CCXC.—Electrometric Studies of the Precipitation of Hydroxides. Part IV. Precipitation of Mercuric, Cadmium, Lead, Silver, Cupric, Uranic, and Ferric Hydroxides by Use of the Oxygen Electrode.

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ATTENTION was directed in Part I (this vol., p. 2110) to the limited applicability of the hydrogen electrode, and consequently resort has been made to the oxygen electrode in order to study the precipitation reactions described in the following pages. Although oxygen electrodes cannot be used to follow with accuracy the changes in hydrogen-ion concentration which may take place during a reaction, they are sufficiently responsive to show the character of the changes and under certain conditions an approximate idea of the hydrogen-ion concentrations may be obtained from the titration curves. The oxygen electrode appears to have been employed for a similar purpose by Ralston (*Trans. Amer. Electrochem. Soc.*, 1923, 43, 87), who found it of considerable use in the hydrolytic purification of electrolytes, such as the freeing of copper sulphate solutions from ferric hydroxide.

It was shown (Britton, J., 1924, 125, 1572) in oxygen electrode titrations of chromic acid that, if the hydrogen-ion concentrations were known of solutions at two remote stages of the titration, rough estimates of the $p_{\rm H}$ of intermediate solutions could be obtained by assuming the voltages to be proportional to the $p_{\rm H}$. This method, however, was found later to introduce errors sometimes as great as a whole $p_{\rm H}$ unit (this vol., p. 1915). The method has been further tested in the present titrations by using solutions which contained a known concentration of free acid, from which the initial p_{π} could be calculated, and continuing the titrations until the solutions had become alkaline and of known $p_{\rm H}$. Table I gives particulars of the solutions titrated and the concentrations of free acid initially present. The titrations were performed with 100 c.c. of solution at 18° in each case by the method described for the previous acid titrations, the normal calomel half-element being used; as junction liquid in titrations 3 and 4 saturated potassium nitrate solution was employed instead of potassium chloride for obvious reasons. Each titration was followed by at least two oxygen electrodes and the solution was kept thoroughly mixed by a rapid current of oxygen, flowing throughout the whole titration.

The curves given by each pair of electrodes were as a rule similar, although by no means coincident, and tended to become closer to

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Titration	100 C.c. of solution contained :		Sodium hydroxide.			
curve			Normal-	C.e.	C.c.	Total.
NO.	tree acid.	sait.	ity.	for acia.	for sait.	
1	0.0212N-	0.02M	0.1018	20.8	39.3	60.1
	HCl	HgCl.				
2	0.0199N	0.02 <i>M</i> -	0.1018	19.6	39.3	58.9
-	H.SO.	CdSO.				
3	0.0202N	0.02M-	0.1005	20.1	39.8	59.9
v	HNO.	Ph(NO ₂).	0 2000			•••
4	0.0202N-	0.02M-	0.1018	19-6	39.3	58.9
*	HNO.	AgNO.	0 2020			
5	0.0199N.	0.02 M.	0.1018	19.6	39.3	58.9
0	H SO	CuSO	0 1010	100	000	000
ß	0.0140V	0.00833 M	0.1005	14.9	49.8	64.7
0	U.014320-	U(NO)	0 1000	110	10 0	0±,
-		$0(110_3)_6$	0 1005	90.1	90.9	50.0
4	0.02021	0.013314.	0.1005	20.1	29.9	99.9
	HCI	FeCl ₃				

TABLE I.

one another on repeated use; continued use, however, impaired the sensitiveness of the electrodes to changes of hydrion concentration. The differences between the typical E.M.F.'s given by the oxygen-normal calomel combination at the beginning and at the end of the titrations, and the corresponding E.M.F.'s which ordinarily would have been given by the hydrogen electrode in solutions of identical hydrion concentration, against the normal calomel half-cell, are given in Table II. These differences are, in effect, the E.M.F.'s of the oxygen-hydrogen cells set up in the various solutions.

TABLE II.

