XXII.—*Hydrogen Electrode Studies of the Precipitation of Basic Chromates, Borates and Carbonates.*

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THE work described in earlier papers (J., 1925, **127**, 2110, 2120, 2142, 2148) showed that a characteristic property of a metallic hydroxide is the hydrion concentration at which it separates from solution. The following electrometric titrations have therefore been carried out to see if the hydrogen-ion concentrations at which various basic precipitates are formed could in any way be correlated with the hydrion concentrations at which the respective hydroxides are precipitated.

I. *Basic Chromates.*

These titrations were made at 18° by the method used in the hydroxide investigations (*loc. cit.*) and chromic acid titration (Britton, J., 1924, **125**, 1572). In Table I are the particulars of the solutions and the p_H's at which precipitation took place.

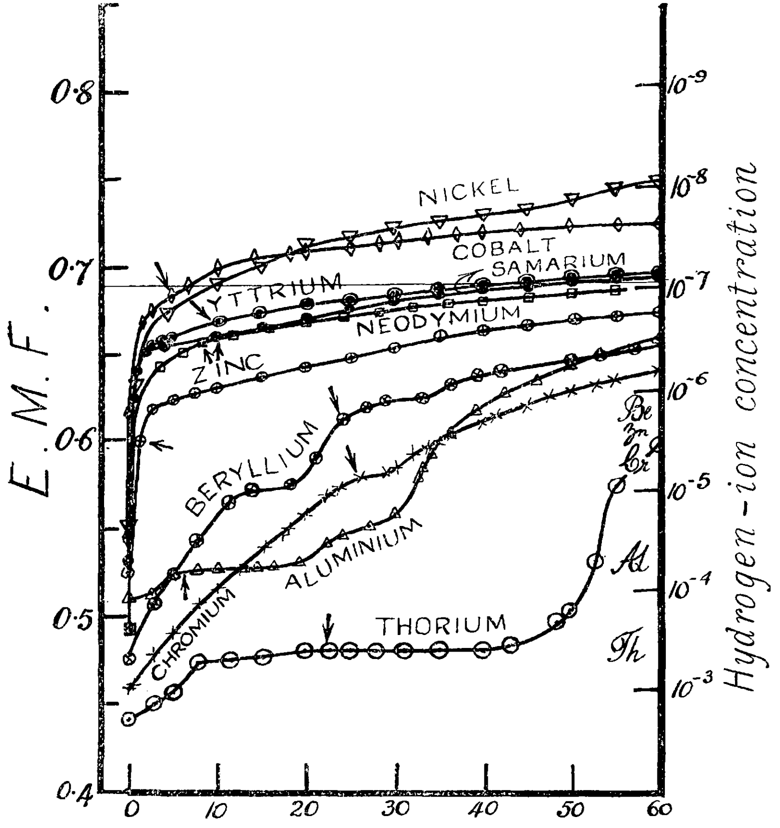
TABLE I.

	Pption of basic chromate began.		Pption of hydroxide began.		
Solution (100 c.c.).	*E.M.F.*	p_H.	*E.M.F.*	p_H.	Pption.
0·01*M*-$ThCl_4$	0·482	3·45	0·484	3·51	Complete
0·00667*M*-$Al_2(SO_4)_3$	0·524	4·18	0·521	4·14	,,
0·01*M*-$Cr_2(SO_4)_3,K_2SO_4$	0·583	5·20	0·591	5·34	,,
0·02*M*-$BeSO_4$	0·613	5·72	0·610	5·69	,,
0·025*M*-$ZnSO_4$	0·600	5·49	0·583	5·20	
0·0132*M*-$Nd(NO_3)_3$	0·657	6·48	0·686	7·00	Partial
0·0133*M*-$SaCl_3$	0·661	6·55	0·676	6·83	,,
0·0133*M*-YCl_3	0·672	6·74	0·674	6·78	,,
0·0247*M*-$CoCl_2$	0·688	7·01	0·676	6·81	,,
0·0200*M*-$NiCl_2$	0·674	6·78	0·666	6·66	Opalescence

M/10-Potassium chromate was used in each titration except that of thorium chloride, in which case the concentration was *M*/20. The data relating to the different hydroxides were taken from the previous papers. The titration curves are given in Fig. 1, the arrows indicating the points at which precipitates first appeared.

Mechanism of the Precipitation of Basic Chromates.—Table I shows that in the majority of the titrations a precipitate did not form until the hydrogen-ion concentration of the solution had become that at which the hydroxide separates. In one or two cases the precipitate first formed was the hydroxide uncontaminated with any chromate. This was particularly the case with aluminium, the initial precipitate being aluminium hydroxide containing some unattacked sulphate. The chief factor controlling the concentration of hydrogen ions is the reaction whereby the acid, produced from the metallic salt by hydrolysis, and the potassium chromate generate hydrochromate ions. The dissociation of these ions is exceedingly small and is rendered still smaller by the increasing concentration of chromate ions from the added potassium chromate. The range of hydrogen-ion concentrations which can be produced in equilibria involving chromate and hydrochromate ions is 10^{-5} to 10^{-8}, as may be seen from the second section of the chromic acid titration curve (Britton, *loc. cit.*). For a considerable range of equilibria the hydrogen-ion concentration remains approximately 10^{-6}. The reason why potassium chromate precipitates basic chromates from salt solutions lies in the inability of the hydrochromate ions to react with the metallic bases and thus maintain them in solution, except in the few instances in which insoluble normal chromates are formed. For example, consider the reactions between freshly precipitated aluminium hydroxide and the hydrochromate ions present in potassium dichromate solutions of different concentrations. It can be shown that the p_H of *M*/10- and *M*/100-$KHCrO_4$ is 3·68 and 4·18 respectively, by assuming the salts to be completely dissociated into $K^{\bullet}$ and $HCrO_4'$, and the latter ions to be dissociated further into an equal number of hydrogen ions and chromate ions. As aluminium hydroxide is precipitated at p_H 4·14, it follows that at the moment of formation of the precipitate the hydroxyl-ion concentration of the solution is $K_w/10^{-4 \cdot 14} = 10^{-10}$. In order that the aluminium hydroxide may react with the hydrochromate ions and consequently dissolve, the hydrochromate ions

FIG. 1.



C.c. $M/10$-K_2CrO_4.
($M/20$-K_2CrO_4 *for thorium curve.*)

must be capable of providing sufficient hydrogen ions to form water with the hydroxyl ions in the solution, *i.e.*, the product [H˙][OH′] must be greater than K_w. If $M/100$-potassium hydrochromate solution be added to freshly precipitated aluminium hydroxide, it will set up a hydrion concentration of $10^{-4 \cdot 18}$, which, being less than the precipitation hydrion concentration, will be incapable of causing solution, or, in other words, [H˙][OH′] will become equal to $10^{-14 \cdot 18}$, a value just less than K_w, $10^{-14 \cdot 14}$. With $M/10$-$KHCrO_4$, $p_H = 3{\cdot}68$, the hydrogen-ion concentration will be less than that necessary for the precipitation of aluminium hydroxide and consequently there will be a tendency for the aluminium hydroxide to dissolve, the product being $10^{-13 \cdot 68}$, which just exceeds the ionic product of water at 18°. If thorium hydroxide, however, be used, no reaction can take place, for its precipitation p_H being 3·5, the product of the hydroxyl-ion concentration and the hydrion concentration arising from either $M/10$- or $M/100$-solution of the potassium acid chromate will be less than K_w.

