloride and sodium tartrate in equimolecular proportions fail to give a complex solution.

The amounts of $N/10$ -sodium hydroxide required to neutralise the acid in these complex thorium tartrate solutions, when boiling, were a little greater than those required when the solutions were cold. Whatever the amount of $N/10$ -sodium tartrate that had been added to 100 c.c. of $M/100$ -thorium chloride, approximately 35 c.c. of $N/10$ -sodium hydroxide were required to neutralise the boiling solution, which shows that the basic tartrate complex had slightly hydrolysed to $\text{ThT}_{0.25}(\text{OH})_{3.5}$.

The fact that basic thorium tartrate cannot be redissolved by alkali except in the presence of sodium tartrate suggests that sodium tartrate or partly neutralised tartaric acid is responsible for its dissolution. It can scarcely be attributed to the formation of salts of a complex acid, and yet it seems to be due to some reaction taking place between the basic complex and the tartrate ions when present in sufficiently high concentration. A tartaric acid solution, on being gradually neutralised with alkali, therefore acquires a correspondingly increasing solvent capacity for both basic zirconium and basic thorium tartrates.

Aluminium.—The curve (Fig. 4) represents the titration of 100 c.c. of $M/200$ -aluminium sulphate with $N/10$ -sodium tartrate by means of the hydrogen electrode. Again, an unexpected increase in hydron concentration was shown during the addition of the first 30 c.c. of tartrate solution (= 3 mols.). No precipitate separated and the solution remained clear. Hence, as the sodium tartrate was added, and sodium sulphate thereby formed, a considerable quantity of tartrate ions, instead of combining with the aluminium, was set free to form hydrotartrate ions, some free acid, and a basic aluminium tartrate complex in the solution. The maximum hydron concentration, $10^{-3.02}$, was attained when 15 c.c. of sodium tartrate solution had been added. This concentration was probably due mainly to hydrogen ions from the first-stage dissociation of the tartaric acid, the hydrotartrate ions having reacted with the aluminium hydroxide.

Titration curves were made of the acid liberated in the solutions obtained by adding various quantities of $N/10$ -sodium tartrate to 100 c.c. of $M/200$ -aluminium sulphate. Ten c.c. of sodium tartrate were insufficient to produce a solution non-precipitable by alkali, but when 20 c.c. [*i.e.*, 2 mols. Na_2T for 1 mol. $\text{Al}_2(\text{SO}_4)_3$] or more were used, the solutions became non-precipitable and the amounts of alkali required to produce neutrality to phenolphthalein varied from 2.4 to 2.7 equivalents (for 1Al). In the boiling solutions, 2.8 equivalents

produced neutrality in each case. Therefore both in cold and in hot solutions a little tartrate remained firmly bound to the aluminium hydroxide. These experiments again seem to show that the non-precipitability is due to the existence of stable basic tartrates, the compositions of which, in the solutions studied, varied from $AlT_{0.3}(OH)_{2.4}$ to $AlT_{0.1}(OH)_{2.8}$.

Beryllium.—A small diminution in the hydrogen-ion concentration occurred in the titration of 100 c.c. of $M/40$ -beryllium sulphate with $N/10$ -sodium tartrate. This was not due to the formation of a less hydrolysed beryllium tartrate, for, as is shown by the curve (Fig. 4), no distinct change in hydrogen-ion concentration occurred when the requisite amount of sodium tartrate (50 c.c.) had been added. The small variation in the hydron concentration was caused by equilibria set up between the added tartrate ions and the hydrotartrate ions, which, by failing to react with the beryllium, left it in the solution in the form of a basic tartrate. The high concentration of hydrotartrate ions was evidently due to their incapacity to react with that part of the beryllium hydroxide which gives rise to "soluble basic salts."

Solutions which contained one or more mols. of beryllium sulphate to one of sodium tartrate were completely precipitated by alkali, although solutions containing the reactants in the molar ratio 1 : 2 did not yield precipitates. The amounts of titratable acid in the complex tartrate solutions were approximately 1.53 equivalents for each molecule of beryllium sulphate taken, and consequently the composition of the final basic complex may be expressed by the formula $BeT_{0.24}(OH)_{1.53}$.