Titration		$E.M.F.$ of $O_2 \mid solution$	tion H ₂ (volts).
No.	Solution.	Beginning.	End.
1	HCl and HgCl ₂	0.98	1.05
2	$H_{2}SO_{4}$ and $CdSO_{4}$	1.09	1.08
3	HNO_3 and $Pb(NO_3)_3$	1.04	1.05
4	HNO ₃ and AgNO ₃	0.96	1.13
5	$H_{2}SO_{4}$ and $CuSO_{4}$	0.94	1.06
6	HNO_3 and $U(NO_3)_6$	0.82	0.96
7	HCl and FeCl ₃	0.97	1.03

Both the hydrogen-ion concentration and the oxidising agents, which may be undergoing titration, have some influence on the oxygen electrode E.M.F. If the latter happens to be either small or almost independent of the hydrogen-ion concentration, then the proportional hydrogen-ion concentration scale may be expected to give a fairly accurate measure of the hydrion concentration. The extrapolated E.M.F.'s of the oxygen-hydrogen cell in the case of the uranium nitrate titration are much lower than usual, and it is probable that the small increase in potential difference was uniformly distributed over the whole titration, for the $p_{\rm H}$'s indicated by the scale at the various stages of the reaction were,

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as far as could be ascertained colorimetrically, in approximate agreement. The low potential differences which were obtained in all the uranium titrations had nothing to do with the ageing of the platinum black, as in many instances freshly platinised electrodes were employed. A regular increase in the potential difference of the oxygen-hydrogen cell could not have taken place in the silver nitrate titrations, for according to the proportional hydrion scale the silver oxide was precipitated at $p_{\rm H}$ 6, whereas calculation from the solubility product of silver hydroxide showed that the true precipitation $p_{\rm H}$ lay between 9 and 10. By comparing the voltage actually observed when the precipitation began, 0.40 volt, with that which would be given by a hydrogen electrode indicating $p_{\rm H}$ 9, each compared with the normal calomel electrode, the E.M.F. of the oxygen-hydrogen cell is found to be 1.21 volts. This value is greater than either the initial (0.96) or the final (1.13)value, and was probably caused by the instability of the silver oxide. The remaining solutions investigated showed much less variation in their extrapolated P.D.'s, and when isolated $p_{\rm H}$'s were found by means of indicators and compared with those given by the scales, they were generally found to agree within half a $p_{\rm H}$ unit.

The differences in the actual voltage readings, which covered equal ranges of hydrion concentration, were usually unequal in any two titrations. Thus the change in $p_{\rm H}$ from 1.7 to 12.0 (say) would be indicated by the hydrogen and normal calomel electrodes by a variation in *E.M.F.* from -0.381 to -0.975 volt, a difference of 0.594 volt. In the case of the lead titration, the oxygen electrode *E.M.F.*'s moved over the same range with an almost equal change in voltage, *viz.*, from 0.667 to 0.067, a difference of 0.600 volt. In the other extreme titration, that of silver nitrate, the *E.M.F.* varied from 0.578 to 0.167 volt, a difference of 0.411 volt only.

In order to represent these titrations graphically (Fig. 1), it has been found necessary to convert the observed voltages into the approximate $p_{\rm H}$ values by simple proportion (this vol., p. 1915); these values are plotted as ordinates, and the number of c.c. of alkali added as abscissæ. Curve No. 4, representing the titration of silver nitrate, is dotted, for, as previously shown, the proportional hydrion scale is inapplicable. The arrows denote the beginning of precipitation.

The precipitation of basic mercuric chloride (curve No. 1) began when $p_{\rm H}$ 7.4 was attained; the precipitate, at first white, became brown as more alkali was added. Precipitation was complete when three-quarters of the amount of alkali required for the complete decomposition of the mercuric chloride had been added. At this point—50.3 c.c. of sodium hydroxide—the addition of more alkali

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caused a rapid increase in p_{π} . The basic chloride was readily decomposed on the addition of an excess of alkali. The fact that exactly 1.5 equivalents of sodium hydroxide were sufficient to



FIG. 1.

alkali had to be added before the solution attained a marked alkalinity. The partial investigation by Toda (Memoirs Coll. Sci. Kyoto, 1921, 4, 305) of the ternary system HgO-HCl-H₂O at 35° failed to establish the individuality of HgCl,,3HgO. A crystalline basic chloride of this composition is stated to occur naturally as kleinite and mosesite, and has also been prepared by several workers (compare Mellor's "Treatise," 1923, Vol. IV, p. 842).

Curve No. 2 shows that the precipitate obtained from the cadmium sulphate solution was also basic. It was heavy and flocculent and its composition must have been CdSO₄,3Cd(OH)₂,xH₂O, for 49 c.c. (=1.5 equivalents) of sodium hydroxide were required for its precipitation. Harned (J. Amer. Chem. Soc., 1917, 39, 252) arrived at the same conclusion by conductimetric titration, and Pickering (J., 1907, 91, 1981) found that a solution of cadmium sulphate was rendered alkaline to phenolphthalein by the addition of 1.46 equivalents of alkali.