The hydroxides higher in the p_H scale (*loc. cit.*, p. 2157) become increasingly reactive with the hydrochromate ions, though very little reaction takes place with those hydroxides which are precipitated from acid solutions. This is due to the fact that as soon as some hydrochromate ions have been converted into chromate ions, the hydrogen-ion concentration becomes considerably reduced and so prevents further reaction. As the hydrion concentration thereby produced is about 10^{-6}, its effect will be most marked with those hydroxides whose precipitation p_H's are above 7. The reaction between those hydroxides, which are precipitated at p_H 7 and above, and the hydrochromate radical becomes more pronounced and consequently potassium chromate causes either partial or no precipitation. Thus it is clear why potassium chromate fails to precipitate magnesium salt solutions. Magnesium hydroxide is precipitated at p_H 10·5 and is therefore able to react with the ions produced in the second stage of the ionisation of chromic acid to an extent sufficient to prevent the attainment of the p_H of precipitation. Manganous hydroxide, too, is sufficiently strong (p_H 8·4) to enter appreciably into combination with the hydrochromate radical. No precipitate is formed when potassium chromate is added to a manganous salt solution, but after some time the solution deepens in colour and eventually a brownish-black precipitate appears. This, however, is due to oxidation of the relatively large amount of manganous hydroxide present in the alkaline solution by the chromate and to some extent by the air (Gröger, *Z. anorg. Chem.*, 1905, **44**, 453).

The latter precipitation reactions may also be considered from the point of view of the alkalinity of the potassium chromate solutions. By assuming complete ionisation of the various salts involved in the hydrolysis of potassium chromate solutions, it can be shown that at 18°, $[H^{\cdot}] = \sqrt{K_2 K_w / C_{K_2CrO_4}}$, K_2 of chromic acid being $4{\cdot}4 \times 10^{-7}$. Therefore p_H of $M/10$-potassium chromate is 9·75 and of the $M/100$-solution, 9·25. Hence the addition of potassium chromate in either of these concentrations to magnesium salt solutions cannot cause precipitation, as the reactants are incapable of attaining an alkalinity corresponding to the p_H of precipitation of magnesium hydroxide. On the other hand, it appears at first sight that if a dilute manganous salt solution contained (say) $M/100$-potassium chromate, the hydrogen-ion concentration which the latter would impart, *viz.*, $10^{-9 \cdot 25}$, would be less than that at which manganous hydroxide is precipitated (p_H 8·4). The reaction between manganous chloride (say) and potassium chromate involves a ready reaction between manganous hydroxide and the hydrions from the first stage of ionisation of chromic acid to form some $Mn(HCrO_4)_2$ and also the more difficult reaction with the hydrions from the second stage. The result is that instead of the reaction being one of simple double decomposition, thus $K_2CrO_4 + MnCl_2 = MnCrO_4 + 2KCl$, the formation of a precipitate depends on how far the following equilibrium reaction is disturbed, $Mn(HCrO_4)_2 + Mn(OH)_2 \rightleftharpoons 2MnCrO_4 + 2H_2O$, which is governed, the oxidation effects which are peculiar to manganous and cobaltous hydroxides being excluded, by the two reactions (*a*) $HCrO_4' + OH' \rightleftharpoons CrO_4'' + H_2O$, and (*b*) $Mn^{\bullet\bullet} + 2OH' \rightleftharpoons Mn(OH)_2$. Equilibrium (*a*) is dependent on K_2 and K_w, and equilibrium (*b*) on $[Mn^{\bullet\bullet}][OH']^2$ or, more directly, the p_H of precipitation. Thus it follows that when $M/10$-potassium chromate is added to a manganous salt solution of the concentration used in these titrations, the p_H of the solution barely attains the precipitation p_H of manganous hydroxide and no precipitate is at first produced. More concentrated solutions of potassium chromate, however, effect partial but almost immediate precipitation of basic manganous chromate.

The behaviour of potassium chromate towards nickel and cobalt salt solutions is of interest. As shown in Table I, nickel hydroxide is precipitated at p_H 6·66 and cobalt hydroxide at p_H 6·81. Yet when $M/10$-potassium chromate is added to solutions of cobalt and nickel salts partial precipitation occurs in the former case and merely an opalescence is produced in the latter. The nickel and cobalt curves show that potassium chromate produces hydrion concentrations less than those at which the respective hydroxides are precipitated by alkali. The partial precipitation of cobalt is probably due to the tendency of cobalt hydroxide to oxidise. Gentle warming of the nickel solution is sufficient to cause precipitation.

The curves showing the course of precipitation of the basic chromates of neodymium and samarium have been included, for unlike the other metals except thorium, they form well-defined, difficultly soluble salts and thus the precipitation of one or the other is determined by (*a*) the hydrogen-ion concentration and (*b*) the solubility of the normal chromate.

These hydrogen-ion relationships of the various hydroxides explain why solutions of potassium dichromate, in spite of their p_H's being greater than the precipitation p_H's of certain hydroxides, fail to cause the precipitation of basic chromates, except from zirconium salt solutions; and even in this case it is far from complete. Unless concentrated solutions be used, in which case the normal thorium chromate may be precipitated, the addition of potassium dichromate to thorium salt solutions fails to give a precipitate, although the p_H of the dichromate solution itself is greater (3·68—4·18 for solutions ranging from 0·1*M* to 0·01*M*) than the hydroxide precipitation p_H, 3·5. Potassium dichromate behaves, towards a weak base like thorium hydroxide, as a salt of a strong monobasic acid containing no reactive hydrogen atom, and on addition to a thorium salt solution merely sets up an equilibrium, $ThCl_4 + 4KHCrO_4 \rightleftharpoons Th(HCrO_4)_4 + 4KCl$, in which the thorium salt is largely hydrolysed, and thereby maintains a hydrion concentration in the solution which is much greater than that required for the precipitation of the hydroxide. An excess of potassium dichromate will have a buffering effect on the hydrolysed chromic acid, but, as the first section of the chromic acid titration curve shows, the excess would have to be considerable before the hydrogen-ion concentration could be reduced to p_H 3·5.

Detailed Study of the Precipitation Reactions.—Thorium. It was mentioned (J., 1923, **123**, 1434) that when *M*/100-thorium nitrate solution was treated with *M*/20-potassium chromate solution in stoicheiometrical amounts, precipitation was partial and the precipitate contained thoria and chromic anhydride in the molecular ratio 1 : 1·38. On substituting the chloride for the nitrate, no variation was found in the composition of the precipitate. Fig. 1 shows that 22·7 c.c. of *M*/20-potassium chromate caused the attainment of the hydroxide precipitation p_H, at which point basic thorium chromate began to be precipitated. The next 30 c.c. caused little change in p_H, but soon afterwards a rapid diminution in hydrogen-ion concentration occurred which marked the end of precipitation. On comparing the inflexion thereby produced with that in the neutralisation curve of chromic acid, it will be observed that it indicates the first half of the neutralisation of all the free chromic acid present in the solution, $KHCrO_4$ being formed. The reaction may be regarded as two simultaneous reactions : first, the gradual hydrolysis of the thorium salt thus, $ThCl_4 + 4H_2O \longrightarrow Th(OH)_4 + 4HCl$, and, secondly, $4HCl + 4K_2CrO_4 \longrightarrow 4KCl + 4KHCrO_4$.