Rosenheim and Woge (*Z. anorg. Chem.*, 1897, **15**, 283) and Rosenheim and Itzig (*Ber.*, 1899, **32**, 3424) isolated two series of complex beryllium tartrates having the general formulæ $R_2[Be_4O_3T_2]$ and $R_2[Be_2OT_2]$, where $R = K, Na, \text{ or } NH_4$. The individuality of these salts is questionable. Salts of the former series were obtained by evaporating hydrogen tartrate salt solutions, saturated with beryllium hydroxide, to syrups and allowing these to solidify, whereas salts of the latter series were prepared in the same way with the one exception that the calculated quantities of beryllium hydroxide were used. The salts were either glassy masses or microcrystalline crusts. Complex salts of the first type cannot give rise to non-precipitability, for, as Rosenheim and Woge state, ammonia produces a precipitate. As already mentioned, solutions containing beryllium sulphate and sodium tartrate in the molar ratio 2 : 1, which is that in $R_2[Be_4O_3T_2]$, are precipitable by alkalis. The latter workers have established, by means of the polarimetric method also used in the case of complex thorium tartrate solutions, that the important complex salt in the

solution was this particular compound, $\text{Na}_2[\text{Be}_4\text{O}_3\text{T}_2]$, from a study of solutions containing mixtures of beryllium sulphate, tartaric acid, and sodium hydroxide. The fact that the products which Rosenheim and Woge obtained by saturating solutions of acid salts with beryllium hydroxide should have corresponded to the formula $\text{R}_2[\text{Be}_4\text{O}_3\text{T}_2]$ is of interest in that the products may be considered as being made up of the neutral tartrate, R_2T , and the basic tartrate, $\text{Be}_4\text{O}_3\text{T}_2$, or $\text{BeT}_{0.25}(\text{OH})_{1.5}$, which happens to be almost that suggested by these experiments to be present in the complex solutions.

Chromium.—The curve (Fig. 4) represents the hydrion concentration changes which occurred during the titration of 100 c.c. of $M/100$ -chrome alum with $N/10$ -sodium tartrate. The hydrion concentrations indicate that the amount of hydrotartrate ions liberated was less than that in the case of the corresponding beryllium titration. The difference appears to be accounted for by the fact that, although the precipitation p_{H} , 5.69, of beryllium hydroxide is a little higher than that of chromium hydroxide, 5.34, one-half of the beryllium hydroxide molecule is associated with the formation of soluble basic salts as compared with one-third in the case of chromium, and consequently a larger equivalent amount of acid is rendered available for reaction. The sodium tartrate caused the violet chromium salt solution to turn green.

The formation of complex chromium tartrate solutions which are not precipitable by alkali depends not so much on the amount of sodium tartrate added as on the treatment to which the solutions have been subjected, and in this respect appears to be similar to that of complex oxalate solutions. There is, however, the one difference that whereas oxalate solutions, on prolonged boiling with alkali, yield a precipitate, those of chromium tartrate in general do not. Chromium tartrate solutions, on boiling, become purplish-red, but if they are now treated with alkali at room temperature they turn green as soon as the precipitation p_{H} of the hydroxide is reached. As in the case of oxalate solutions, boiling caused the liberation of acid and the simultaneous formation of inert basic salt.

Zinc.—The curve (Fig. 4) is that of the titration of 100 c.c. of $M/50$ -zinc sulphate with $N/10$ -sodium tartrate. Although the sodium tartrate did not precipitate zinc hydroxide, the hydrion concentration on addition of the first 40 c.c. (when the molecular ratio was $\text{Na}_2\text{T} : \text{ZnSO}_4$) was reduced to nearly the precipitation p_{H} , 5.2, of zinc hydroxide. Titrations were made with sodium hydroxide and phenolphthalein of the acid liberated when varying quantities of $N/10$ -sodium tartrate were added to 100 c.c. of $M/50$ -zinc sulphate; the results are in Table V, where a = mols. of sodium tartrate per

mol. of zinc sulphate, and b and c = equivs. of sodium hydroxide required to produce a precipitate and neutrality, respectively.