Curve No. 3, illustrating the precipitation of lead as a basic nitrate, is remarkable for the considerable change in hydrion concentration which is shown to have taken place. The mode by which the precipitate was formed is yet another example showing that precipitation is often brought about by the coagulation of a colloidal solution, initially formed. A faint opalescence occurred on the addition of 20.5 c.c. of sodium hydroxide ($p_{\rm H} = 6$), but immediately after another 0.5 c.c. had been added a heavy, white precipitate appeared, only to pass, in the course of a few seconds, into colloidal solution. Further additions of alkali merely intensified the turbidity of the solution, which became opaque after the addition of 33.5 c.c. The colloidal solution coagulated when 38 c.c. of alkali had been added. Once again, 1.5 equivalents of alkali were required for complete precipitation, showing that the composition of the precipitate was $Pb(NO_3)_{2,3}Pb(OH)_{2,x}H_2O$. The existence of such a salt has been claimed by several workers.

Silver does not appear to give a basic precipitate under these conditions, as will be seen from curve No. 4.

The precipitation of basic copper sulphate is an excellent example to show how the composition of the precipitate may be influenced by the manner in which the precipitant is added. When the sodium hydroxide was added slowly to a copper sulphate solution, and the solution was thoroughly agitated, the precipitate was pale blue, amorphous, and heavy, but when the alkali was added quickly. no care being taken to ensure thorough mixing, the precipitate was green and gelatinous and, in contrast to the former precipitate, turned black either on standing or on heating. Provided the amount of alkali added was insufficient to render the solution

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alkaline, the gelatinous precipitate, on shaking, gradually became converted into the less basic, amorphous precipitate. The precipitate obtained in the titration was amorphous and, as will be concluded from the amount of alkali (1.47 equivalents) required for its precipitation and to render the solution alkaline, contained CuO and SO_3 in the molar ratio 4:1. In his experiments on copper sulphate solutions, Pickering (loc. cit.) found that whilst 1.53 equivalents of sodium hydroxide actually produced complete precipitation as basic sulphate, the solution on treatment with alkali did not become alkaline to phenolphthalein until about 1.7 equivalents had been added. This initial alkalinity gradually disappeared until approximately 1.8 equivalents had been added. It is evident that Pickering obtained complete precipitation as CuSO4,3Cu(OH)2,xH2O in one case. The fact that the initial alkalinity did not coincide with the end of precipitation was due to the way in which the alkali was added during the testing with phenolphthalein. In the present electrometric titration, complete precipitation and alkalinity to phenolphthalein took place simultaneously. Pickering believed that the greater amount of alkali pointed to the precipitation of a mixture of basic sulphates, 4CuO,SO₃ and 10CuO,SO₃; the individuality of the latter he thought to be sufficiently established by the amount of alkali required to cause final alkalinity. Harned (loc. cit.), by titrating with a copper electrode, also found that precipitation was complete when 1.7 equivalents of sodium hydroxide had been added. Harned's observation, as was Pickering's, was due to the manner in which the precipitant was added. In a subsequent paper, it will be shown that the pale blue, amorphous precipitate is a definite basic salt, 4CuO,SO₃,4H₂O.

The uranic solution used in the titration was prepared by dissolving so-called uranyl nitrate in nitric acid. The colour of the solution was pale yellow, but important changes in the intensity occurred during the titration. Curve No. 6 shows that a slight inflexion occurred immediately after the acid in excess of that required to form uranic nitrate had been neutralised with 14.9 c.c. of alkali; this, perhaps, may be due to the presence of sexavalent uranium nitrate in the solution (compare the titrations of the chlorides of zirconium and ferric iron). This small inflexion was repeatedly obtained. No appreciable change in colour was observed until 45 c.c. of sodium hydroxide had been added, the composition of the solute then being $U(NO_3)_{238}(OH)_{3:62}$. Thereafter the solution, though remaining clear, gradually became deeper in colour until 55.8 c.c. of alkali had reacted, the solution then containing $U(NO_3)_{108}(OH)_{4:92}$; at this stage a yellow precipitate began to