As stated above, it would be expected that thorium hydroxide would show a negligible tendency to react with the small concentrations of hydrions which arise from the dissociation of hydrochromate ions. Yet the thorium hydroxide which was precipitated contained appreciable amounts of chromic anhydride. Two reasons may be offered: (*a*) co-precipitation of thorium chromate, and (*b*) adsorption of chromic anhydride, through chemical forces at play between the weak base, thorium hydroxide, and the weak acid, $HCrO_4'$. The precipitates, apart from being yellow, resembled thorium hydroxide and appeared to contain no crystalline thorium chromate. Thorium chromate is much more soluble than the hydroxide, and seeing that the thorium- and chromate-ion concentrations were insufficient to produce a precipitate of the normal chromate before the hydroxide precipitation p_H was attained, it appears improbable that the basic chromate contained any normal chromate. The large chromic anhydride content of the basic precipitate was probably caused by a process akin to adsorption in which the chemical tendencies of the weak acid and the weak base played an important part.

An approximate estimate of the composition of the precipitate may be obtained from the titration curve. Precipitation was complete when 53 c.c. of $M/20$-potassium chromate had been added, *i.e.*, an amount corresponding to the mid-point of the inflexion. If thorium hydroxide alone had been precipitated, then, as shown by the previous equations, 4 mols. of potassium chromate to 1 mol. of thorium chloride would have been required, or 80 c.c. in the titration; as compared with 2 mols., or 40 c.c. of $M/20$-potassium chromate, if the normal chromate had been formed. But actually 53 c.c. were required, and therefore by alligation the basic chromate precipitate must have contained $27Th(CrO_4)_2,13Th(OH)_4$, or $ThO_2,1{\cdot}35CrO_3$. The precipitate contained 54·55% of ThO_2 and 28·47% of CrO_3, and therefore agreed with the formula $ThO_2,1{\cdot}38CrO_3,4{\cdot}57H_2O$, which is similar to that suggested by the curve.

Aluminium. Precipitation began when 5 c.c. of $M/10$-potassium chromate had been added, the p_H attained being that required for the precipitation of aluminium hydroxide. At first, the precipitate was white basic aluminium sulphate, but gradually became yellow and contained some chromate (compare Gröger, *Ber.*, 1902, **35**, 3420). The curve shows that very little change in p_H ensued until 20 c.c. of potassium chromate had been added. The main inflexion occurred and precipitation became complete when between 32 and 35 c.c. were added. The precipitate was gelatinous and contained chromate, much of which could be removed by washing.

The experiments of Gröger on the solubility of aluminium hydroxide in chromic acid solutions throw some light on the reactivity of the acid. He found that the number of molecules of chromic anhydride required to hold 1 mol. of alumina in solution varied from 4·46 to 5·02, and therefore concluded that both aluminium chromate and dichromate were capable of existence in solution. The explanation lies in the mode of dissociation of chromic acid. The first stage of the ionisation permits of the ready solution of aluminium hydroxide, thus $Al(OH)_3 + 3H_2CrO_4 \rightleftharpoons Al(HCrO_4)_3 + 3H_2O$, which requires 6 mols. of CrO_3 to 1 mol. of Al_2O_3, but the amount of hydrions produced in the second stage of the dissociation will depend on the concentration of chromic acid used. If it be large, the great concentration of hydrochromate ions will tend to suppress the second stage of dissociation and consequently there will be proportionally fewer hydrions available for reaction than in a more dilute solution. Hence it is clear why Gröger required variable amounts of chromic acid which corresponded to somewhat less than 6 mols.

Chromium. Maus (*Pogg. Annalen*, 1827, **9**, 127) and later Storer and Eliot (*Proc. Amer. Acad. Arts Sci.*, 1862, **5**, 192) found that brown precipitates of basic chromium chromate were produced by the action of potassium chromate on solutions of chromium salts, from which the chromic acid could be removed by repeated washing. The latter investigators stated that the abstraction did not stop when the precipitate had attained any particular composition and, from an equation based on the molecular proportion of potassium chromate which they found necessary for precipitation, concluded that CrO_2, *i.e.*, Cr_2O_3,CrO_3, must have first been formed.

The titration curve shows that the factor which determined precipitation was the hydrogen-ion concentration, for when 26 c.c. of $M/10$-potassium chromate had been added and the p_H had become 5·2, as compared with 5·34 found for the hydroxide, the basic chromate began to separate. The amount of potassium chromate required was 2·6 mols. to 1 mol. of chromic sulphate, and thus happens to be about half the quantity (5 mols.) found by Storer and Eliot. As the point of precipitation is determined by the hydrion concentration, the amount of potassium chromate required appears to be a function of the concentration of the reactants. The p_H change prior to precipitation was indicated by a line which was nearly straight, comparable with the section, corresponding to the addition of the first equivalent (to 1 Cr) of sodium hydroxide, in the alkali titration curve (*loc. cit.*). The fact that 2 mols. of sodium hydroxide had to be added to 1 mol. of chromium sulphate before precipitation began was due to the peculiar property of tervalent chromium of forming "soluble basic salts," such that in a solution of the sulphate one molecule of sulphuric acid is in a state of loose combination which may perhaps be expressed by the equilibrium $Cr_2(SO_4)_3 + 2H_2O \rightleftharpoons (OH)_2Cr_2(SO_4)_2 \ldots . H_2SO_4$, the looseness of the combination being indicated by the dotted line. This molecule of sulphuric acid, on its gradual release, reacted with two molecules of potassium chromate, thus : $H_2SO_4 + 2K_2CrO_4 = 2KHCrO_4 + K_2SO_4$, and the remaining 0·6 mol. of potassium chromate set up an equilibrium with the hydrochromate ions so formed to produce the requisite hydrion concentration for precipitation.

The precipitates formed by treating chromium sulphate solution (alum) with varying proportions of potassium chromate, corresponding to 30, 60 and 90 c.c. in the titration, were analysed. After being freed from mother-liquor by suction and a little washing by decantation, the first precipitate was green and had the composition $Cr_2O_3,0{\cdot}079CrO_3,xH_2O$, and was thus almost pure chromium hydroxide; the second was brown and contained more chromate, $Cr_2O_3,0{\cdot}574CrO_3,xH_2O$; and the third, still more, its composition being $Cr_2O_3,0{\cdot}871CrO_3,xH_2O$.

Beryllium is another of the elements that form soluble basic salts and this property appears to be reflected in the titration curve, the p_H at which precipitation began not being attained until 24 c.c. of $M/10$-potassium chromate had been added, *i.e.*, 1·2 mols. for 1 mol. of beryllium sulphate.

The alkali curve (*loc. cit.*) shows a characteristic inflexion during the reaction with the first equivalent of sodium hydroxide; precipitation occurred at p_H 5·69 (given at the top of an inflexion), when 1·04 equivalents had been added. A similar inflexion occurred in the chromate titration curve and precipitation began at p_H 5·72, indicated by a point in a similar position. The equivalent amount of potassium chromate which produced this change was 2·4 times that of the alkali and consequently the change in hydrion concentration was due to reaction between a loosely bound equivalent of acid in the beryllium sulphate molecule and potassium chromate, hydrochromate ions being formed which eventually entered into equilibrium with the added chromate ions.