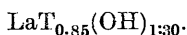
TABLE V.

a	2	2.5	3	4	5
b	0.41	1.00	—	—	—
c	1.14	1.13	1.19	1.14	1.03

The table shows that the minimum quantity of sodium tartrate required to prevent precipitation by alkali was 3 mols. for 1 mol. of zinc sulphate (= 120 c.c.). This quantity is much greater than those required in the case of the weaker bases. Moreover, all the solutions referred to in the table gave a precipitate when boiled with alkali. The change in hydron concentration after 40 c.c. of sodium tartrate solution had been added shows that not all the hydriions of the tartaric acid had reacted, and the amounts of alkali required to neutralise the acid which had failed to react indicate that the compositions of the basic tartrates in the complex solutions varied from $ZnT_{0.49}(OH)_{1.03}$ to $ZnT_{0.41}(OH)_{1.19}$.

Lanthanum.—When sodium tartrate was added to a lanthanum nitrate solution, a white, flocculent precipitate formed at p_H between 6 and 7 [Found in the air-dried precipitate: La_2O_3 , 34.6; C (by "wet" combustion), 15.5. $La_2(C_4H_4O_6)_3 \cdot 12H_2O$ requires La_2O_3 , 34.75; C, 15.4%]. Czudnowicz (*J. pr. Chem.*, 1860, **79**, 39) and Holmberg (*Z. anorg. Chem.*, 1907, **53**, 87) prepared this salt, but based their formulæ on the lanthana content only, and reported that the water corresponded to $9H_2O$. Clève (*Bull. Soc. chim.*, 1874, **21**, 202) stated that the water content of the salt dried in a desiccator was $3H_2O$.

Lanthanum tartrate, although insoluble in water (Rinbach and Schubert, *Z. physikal. Chem.*, 1909, **67**, 192), is so readily soluble in mineral acids that when tartaric acid is added to a solution of a lanthanum salt of a strong acid no precipitate is formed; but one is obtained from a solution of lanthanum acetate. It is also readily soluble in alkalis and dissolves in an excess of sodium tartrate or tartaric acid solution. The following experiments were made to ascertain something of its nature in solution. Lanthanum tartrate was precipitated on addition of 30 c.c. of $N/10$ -sodium tartrate to 30 c.c. of $N/10$ -lanthanum nitrate. The solution became alkaline to thymol-blue on addition of 11.2 c.c. of $N/10$ -sodium hydroxide, and the precipitate completely dissolved on addition of 13 c.c. The amount of alkali required for re-solution shows, if it be assumed that the alkali had been converted into sodium tartrate, that the lanthanum had passed back into solution as a basic tartrate,



In another experiment, 50 c.c. of $N/10$ -sodium tartrate were added to 30 c.c. of $N/10$ -lanthanum nitrate, and the solution containing the suspended precipitate was titrated, by means of the hydrogen electrode, with $N/10$ -sodium hydroxide. The precipitate dissolved at p_H 7.9, when 12 c.c. of alkali had been added, the soluble basic tartrate then being $\text{LaT}_{0.90}(\text{OH})_{1.20}$, but the inflexion indicating the attainment of marked alkalinity did not occur until 14.4 c.c. had been added, and therefore the soluble basic lanthanum tartrate had become slightly decomposed to $\text{LaT}_{0.78}(\text{OH})_{1.44}$. The curve obtained on adding more alkali showed that the basic tartrate was undergoing further decomposition. The following experiment gives some idea of the extent of the decomposition which takes place in alkaline solutions. Lanthanum tartrate (0.1960 g.) was shaken mechanically with 100 c.c. of 0.014*N*-sodium hydroxide for 24 hours; all the tartrate had then dissolved. The solution was titrated by means of the hydrogen electrode with $N/10$ -hydrochloric acid, and the excess of free alkali was equivalent to 6.35 c.c. of the acid. The lanthanum tartrate therefore existed in the alkaline solution as $\text{LaT}_{0.59}(\text{OH})_{1.82}$, and was much more basic than those mentioned above. In this titration, the basic lanthanum tartrate began to be precipitated when the free alkali had just been neutralised, and the p_H then attained was that required for the precipitation of lanthanum hydroxide.

Discussion.