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separate. It happened that this change corresponded exactly to a new section of the curve, and the point of inflexion corresponded to the solution in which the change in shade of yellow was first noticed. The diminished hydrion concentrations of the deeply coloured solutions, about $p_{\rm H}$ 3.7, were close to that at which precipitation began, $p_{\rm H}$ 4.2. The deepening in colour of the highly basic solutions seems to have been due to a gradual increase in the size of the basic particles, the uranium hydroxide being held in solution in a state closely akin to that of a colloid. The hydrion concentration of the solution when 48 c.c. of alkali had been added was $10^{-3.7}$; the solution then contained the proportions of uranium and nitrate present in uranyl nitrate but was much deeper in colour than that obtained by dissolving uranyl nitrate crystals. The explanation of this difference probably lies in the fact that uranyl nitrate is crystallised from strongly acid solutions. On solution in water, it tends to revert to a state which is probably colloidal, as shown by the changes in colour and in conductivity which it undergoes on standing and especially at higher temperatures (Dittrich, Z. physikal. Chem., 1899, 29, 449). If the increase in conductivity which takes place on standing is due to the formation of particles which are essentially colloidal, these particles must be capable of some kind of ionisation. There seems to be very little support for the belief that uranyl salt solutions contain the "uranyl" kation; none is to be found in conductivity measurements, which show that the increases in conductivity with dilution of solutions of the nitrate, chloride, and sulphate are anomalous.

The diagram shows that precipitation was complete when 64 c.c. of alkali had been added as compared with the 64.7 c.c. which were required for the complete formation of uranic hydroxide. Hence the precipitate was uranic hydroxide containing a very small quantity of undecomposed nitrate. The text-books state that alkalis precipitate "diuranates" and not uranium hydroxide; *e.g.*, with sodium hydroxide, the precipitate is stated to be Na₂U₂O₇ (compare Roscoe and Schorlemmer's "Treatise," Vol. II, p. 1154, revised 1923). Jolibois and Bossuet (*Compt. rend.*, 1922, **174**, 1625) found that the precipitates produced by the action of sodium hydroxide on uranyl nitrate solutions contained no nitrate; the small quantities of sodium hydroxide present, varying from 1.2 to 8% they considered to be adsorbed.

Dilute acid solutions of uranium nitrate or uranyl salt solutions themselves, when gently heated, underwent some profound change; the colour became deeper and the reverse change on cooling took place very slowly. They became alkaline to phenolphthalein when

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the theoretical amount of alkali was added but a precipitate separated only when an appreciable excess of alkali had been added or the solution had been boiled for some time. The opalescence of the alkaline colloidal solution depended on the temperature to which the original solution had been heated. The deep yellow solutions formed by gentle heating were almost clear, whereas those which had been boiled became visibly colloidal. If not too great an excess of alkali had been added, the resulting colloidal solutions remained quite stable for several days. They were coagulable on addition of 1 or 2 c.c. of saturated potassium chloride solution. Heating thus appeared to have caused some change in the state of aggregation of the particles of uranium hydroxide or more likely of highly basic salt, which were probably in equilibrium with free nitrate ions and were thereby enabled to enter into reaction with alkalis so that the uranium hydroxide complexes remained in colloidal solution.

Curve 7 represents the titration of an acid solution of ferric chloride and correlates the changes in hydrion concentration with the changes in colour. It is something more than a coincidence that the colours of solutions containing basic salts should be similar to those of their respective hydroxides. The colour of solutions of both the basic salts of chromium with strong acids and chromium hydroxide is green, and the uranium solutions are pale yellow but become intensely yellow as they become more basic and are then identical in colour with uranium hydroxide. As is well known, ferric chloride solutions freshly prepared or containing an excess of free acid, are only slightly coloured; on standing, the solution reddens and its colour approaches that of red ferric hydroxide. In the present titration the end of the neutralisation of the free acid appears to be indicated by an inflexion, at 20.1 c.c. of sodium hydroxide. As the solution was rendered more basic, the colour gradually changed from yellow to red. It became quite red after addition of 30 c.c. of sodium hydroxide, when the composition of the solute had become Fe(OH)_{0.74}Cl_{2.26}, and with 39 c.c. it began to opalesce. Afterwards the solution became increasingly colloidal and became opaque at $p_{\rm H}$ 3, which, as will be seen from the curve, occurred just when the sudden change in hydrion concentration had begun. Coagulation set in when the p_{π} had become 6.6 and 58 c.c. of alkali had been added, the composition of the basic chloride then being $Fe(OH)_{2.85}Cl_{0.15}$.