Bleyer and Moorman (*Z. anorg. Chem.*, 1912, **76**, 70; see also Orlov, *ibid.*, 1913, **79**, 365) found that the interaction of potassium chromate and beryllium sulphate in solution produced very highly basic chromate precipitates, the chromate content of which seemed to increase slightly with the amount of potassium chromate added. Thus with 2 mols. of potassium chromate to one of beryllium sulphate the precipitate contained $BeO,0{\cdot}036CrO_3$, and with 4 mols. of potassium chromate, $BeO,0{\cdot}07CrO_3$, some unattacked sulphate being present in each precipitate. Bleyer and Moorman, having found that chromic acid solutions saturated with beryllium hydroxide contained the two in equimolecular proportions, stated that beryllium chromate existed in solution. Solutions of strong acids saturated with beryllia are invariably basic, and, as shown by the titration curve of beryllium sulphate and sodium hydroxide (*loc. cit.*), the solution had to be rendered basic to an extent shown by the formula $Be(SO_4)_{0·5}(OH)$ before precipitation commenced. Similarly, the proportions in Bleyer and Moorman's solutions show that they were basic to the same extent, *viz.*, $Be(HCrO_4)(OH)$, chromic acid being too weak in its second stage of dissociation to react with beryllium hydroxide to any appreciable extent.

Zinc. Table I shows that the p_H of precipitation of basic zinc chromate was 5·49 and therefore a little higher than that of the hydroxide, 5·20. The rapidity with which the p_H changed during the addition of the first c.c. of potassium chromate rendered it difficult to ascertain with any degree of precision the exact point at which the precipitate appeared. The precipitate was basic and consequently the hydrion concentration of the solution was controlled mainly by the equilibrium between the liberated hydrochromate ions and chromate ions. Gröger's analyses (*Monatsh.*, 1904, **25**, 520) showed that the precipitates obtained by treating zinc sulphate solutions with potassium chromate were indefinite and contained some sulphate, but the precipitates obtained from zinc chloride solutions were free from chloride, evidently due to the greater ease with which chlorides are hydrolysed. Varying amounts of potassium chromate were retained but were removable by washing.

An insoluble normal zinc chromate has been stated to exist by Schultze (*Z. anorg. Chem.*, 1895, **10**, 148) and Briggs (*ibid.*, 1908, **56**, 254), but the latter's data are unconvincing. It was thought that, if a difficultly soluble chromate did exist, its solubility might be too large for it to be precipitated by double decomposition through the attainment of the p_H at which the basic chromate separated, but that it might be precipitated from a chromic acid solution of zinc oxide by the gradual addition of potassium chromate so that the p_H should be kept below that necessary for the precipitation of the basic chromate (compare Britton, J., 1924, **125**, 1875). Indefinite basic chromates were always obtained; *e.g.*, one air-dried precipitate, $ZnO,0·605CrO_3$, contained 55·03% ZnO and 40·90% CrO_3, and another contained 58·10% ZnO and 33·00% CrO_3, corresponding to $ZnO,0·462CrO_3$.

Some criticism appears to be necessary of Gröger's conclusions (*Z. anorg. Chem.*, 1911, **70**, 135) from his study of the 25°-isotherm of the system $ZnO–CrO_3–H_2O$, in which he claims to have established the identity of several definite basic chromates of zinc. The "rests" were considered, without experimental proof, to be the actual solid phases alone. If the molar concentrations of Gröger's liquid phases of ZnO be plotted against those of CrO_3, it will be found that all the points lie on a continuous curve, whereas had definite basic salts been formed the curve should display a number of "breaks," indicating the univariant points.

Although Gröger's conclusions can scarcely be regarded as valid, the analyses of his liquid phases are important in that they give the solubility of zinc oxide in chromic acid solutions varying in concentration from 0·006*M* to 9·7*M*, and therefore should give some idea of the reactivity of chromic acid towards zinc oxide. The number of molecules of chromic acid, H_2CrO_4, required to dissolve one molecule of zinc oxide varied continuously with increasing concentration of acid from 1·20 to 2·03, which led Gröger to conclude that the more dilute solutions contained both zinc chromate, $ZnCrO_4$, and zinc dichromate, $ZnCr_2O_7$, whilst the highly concentrated solutions contained only zinc dichromate. The fact that approximately two molecules of chromic acid were required for the most concentrated acid solutions was due to the reaction having taken place between zinc oxide and the hydrions of the first dissociation, thus: $ZnO + 2H_2CrO_4 \longrightarrow Zn(HCrO_4)_2 + H_2O$, the large concentration of hydrochromate ions having inhibited further ionisation and consequent reaction, whereas in the dilute solutions some of the hydrions from the second stage of ionisation became available for reaction, with the result that less than 2 mols. of chromic acid were required.

Cobalt and Nickel. The reactions of these two metals have already been discussed (*vide supra*).

Reference may be made to Weil's proposal (*Bull. Soc. chim.*, 1911, **9**, 20) to use potassium chromate for the separation of cobalt from nickel. Although potassium chromate does not precipitate basic nickel chromate at room temperature, the titration curve shows that the hydrion concentration produced by addition of potassium chromate to a nickel salt solution is such that the basic salt is on the point of being precipitated. A method depending on such a small difference in solubility can give but a rough separation, for there will be a great tendency for the gelatinous basic cobalt chromate to carry down much nickel.

Rare Earths.—Yttrium. Basic yttrium chromate began to be precipitated at the same p_H as its hydroxide, but precipitation was far from complete and the precipitate was highly basic. The air-dried precipitate formed by the interaction of stoicheiometrical amounts of yttrium chloride and potassium chromate (40 c.c. of

$M/10$-K_2CrO_4 in the titration) solutions contained 38·61% Y_2O_3 and 22·29% CrO_3, corresponding to the formula $Y_2O_3,1{\cdot}30CrO_3$. The filtrate from this precipitate was treated with more potassium chromate, and the new precipitate was still more basic and contained $Y_2O_3,0{\cdot}93CrO_3$.

Neodymium and Samarium. These two elements form well-defined but comparatively insoluble chromates (Britton, J., 1924, **125**, 1875); the power of these earths to unite with chromic acid in its two stages being, no doubt, due to the small solubility of the salts formed, rather than to the strength of the bases. The solubilities of praseodymium chromate and lanthanum chromate are so small that when potassium chromate is added to the respective salt solutions the conditions requisite for the precipitation of the normal chromates are obtained before the hydroxide p_H is reached. This is not so with neodymium and samarium chromates, for they are sufficiently soluble to allow the p_H at which the hydroxide is precipitated to be attained before the respective solubility products of the chromates are exceeded, and consequently basic chromate precipitates are produced. When neodymium nitrate solution was treated with potassium chromate, a flocculent precipitate was obtained which on microscopic examination was seen to contain crystalline needles similar to those of the normal chromate. The following analyses refer to precipitates so obtained: (1) Nd_2O_3, 44·13; CrO_3, 34·59%, corresponding to $Nd_2O_3,2{\cdot}64CrO_3,9{\cdot}02H_2O$, and (2) Nd_2O_3, 47·95; CrO_3, 31·81%, corresponding to $Nd_2O_3,2{\cdot}23CrO_3,7{\cdot}88H_2O$. The fact that precipitation began at p_H 6·48 instead of at 7·0, coupled with the nature of the precipitates and the relatively high CrO_3 content, indicates that the formation of these precipitates constitutes a comparatively rare example of the co-precipitation of the crystalline normal salt and an indefinite basic salt.