The foregoing investigations show that complex tartrate solutions are essentially basic in nature. This is especially evident in the cases of the complex zirconium and thorium tartrate solutions produced by the re-solution, probably without change in composition, of the basic tartrates first precipitated. Unlike the complex solutions which were sometimes formed with acetates and oxalates, those of the tartrates are extremely stable. The basic tartrates, like the basic aggregates in solution, are strongly resistant to alkalis, which probably explains their non-precipitability by such means.

The existence of these basic tartrate complexes would also account for the properties of Fehling's solution. The fact that the ease of reduction to cuprous oxide is comparable with that of freshly precipitated cupric hydroxide suggests that the condition of the cupric salt in alkaline tartrate solutions is in some way related to that of cupric hydroxide itself, as would obtain in basic tartrate complexes.

The condition of copper tartrate on passing into these complex alkaline tartrate solutions is, at any rate, basic. For example, Kahlenberg (*Z. physikal. Chem.*, 1895, **17**, 586), Masson and Steele (*J.*, 1899, **75**, 725), and Pickering (*J.*, 1911, **99**, 169) found that the quantity of sodium or potassium hydroxide necessary to produce

alkalinity in a solution of copper tartrate varied from 1.25 to 1.36 mols., and therefore the basic complexes in the solutions must have varied from $\text{CuT}_{0.38}(\text{OH})_{1.25}$ to $\text{CuT}_{0.32}(\text{OH})_{1.36}$.

Previous workers attempted to account for the anomalies of complex tartrate solutions by regarding the heavy metal as being present in a complex anion. Masson and Steele obtained a substance, $\text{K}_3\text{Cu}_4\text{C}_{12}\text{H}_7\text{O}_{18}\cdot 5\text{H}_2\text{O}$, by precipitation with alcohol from a copper tartrate solution which had been neutralised with 1.25 equivalents of potassium hydroxide. The substance, which was isolated as a dark blue, gummy mass (and therefore was of questionable character), was in effect composed of $3\text{K}_2\text{T}$ and $8\text{CuT}_{0.375}(\text{OH})_{1.25}$ and was probably a mixture of potassium tartrate with a preponderance of basic copper tartrate. Their migration experiments on solutions of this substance are important in that they show that some copper had passed into the portion carrying the negative charge, but this may have been due equally well to the colloidal nature of the basic copper tartrate as to the presence of a complex copper anion. Pickering also obtained flocculent precipitates from copper tartrate solutions by adding alcohol. The unwashed precipitates (whose constitutions he tried to establish by regarding some of the copper as quadrivalent) contained variable quantities of potassium salt, all of which, together with some copper, could be removed by washing. Wark (J., 1923, **123**, 1815, 1826; 1924, **125**, 2004) has suggested that the complexity of solutions containing copper and malic acid is due to the formation of cuprimalic acid, $\text{HCuC}_4\text{H}_3\text{O}_5$, isomeric with the normal cupric malate.

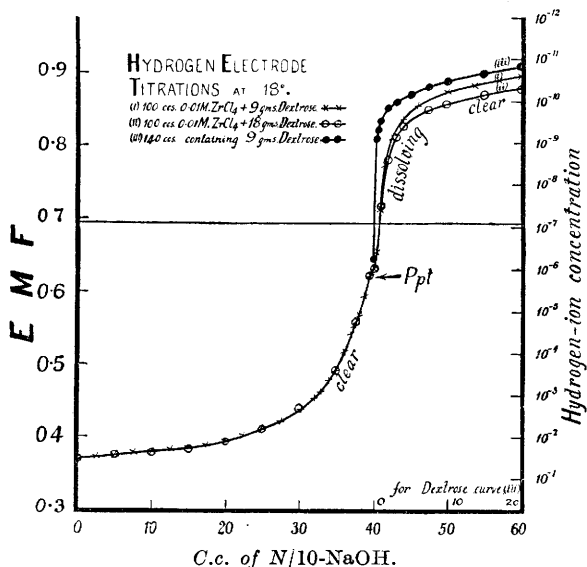
The formation of the complex tartrate solutions of zirconium and thorium by the re-solution of the basic precipitates seems to have been due to the sodium tartrate which was present, although it has not been possible to associate any precise quantity of the latter with that of the respective basic tartrates. Many attempts have been made to account for the complexity of tartrate solutions by assuming that their formation involves reactions with the hydrogen atoms of the hydroxy-groups. It is difficult, however, to imagine that zirconium hydroxide, for example, one of the weakest bases, should be capable of so reacting, when strong bases show so very little aptitude. If the hydroxy-groups of tartaric acid are weakly acidic (their acidity is so small that it is not measurable by any physical method), they might be able to react with metallic bases, provided that the products formed were insoluble and therefore were removed from the sphere of action. Such a condition would probably be satisfied if the bases which had combined passed into the dispersed particles of a colloidal solution.