As the colloidal solution persisted until nearly all the chloride had reacted, experiments were made to see if it were possible to prevent coagulation while the solution was being subjected to a sudden fall in hydrion concentration. As in the case of basic

uranium nitrate solutions, this possibility depended on the changes which had taken place in the ferric chloride solutions before treatment with alkali. Aqueous solutions of ferric chloride more dilute than N/25, on boiling, acquired a deep red colour, and often remained colloidal on treatment with N/10-alkali in slight excess. Small. red, amorphous precipitates separated in some cases, but even then the precipitation was incomplete and the solids did not settle until several hours had elapsed. The presence of a little hydrochloric acid in the solutions before heating had some stabilising effect on the colloidal solutions which were subsequently produced. In one case the colloidal solution remained stable for nearly 3 months. This solution was prepared by adding 55 c.c. of N/10-sodium hydroxide to 500 c.c. of a boiling solution containing 100 c.c. of N/25-ferric chloride and 10 c.c. of N/10-hydrochloric acid. Tt seems certain that the red colour of boiled ferric chloride solutions was due to dispersed ferric hydroxide particles, and consequently the increase in the size of the basic chloride particles caused by rendering the solution alkaline was not so great as that occurring in an unboiled solution, and therefore did not produce coagulation. The increased stability of the colloidal solutions prepared from acidified ferric chloride solutions was probably due to the effect of the acid in suppressing the growth of the colloidal particles on boiling, thereby giving rise to a more highly dispersed and more stable colloidal solution. Prolonged boiling decomposed these alkaline colloidal solutions, and they were readily coagulated on addition of electrolytes in sufficient amounts.

It is probable that the solubility product of very weak bases such as ferric hydroxide has very little meaning, but in view of the recent work of Jellinek and Gordon (Z. physikal. Chem., 1924, 112, 235) it is interesting to compare their value for [Fe^{···}][OH']³, viz., 10^{-37'9}, with that given by the titration curve. They measured the hydrogen-ion concentrations with the hydrogen electrode of solutions of ferric chloride, containing potassium chloride to coagulate the colloidal solutions, to which varying amounts of sodium hydroxide had been added. The concentration of ferric ions in the mother-liquor was determined colorimetrically as thiocyanate. The latter method is probably unsatisfactory, because the acid used would materially affect the concentration of ferric ions in a basic ferric chloride solution. If it be assumed that in the titration the appearance of opalescence marked the point at which ferric hydroxide actually began to separate, and that the amount of free ferric ions was equivalent to the remaining amount of alkali to be added to decompose the ferric chloride completely, the value for the solubility product becomes 10^{-37.7}. Thus opalescence occurred

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on the addition of 39 c.c. of N/10-alkali; $p_{\rm H} = 2.3$. Hence $[OH'] = 10^{-11.8}$ and $[Fe^{\cdots}] = 20.9/39.8 \cdot 100/139 \cdot 0.0133 = 10^{-2.3}$ Müller ("Das Eisen und seine Verbindungen," 1917, p. 281) calculated the value $6.5 \times 10^{-4.7}$ from Bodländer's formula (Z. physikal. Chem., 1898, 27, 66).

Arrangement of Metals in the Order of the Hydrogen-ion Concentrations required for the Precipitation of their Hydroxides.

It was stated in Part I that no principle has yet been found which leads to a satisfactory arrangement of the metals such that the order is that of the basic strengths of their hydroxides. The titrations described in the foregoing pages show that for each hydroxide there is a definite hydrogen-ion concentration at which its precipitation normally takes place. It is true that the majority of the hydroxides are thrown out of solution as basic precipitates, but the hydrogen-ion concentrations at which these are precipitated probably do not differ greatly from those of the particular hydroxides. The table gives the metals in the order of the hydrogen-ion concentrations at which their respective hydroxides are precipitated from dilute solutions. Although it is not certain that this order is that of the actual basic strengths of the hydroxides, it can be stated, as will be shown later, that it is these hydrogen-ion concentration relationships which underlie many of the reactions of the various metallic salt solutions.