Samarium chromate has a greater solubility than neodymium chromate and does not appear to be precipitated with the basic chromate. As the titration curve shows, the basic chromate was precipitated at p_H 6·55, which was somewhat lower than the hydroxide p_H. It was yellow and flocculent and when dried and examined under the microscope appeared to be entirely amorphous. Its separation was partial. The air-dried precipitate from the titration contained 25·1% CrO_3 as compared with 37·84% in $Sa_2(CrO_4)_3,8H_2O$.

II. *Basic Borates.*

Electrometric titrations were carried out at 18° with $0{\cdot}05M$-borax solution and salt solutions, which were so chosen that the precipitation reactions could be studied over as wide a range of hydrogen-ion concentration as possible. Details of the solutions used and the p_H's at which precipitates first appeared are in Table II.

TABLE II.

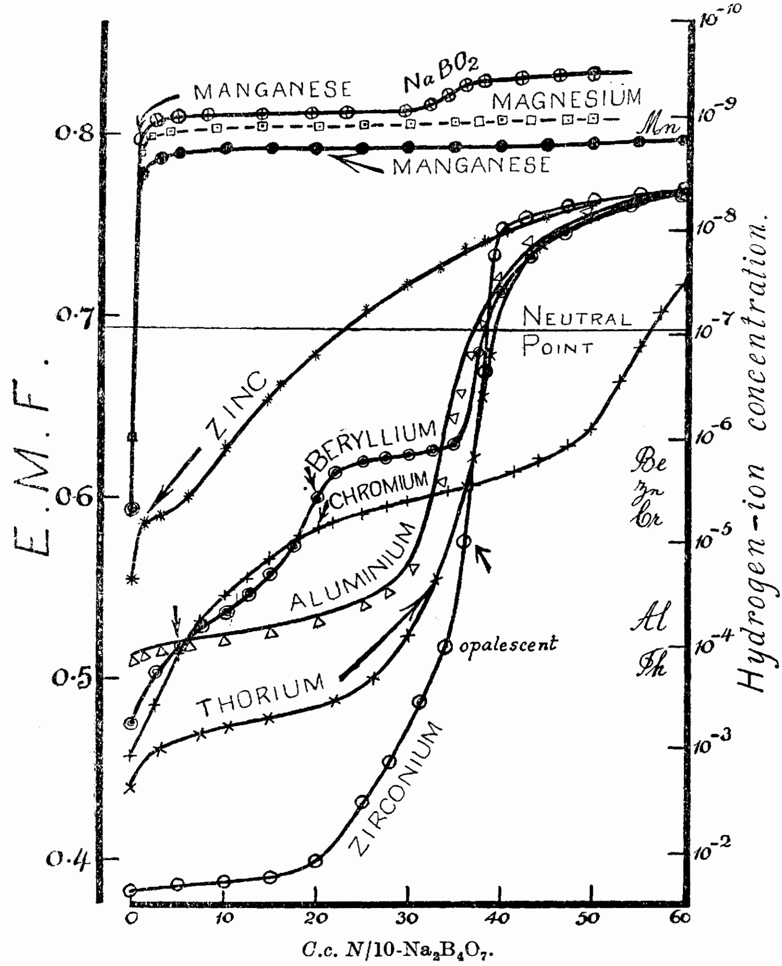
	Pption of basic borate began.		Pption of hydroxide began.		
Solution (100 c.c. .	*E.M.F.*	p_H.	*E.M.F.*	p_H.	Pption.
0·01*M*-$ZrCl_4$	0·517	4·07	0·390	1·86	Complete
0·01*M*-$ThCl_4$	0·554	4·70	0·484	3·51	,,
0·0067*M*-$Al_2(SO_4)_3$	0·521	4·14	0·521	4·14	,,
0·01*M*-$Cr_2(SO_4)_3,K_2SO_4$	0·586	5·25	0·591	5·34	,,
0·02*M*-$BeSO_4$	0·613	5·72	0·610	5·69	,,
0·02*M*-$ZnSO_4$	0·587	5·27	0·583	5·20	,,
0·02*M*-$MnCl_2$	0·792	8·82	0·770*	8·43*	Partial
			0·794	8·85	
0·02*M*-$MgSO_4$	—	—	0·885	10·49	None

The titration curves are given in Fig. 2, the arrows showing the points at which precipitation began. The top curve in the diagram represents the titration of 100 c.c. of 0·02*M*-manganous chloride with 0·1018*M*-sodium metaborate.

Table II shows that, except in the case of zirconium and thorium, addition of borax solution did not cause precipitation to begin until the p_H at which the hydroxide is precipitated had been attained. The titration curves in Fig. 2, apart from that of zinc, are similar in shape to those representing the alkali titrations. Moreover, those curves which correspond to precipitation taking place in the acid zone show that the amounts of *N*/10-borax solution which caused the solutions to become alkaline, precipitation having become complete, were approximately the same as those required in the sodium hydroxide titrations. It appears, therefore, as far as the weaker bases are concerned, that sodium pyroborate has simply a hydrolysing action in precipitating the hydroxides, and in fact behaves as if no borate were present at all. The hydroxides which were precipitated contained some unattacked acid radical of the original salt, as may be seen from the amounts of *N*/10-borax required to render the solutions neutral, if it be assumed that the borate radical did not enter into combination. Thus in the zirconium titration, 38·5 c.c. were required as compared with the theoretical amount, 40 c.c.; thorium, 38·0 instead of 40 c.c.; aluminium, 36·0 instead of 40; chromium, 55 instead of 60; and beryllium, 37·6 instead of 40 c.c.

Provided that no insoluble normal borates are formed, it follows on theoretical grounds that boric acid, HBO_2, with its exceptionally small dissociation constant, is incapable of producing hydrogen-ion concentrations large enough to cause dissolution of any of the hydroxides which are precipitated at p_H less than 7. As far as the reactivity of boric acid is concerned, boric acid behaves as a monobasic acid. If 5×10^{-10} be taken as an average value of $K = [H^{\cdot}][BO_2']/[HBO_2]$, it follows that in a $M/10$-boric acid solution the hydrogen-ion concentration is $10^{-5.2}$, and $10^{-5.6}$ in a $M/100$-solution. The hydroxides of beryllium, zinc, chromium, aluminium, thorium and zirconium are all precipitated at p_H less than 5·69, and consequently the hydrion concentrations of $M/10$- and $M/100$-solutions of boric acid are too small to have any solution effect on these hydroxides. Taking the case of beryllium hydroxide, which is precipitated at the highest p_H of the series under consideration,

FIG. 2.



in order that the reaction $Be(OH)_2 + 2HBO_2 \longrightarrow Be(BO_2)_2 + H_2O$ may proceed, water must be formed and therefore the product of the concentration of hydroxyl ions due to beryllium hydroxide, *viz.*, $10^{-14\cdot14}/10^{-5\cdot69} = 10^{-8\cdot45}$, and that of the hydrions from the boric acid, about $10^{-5\cdot2}$, must exceed K_w. In this case it is $10^{-13\cdot9}$, and only just exceeds K_w, and consequently beryllium hydroxide may perhaps be expected to exhibit the slightest tendency to dissolve. Any solution, however, would cause an increase in the concentration of BO_2' ions, which would depress the ionisation of boric acid and so prevent further solution. Boric acid does not dissolve either of these bases to any appreciable extent.