Many hydroxy-compounds, such as the sugars and glycerol, have

a definite, though very slight, acid character (compare Michaelis and Rona, *Biochem. Z.*, 1913, **49**, 248) and their dissociation constants can be measured. The dissociation constant of glycerol as a monobasic acid at 17.5° is 7×10^{-15} , and, in fact, the presence of glycerol in an alkali solution has a barely measurable effect on the p_H . Yet its effect on a zirconium chloride or ferric chloride solution may be such that alkalis fail to precipitate the hydroxide.

The reaction which must take place between the glycerol and the metallic base provides an explanation of the well-known protective action on ferric oxide hydrosols prepared by dialysis of ferric

FIG. 5.



chloride-glycerol solutions. It is significant, too, that the hydrosols so prepared are clear in transmitted light. The glycerol may retard the growth of the colloidal particles.

If the behaviour of the hydroxy-groups of tartaric and other hydroxy-acids is due to their feebly acid character, then it seems that complex tartrate solutions are essentially protected colloidal solutions. The following electrometric titrations were carried out to test this view. Michaelis and Rona (*loc. cit.*) having shown that dextrose is a stronger acid ($K = 6.6 \times 10^{-13}$; compare Britton, J., 1925, **127**, 1902) than glycerol, it was decided to use the former in the titrations. A solution (100 c.c.), $M/100$ with respect to zirconium chloride and $M/2$ with respect to dextrose (9 g. in 100 c.c.), was titrated with $N/10$ -sodium hydroxide at 18° by means of the

hydrogen and the normal calomel electrode. The curve is shown in Fig. 5, the points obtained being marked by crosses. A very slight opalescence was produced by 38.5 c.c. of the alkali ($p_H = 5.22$), and a precipitate by 39.5 c.c. ($p_H = 5.89$). This began to dissolve when 40 c.c. (*i.e.*, 4NaOH : ZrCl₄) had been added, and the solution was cleared by 50 c.c. In the titration of zirconium chloride solution alone (J., 1925, 127, 2125), the solution first became visibly colloidal with 1.5 equivalents of alkali ($p_H = 1.86$), but in the present titration the effect of the dextrose was manifested in the delay of precipitation until nearly the whole of the alkali required to convert the zirconium chloride into the hydroxide had been added and the hydrogen-ion concentration had become extremely small, *viz.*, 10^{-6} . The fact that the solution remained clear until 3.85 equivalents of alkali had been added suggests that, although the dextrose was incapable of influencing the hydrogen-ion concentration of the solution, it had the effect of repressing the growth of the basic particles below the limit necessary to produce visible colloidal. Table VI, compiled from the observed voltages, shows that during the addition of the first 40 c.c. of alkali the zirconium chloride was more basic than ZrCl(OH)₃. The ionisation of dextrose is much too small to affect the hydrogen-ion concentrations of solutions whose p_H is less than 6, and consequently the hydron concentrations of the basic zirconium chloride solutions have been regarded as coming entirely from the hydrolysed acid.

TABLE VI.