Hydrion conc.		Hydrion conc.		Hydrion conc.	
10-11 10-10 10-9	Magnesium Silver Manganous		Cadmium Praseodymium Neodymium Vttrium	10-5	Copper Chromium
10- ⁸	Lanthanum Mercuric Cerous	10-7	Samarium Ferrous (?) Lead (?)	10-4	Uranic Thorium
	Nickel	10 •	Beryllium	10 -	Stannous Zirconium Ferric

An arrangement now widely adopted is that based by Abegg and Bodländer (Z. anorg. Chem., 1899, **20**, 453) on their theory of electroaffinity, which states that the electrolytic potential constitutes an approximate measure of the basic strength of the metal. Comparison with the present arrangement brings out the following important differences. According to the position of aluminium in the table, aluminium hydroxide is an extremely weak base, weaker than chromium hydroxide, yet aluminium occurs higher than chromium in the electropotential series. There is no doubt

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that both aluminium and chromium hydroxides are much weaker bases than manganous hydroxide, and this is also indicated by the present scheme, but according to the electropotential series they are both placed above manganese. Heyrovský (Proc. Roy. Soc., 1923, A, 102, 628) has pointed out that the thallous potential is small, which necessitates placing thallium relatively close to hydrogen in the electropotential series, in spite of the fact that thallous hydroxide is a strong base and is not precipitated by alkalis. If it be assumed that the electrolytic potentials of metals under identical conditions are a measure of their electroaffinities, *i.e.*, the free energies by which the elements take up electric charges, it cannot be concluded, as was admitted by Abegg and Bodländer, that the potentials as determined are in any way parallel to the electroaffinities, for nothing is known of the relative atomic solubilities of the various metals in water. Unless it is known that the number of atoms of the different metals which pass into solution is the same, no guarantee can be obtained that an arrangement accruing therefrom is in any way true. Heyrovský attempted to amend the above method by introducing such factors as the mass of the kation, and obtained an order which he stated "comes out right." Hevrovský's system indicates that lead hydroxide is a stronger base than magnesium hydroxide, and that mercuric oxide is a very weak base, weaker than zinc hydroxide. The present table suggests the contrary in both cases. It is well known that water becomes alkaline (to litmus) when shaken with mercuric oxide, but remains neutral when shaken with zinc oxide.

It is probable that the present table provides as satisfactory an arrangement as any that has been hitherto advanced, as far as the general reactions which involve the strength of the base are concerned. The position of the hydroxides in the table is the important factor in processes for separating hydroxides or basic salts, as was shown to be the case in the separation of thoria from the rare earths (see Part III). The basic acetate and basic succinate methods for the separation of manganese from iron depend on the great difference in hydrogen-ion concentration required to precipitate their respective hydroxides. Lundell and Knowles (J. Amer. Chem. Soc., 1923, 45, 676) have shown that the separation may equally well be performed by fractional precipitation with ammonia in presence of ammonium chloride, the precipitation of the ferric hydroxide being controlled by rendering the solution just alkaline to methyl-red, *i.e.*, about $p_{\rm H}$ 6.3. The reason for this is apparent from the hydrion table of the hydroxides. The table also explains why mercuric oxide can be used as a separating agent for various bases. Thus E. F. Smith and Heyl (Z.

anorg. Chem., 1894, 7, 87) showed that mercuric oxide caused the complete precipitation in the cold of ferric, aluminium, and chromium hydroxides, the partial precipitation of zinc, cobalt, nickel, uranium, beryllium, cerous, and lanthanum hydroxides, and failed to precipitate manganous hydroxide. The table shows that the hydrogen-ion concentration peculiar to mercuric oxide is greater than that required to precipitate manganous hydroxide, is approximately equal to that required for lanthana, is somewhat less than that required by those hydroxides which were partly precipitated, and is considerably less than that of the three bases which were completely precipitated.

Summary.

(1) The reactions between sodium hydroxide and salt solutions of certain metals have been followed with the oxygen electrode, the hydrogen electrode being inapplicable.

(2) A scale of hydrogen-ion concentrations has been applied to the observed voltages, accurate to the extent of about 0.5 $p_{\rm H}$ unit except in the case of the silver nitrate titration.

(3) Basic precipitates, probably containing definite basic salts, were obtained from solutions of mercuric chloride, copper sulphate, cadmium sulphate, and lead nitrate.

(4) The precipitate obtained from uranium nitrate solution was the hydroxide containing a little nitrate, and not sodium diuranate as is often stated.

(5) Significant changes in colour were observed in the titrations of both uranic and ferric salts.

(6) The twenty-five hydroxides which have been investigated have been arranged in the order of their respective precipitation hydrogen-ion concentrations.

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