The hydrogen-ion concentrations of the solutions at the end of these titrations were such as would be given by borate mixtures comprising the total quantity of boric acid added and the alkali in excess of that required for the precipitations, and therefore confirm the view that no boric acid, or relatively little, was contained in the precipitates. Thus in the titrations of zinc, beryllium, aluminium, thorium and zirconium, it will be seen from Fig. 2 that the hydrion concentration when 60 c.c. of $N/10$-borax had been added was $10^{-8\cdot3}$ in each case. By subtracting the 40 c.c. of $N/10$-sodium hydroxide which were neutralised during the precipitations, it is found that the solutions contained alkali equal to 20 c.c. of $N/10$-sodium hydroxide and boric acid equal to 120 c.c. of $N/10$-HBO_2, the boric acid having been one-sixth neutralised. The p_H of a $0\cdot2N$-solution of boric acid neutralised to the same extent is, according to Sörensen, 8·29 (Prideaux, "Theory of Indicators," 1917, p. 279), and as the variation in p_H produced by the difference in concentration of the two solutions is very small, it will be seen that the agreement is sufficiently good.

Although the changes in hydrion concentration which took place in the acid zone of the titrations are almost identical with those which were obtained when the precipitant was sodium hydroxide, in the case of the weakest two bases, zirconia and thoria, the p_H's of precipitation do not compare favourably with the corresponding hydroxide p_H's. Zirconium hydroxide is generally precipitated at a p_H somewhere on the very slightly inclined part of the curve. In the precipitation of zirconium chloride solution with sodium hydroxide (J., 1925, **127**, 2124) the p_H was 1·86, but in the present titration the solution remained perfectly clear until the inflexion in the curve had been passed and the p_H had become 4·06; opalescence then began. This was when 3·4 atoms of chloride of the zirconium tetrachloride had been replaced by hydroxyl groups and, notwithstanding its highly basic nature, the solution had remained perfectly clear. With thorium chloride, the effect was similar; the solution remained quite clear until 3·3 atoms of chloride had been replaced and the curve had begun to incline, the p_H being 4·70 instead of 3·51 obtained by using alkali. Hence it appears that the boric acid was having some restrictive influence on the size of the particles. It is probable that the tendency, although very slight, which boric acid may have to combine with thoria and zirconia exerts its greatest influence just at the point where the hydroxide or basic salt is about to pass into colloidal solution prior to precipitation. If this be the case, it seems reasonable that the boric acid, in trying to react with the nascent hydroxide, tended to keep it in solution by impeding the growth of the particles. Two experiments were made to determine whether the delayed precipitation from a thorium chloride solution whose p_H is that at which precipitation normally takes place is a matter of time: To thorium chloride solutions of the concentration used in the titration were added amounts of borax equal to 2 and 3 equivalents; in neither case did a precipitate separate during a period of several weeks.

In the chromium titration, the solution became green on addition of the borax and precipitation occurred when 21·9 c.c. of *N*/10-solution had been added, or 1·09 equivalents for each atom of chromium.

The beryllium curve again is similar to the alkali curve, and precipitation was also delayed until 21·9 c.c. (= 1·09 equivalents to 1 atom of Be) had been added.

The zinc curve shows hydrogen-ion changes which were due mainly to equilibria which must have been set up between borate ions and boric acid. The precipitation p_H was the same as that when alkali was used.

The incomplete precipitation which took place from *M*/50-manganous chloride solution will be understood when it is remembered that the p_H of *N*/10-borax itself, *viz.*, 9·11, is only slightly greater than the p_H at which manganous hydroxide is precipitated. Table II gives two p_H values for manganous hydroxide; the one marked with an asterisk is low, probably on account of oxidation of manganous hydroxide, and the other, which is approximately correct, was extrapolated from the alkali titration curve. In the borax titration the precipitate did not appear until 20 c.c. of *N*/10-borax had been added and p_H 8·82 attained. The precipitate was white and remained dispersed until 50 c.c. had been added, and, unlike the hydroxide, it did not immediately turn brown through oxidation. It readily did so when washed. (It is this protective action which is conferred on manganous hydroxide by union with some boric acid which makes the substance of use as a " drier " in paints and varnishes.) The fact that it was precipitated at the hydroxide p_H suggests that the white precipitate was basic, and not manganous borate as was stated by Hartley and Ramage (J., 1893, **63**, 133). Their precipitates were obtained by pouring solutions of manganous sulphate into solutions of borax until no further precipitation occurred. From widely differing estimations of the manganese content only, they concluded that they had prepared a definite borate having the formula $MnH_4(BO_3)_2$ when dried at 100°, and they state that $MnH_2B_2O_5$ and $Mn(BO_2)_2$ were formed by dehydrating it still more. They also state that manganous borate was produced by the interaction of manganous sulphate and sodium metaborate. The precipitate produced by the action of *N*/10-borax on *M*/50-manganous chloride solution was both indefinite and basic and contained $MnO,1{\cdot}47HBO_2$. In the titration of *M*/50-manganous chloride with 0·1018*N*-sodium metaborate, the precipitate appeared when 1 c.c. of precipitant had been added and the p_H had become 8·77. This precipitate was, like the hydroxide, quickly oxidised and was strongly basic.

Laurent (*Comp. rend. Trav. Chim.*, 1850, **6**, 33) observed that manganous salt solutions were not precipitated with potassium hexaborate. It will be seen from the hydrogen-ion concentrations of the various borate "buffer" mixtures that the p_H of a boric acid solution, a third of which has been neutralised with alkali and which thus corresponds to Laurent's reagent, is about 8·7; this falls just below the p_H at which the hydroxide is precipitated. When, however, the borate solution is added to a manganous salt solution, some of the alkali is neutralised and the p_H falls a little further below 8·7.

According to Gmelin-Kraut ("Handbuch anorg. Chem.," 1908, iii, [2], p. 324), Berzelius found that when a magnesium salt had been added to a manganous salt solution, borax failed to give a precipitate. Neutral salts, such as sodium chloride, sodium sulphate, calcium chloride and potassium chloride, also produce this effect, but to a lesser extent; *e.g.*, a solution from which precipitation had been prevented with magnesium sulphate remained clear on standing, whereas by using either potassium chloride or any of the other salts brown precipitates appeared after 12 hours. Precipitates obtained by means of borax may be forced back into solution by the addition of these salts. Since the highest p_H that could be produced by borax solutions was far removed from the precipitation p_H of manganous hydroxide, it appeared that the behaviour of these salts in preventing precipitation of basic manganous borate lay in their power to diminish the p_H below that necessary for precipitation. For example, when 10 c.c. of a saturated solution of magnesium sulphate were added to 100 c.c. of *N*/10-borax solution whose initial p_H was 9·11, the p_H fell to 8·58; with 40 c.c., p_H was 8·10; and with 50 c.c., 8·06. The effect of potassium chloride was not so marked. The addition of much potassium chloride to a *N*/10-borax solution depressed the p_H only from 9·11 to 8·82—a value, it will be noticed, corresponding to incipient precipitation.