C.c. of N/10- NaOH.	<i>E.M.F.</i>	% Hydrolysis of un- neutralised part.	Atoms of Cl in ZrCl ₄ neutralised.	Composition of basic zirconium chloride. Atoms per 1Zr.		Mols. of free HCl referred to 1Zr.
				Cl.	OH.	
0.0	0.370	77.8	0	0.89	3.11	3.11
55.0	0.374	79.5	0.5	0.78	3.22	2.72
10.0	0.379	79.8	1.0	0.61	3.39	2.39
15.0	0.386	75.7	1.5	0.61	3.39	1.89
20.0	0.395	68.7	2.0	0.63	3.37	1.37
25.0	0.413	46.5	2.5	0.80	3.20	0.70
30.0	0.438	26.8	3.0	0.73	3.27	0.27
35.0	0.491	6.7	3.5	0.47	3.53	0.03
37.5	0.552	1.2	3.75	0.25	3.75	0.003
38.0	0.566	1.1	3.8	0.20	3.80	0.002
39.0	0.598	0.5	3.9	0.10	3.90	0.0005
39.5	0.623	0.4	3.95	0.05	3.95	0.0002
40.0	0.634	0	4	0	4	0

The last column shows that when the solution began to opalesce, with 38.5 c.c. of alkali, the amount of free acid had become negligible. It is remarkable that the dextrose was able to maintain the highly basic zirconium chloride (columns 5 and 6) in a solution which was quite clear. Borax and sodium carbonate also delay precipitation

by alkali until somewhat more than 3 equivalents have been added (this vol., p. 125).

In order to ascertain whether the dextrose had entered into any reaction which might have influenced the p_H of the solution during the re-solution of the zirconium hydroxide in the sodium hydroxide, a solution of 140 c.c. (*i.e.*, the volume of the titrated solution when the stoichiometrical amount of alkali had been added) containing 9 g. of dextrose was titrated with $N/10$ -sodium hydroxide. The data and dissociation constant figures of dextrose as a monobasic acid are given in a previous paper (J., 1925, **127**, 1902). In Fig. 5 the titration curve is the one beginning at 40 c.c. of $N/10$ -sodium hydroxide given at the top of the diagram. By comparing the two curves, it will be seen that the presence of the zirconium hydroxide in the one solution caused a perceptible diminution in p_H , and consequently the hydroxide on dissolution must have combined in some way with the dextrose. It is difficult to understand how the zirconium hydroxide effected this increase in hydrogen-ion concentration. Had it reacted simply with the dextrose to form inert colloidal aggregates, this, in effect, would have been equivalent to the removal of some dextrose from the solution and therefore would have given rise to a diminished hydrion concentration. An increased hydrogen-ion concentration seems to be possible only by assuming that the zirconium hydroxide had, in combining with the dextrose, given rise to a complex acid slightly stronger than dextrose itself. All that the titration can be said to show is that dextrose does enter into some kind of reaction with the zirconium hydroxide in effecting its dissolution in alkali solutions.

A second titration was that of 100 c.c. of $M/100$ -zirconium chloride and $M/1$ -dextrose solution (18 g. in 100 c.c.). The increased amount of dextrose was without further effect during the addition of the first 40 c.c. of alkali, but tended to cause a more rapid re-solution of the zirconium hydroxide as the excess of alkali was added. The data for this curve are indicated by circles in Fig. 5.

Summary.

(1) Sodium acetate at the ordinary temperature fails to precipitate weak bases, although the precipitation p_H 's of the respective hydroxides may be exceeded. An exception is the reaction with thorium sulphate solution. There is good evidence that weak metallic bases exist in complex acetate solutions as basic acetates.

(2) Sodium oxalate produces a basic precipitate from zirconium chloride solution through the incapacity of the hydrions from the second stage of dissociation of oxalic acid to react with zirconium hydroxide, but the precipitate dissolves in excess of the reagent.

The oxalate does not produce precipitates from solutions of salts of slightly stronger bases, *e.g.*, aluminium and chromium hydroxides, even although it is probable that very little reaction can take place between them and the hydro-oxalate ions. Observations on solutions of chromium hydroxide in oxalic acid and of potassium chromium oxalate suggest that both their properties and the existence of the series $3R_2C_2O_4, Cr_2(C_2O_4)_3$ arise from the nature of the reactants.

(3) The reaction of sodium tartrate with salts of thorium and aluminium in solution is remarkable in that increased hydron concentrations are at first produced; in the case of thorium, a basic tartrate precipitate is formed, even although the hydron concentration is considerably higher than that necessary for the precipitation of the hydroxide.

(4) Hydrogen electrode titrations of zirconium chloride solutions containing dextrose with sodium hydroxide show that some reaction must take place between the zirconia and the hydroxy-groups of dextrose.

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