The dotted curve shows the changes produced in hydrogen-ion concentration during the addition of *N*/10-borax solution to a *M*/50-solution of magnesium sulphate. No precipitate was obtained, for the p_H of the borax solution was below that, 10·49, requisite for the precipitation of magnesium hydroxide. Borax produces in the boiling solution a precipitate which redissolves on cooling. No precipitate was obtained with *N*/10-sodium metaborate solution, for although its p_H was 10·85, the p_H of the mixture became a little lower than the necessary value.

III. *Basic Carbonates.*

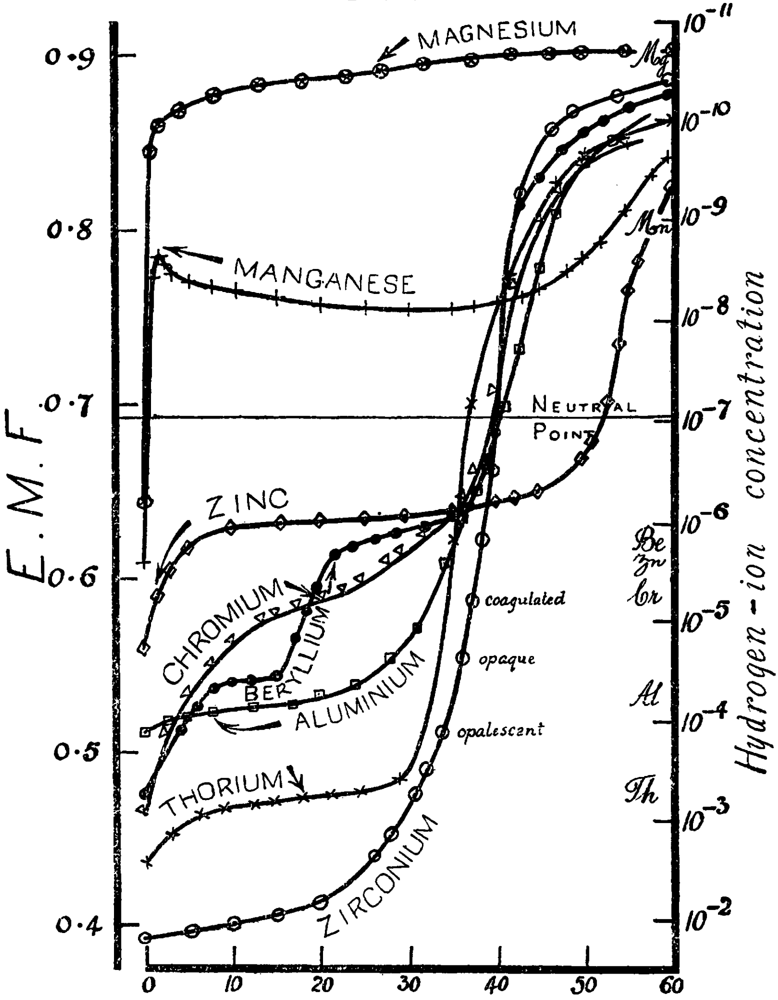
The hydrogen electrode titration method has been applied in a study of the relationships involved in the precipitation of basic carbonates. By using a plentiful supply of hydrogen electrodes which were efficient in ordinary solutions, potential differences between them and the normal calomel electrode were obtained, in these carbonate titrations, which were readily reproducible and were unaffected by any liberated carbon dioxide. Table III gives the particulars of the several titrations, and Fig. 3 shows the titration curves, the points at which precipitation began being again denoted by arrows. The sodium carbonate was decinormal in every case except the chromium titration, where it was 0·166*N*.

TABLE III.

	Pption of basic carbonate began.		Pption of hydroxide began.		
Solution (100 c.c.).	*E.M.F.*	p_H.	*E.M.F.*	p_H.	Pption.
0·01*M*-$ZrCl_4$	0·511	3·95	0·390	1·86	Complete
0·01*M*-$Th(NO_3)_4$	0·476	3·35	0·484	3·51	,,
0·0067M-$Al_2(SO_4)_3$	0·523	4·16	0·521	4·14	,,
0·01*M*-$Cr_2(SO_4)_3,K_2SO_4$	0·587	5·27	0·591	5·34	,,
0·02*M*-$BeSO_4$	0·612	5·70	0·610	5·69	,,
0·02*M*-$ZnSO_4$	0·589	5·30	0·583	5·20	,,
0·02*M*-$MnCl_2$	0·784	8·68	0·794	8·85	,,
0·02*M*-$MgSO_4$	0·891	10·54	0·885	10·49	Turbidity

The titration curves are of the same type as those obtained in the preceding hydrolytic precipitation titrations, and in every case but zirconium, precipitation began at hydrion concentrations equal or very nearly equal to those necessary for the corresponding hydroxides. $N/10$-Sodium carbonate, unlike the reagents used in the previous titrations, when added to the magnesium sulphate solution, produced an alkalinity corresponding, but only just so,

FIG. 3.



C.c. $N/10 \cdot Na_2CO_3$.

to the p_H at which the hydroxide is precipitated, which did not occur until 27 c.c. had been added. The precipitate formed even after 100 c.c. of sodium carbonate had been added did not amount to more than a slight turbidity.

The stoicheiometrical quantity of sodium carbonate required for simple double decomposition was equivalent to 40 c.c. of *N*/10-sodium carbonate, except in the case of chromium, where it was 36 c.c. The curves for zirconium, thorium, aluminium, beryllium and chromium show that the mother-liquors became alkaline when approximately theoretical quantities of sodium carbonate had been added. The hydrion concentrations at the end of the titrations, although differing somewhat owing to the escape of different amounts of carbon dioxide during the precipitations, were such as would be produced by mixtures of sodium bicarbonate and carbonate (compare Prideaux, "Theory of Indicators," p. 299; Auerbach and Pick, *Arb. K. Gesundheitsamt.*, 1911, **38**, 243). The changes in hydrion concentration which took place during the precipitation of the basic carbonates from solutions whose hydrogen-ion concentrations were greater than 10^{-6} were scarcely at all affected by the carbon dioxide that was liberated. The carbon dioxide set free during the precipitation of basic zinc carbonate, however, had so marked an effect on the hydrogen-ion concentration that the inflexion corresponding to the formation of sodium bicarbonate from the liberated carbon dioxide and the added sodium carbonate did not occur until 54 c.c. of the latter had been added.

The curve for manganese shows that the addition of *N*/10-sodium carbonate, after the first 2 c.c., produced a diminution in p_H, which reached a minimum, 8·2, when 30 c.c. had been added. The precipitate appeared when 1·4 c.c. had been added and p_H 8·68, *i.e.*, nearly the hydroxide p_H, had been attained. The precipitate first formed was basic, as may be seen from the curve, which shows that more than 40 c.c. of sodium carbonate had to be added before the p_H of sodium bicarbonate was attained, *viz.*, 8·7.* The precipitate, although basic, did not turn brown through oxidation by the air. It is remarkable that the increase in hydrion concentration which occurred during the titration did not cause the basic carbonate to re-dissolve. This, however, was a case of two precipitations, one of the basic carbonate due to the p_H's ruling at the beginning and at the end of the reaction, and the other of the normal carbonate, which was precipitated when the hydrion concentration of the solution was enhanced. Sodium bicarbonate when added to a manganous chloride solution, preferably saturated with carbon dioxide, causes the precipitation of manganous carbonate only, for it cannot produce a sufficiently low hydrion concentration to enable

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* It may be calculated from Noyes's formula (*Z. physikal. Chem.*, 1893, **11**, 495), by taking K_1 and K_2 of carbonic acid to be 3×10^{-7} and $1{\cdot}3 \times 10^{-11}$, respectively, that the p_H of dilute solutions of sodium bicarbonate is about 8·7.

the basic carbonate to separate from solution; *e.g.*, the hydrion concentration of a manganous chloride solution was gradually reduced by the addition of a solution of sodium bicarbonate until p_H was 7·6; a white precipitate of manganous carbonate then began to form. Hence, in order to ensure the precipitation of the normal carbonate, the precipitant must be incapable of causing the p_H to be attained at which the hydroxide is precipitated.

Normal zinc carbonate has been prepared. The titration curve shows that in order to precipitate this salt uncontaminated with basic carbonate a reagent must be used which, besides causing the solubility product $[Zn^{\cdot\cdot}][CO_3'']$ to be exceeded, will maintain a hydrogen-ion concentration greater than that at which the basic carbonate would separate. Sodium bicarbonate with its p_H of 8·7 would be useless, even though the carbon dioxide which would be set free during the precipitation would tend to increase the hydrion concentration. It would be necessary to have the solution saturated with carbon dioxide under a very high pressure before any addition of sodium bicarbonate. Smith (*J. Amer. Chem. Soc.*, 1918, **40**, 883) has determined the solubility of zinc carbonate in solutions of carbon dioxide under pressures ranging from 4·12 to 40·6 atmospheres. His results may be used to calculate the hydrogen-ion concentrations of the various solutions which, being in equilibrium with zinc carbonate, were just on the point of precipitating zinc carbonate, if it be assumed, as was done by Bodländer (*Z. physikal. Chem.*, 1900, **35**, 23), that metallic bases exist in carbonic acid solutions in the form of bicarbonates. If zinc oxide exists as $Zn(HCO_3)_2$, the concentration of HCO_3' ions is equal to twice the concentration of dissolved zinc oxide, and, the extremely small concentration of hydrions arising from carbonic acid in its second stage of dissociation being neglected, it follows that $[H^{\cdot}] = [H_2CO_3]K_1/[HCO_3'] = ([CO_2] - 2[ZnO]). 3 \times 10^{-7}/2[ZnO]$. It was thus calculated that the p_H's of Smith's solutions varied continuously from 4·94 to 4·33. Even when the pressure of carbon dioxide is very high, the p_H at which the normal carbonate is precipitated is not very much less than that at which the hydroxide is precipitated.

Mikusch (*Z. anorg. Chem.*, 1908, **56**, 365) determined the solubility of zinc oxide in carbon dioxide solutions in equilibrium with basic zinc carbonate. By means of the above formula, it was found that the p_H's of his solutions lay between 6·05 and 6·15. These hydrion concentrations, though somewhat higher than that at which basic zinc carbonate began to separate in the present titration, *viz.*, p_H 5·3, happen to be those that obtained during the main course of the precipitation. As zinc carbonate exists in equilibrium with hydrogen ions at a relatively high concentration, it follows that water will decompose zinc carbonate to give the less soluble basic carbonate.

The hydrogen-ion concentration which had to be attained in the magnesium titration before sodium carbonate produced a precipitate shows that, contrary to the statements of several workers, the precipitate was basic. The solubility product of magnesium carbonate, $MgCO_3,3H_2O$, at 18° is $1{\cdot}2 \times 10^{-4}$ (Johnson, *J. Amer. Chem. Soc.*, 1915, **37**, 2014), and consequently, if complete dissociation be assumed, the solubility of magnesium carbonate is $1{\cdot}1 \times 10^{-2}$ mol. per litre. The solubility of magnesium hydroxide, obtained from the solubility product, 2×10^{-11}, is $2{\cdot}7 \times 10^{-4}$ mol. per litre. Hence, to precipitate the more soluble magnesium carbonate, a precipitant must be used which will supply the necessary carbonate ions without introducing the concentration of hydroxyl ions that causes the separation of magnesium hydroxide. As magnesium hydroxide is precipitated at p_H 10·5, it is obvious that sodium bicarbonate (p_H 8·7), even although added in large excess, cannot produce the corresponding concentration of hydrogen ions, and therefore cannot precipitate basic magnesium carbonate. It can, however, supply the carbonate ions which, provided that the magnesium salt solution is sufficiently concentrated, will cause magnesium carbonate to separate. Boussingault (*Ann. Chim. Phys.*, 1825, **29**, 285) found that sodium sesquicarbonate, $Na_2CO_3,2NaHCO_3$, also could be used for this purpose. The data of Auerbach and Pick (*loc. cit.*) show that the p_H of such a mixture, decinormal with respect to carbonic acid, is approximately 9·9, which is just a little below the value required for the precipitation of the hydroxide.

No normal carbonates of chromium, beryllium, aluminium, thorium, and zirconium are known, and, as would be expected, the precipitates they form are highly basic. The shape of the beryllium titration curve appears to be peculiar to that element, and the precipitate did not appear until 22 c.c. (= 1·1 equivs. Na_2CO_3 to 1 mol. $BeSO_4$) of sodium carbonate had been added. In the chromium and thorium titrations, precipitation did not begin until 20 c.c. (1·85 equivs. to 1 Cr) and 18 c.c. (1·8 equivs.), respectively, of sodium carbonate had been added. As may be seen from Table III, the precipitation which took place from thorium chloride solution with sodium carbonate was due to the attainment of the p_H at which the hydroxide is precipitated and therefore the precipitate was basic. Chauvenet (*Compt. rend.*, 1911, **153**, 66), having found that the analysis of such a precipitate corresponded to the formula $ThO_2,CO_2,8H_2O$, stated that it was normal thorium orthocarbonate, $ThCO_4,8H_2O$, a salt of a purely hypothetical acid. In the case of the zirconium titration the curious effect noted in the borate titration was again observed, opalescence not beginning until 3·4 equivalents of sodium carbonate had been added and the relatively high p_H of 3·95 had been attained. In the borate titration the p_H was 4·06, and 3·4 equivalents of borax were required. As mentioned above, this phenomenon is believed to be due to suppression of the growth of the basic particles owing to a slight solvent action of the liberated weak acid.

Summary.

(1) The hydrogen-ion concentrations which govern the precipitation of basic salts containing weak acid radicals—chromates, borates, and carbonates—have been investigated.

(2) These basic precipitates are formed at the same p_H as the respective hydroxides; cases occurred of delayed precipitation from zirconium and thorium chloride solutions.

(3) The precipitability of the different bases as basic salts depends on the capacity of the precipitant to produce the p_H at which the hydroxide is precipitated. In cases where this p_H is only just attained, the precipitation is partial.

(4) The conditions for the precipitation of normal salts have been discussed wherever possible.

(5) The mode of dissociation of chromic acid (J., 1924, **125**, 1572) has been shown to account for the action of alkali-metal chromates in precipitating basic salts.

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