379. *Electrometric Studies of the Precipitation of Hydroxides. Part VII. Glass-electrode Titrations of Mercuric Salt Solutions.*

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In general, none of the anions, NO_3', Cl', and SO_4'', has an appreciable effect on the p_H values at which the metallic bases undergo precipitation, evidently owing to the fact that the corresponding salts of any particular metal ionise to similar extents in solutions of the same concentration. With bivalent mercury, however, conductivity measurements reveal that the salts of strong oxyacids are considerably dissociated, whilst the reverse is true of the chloride, bromide, cyanide, nitrite, and acetate, in many cases owing to complex-ion formation.

Britton (J., 1925, **127**, 2128) found that precipitation does not begin when sodium hydroxide is added to mercuric chloride solution until p_H 7·4 is attained, and Britton and Robinson (*Trans. Faraday Soc.*, 1932, **28**, 531) have shown that the solubility-product principle holds qualitatively during the precipitation of a basic salt. Hence, in view of the widely differing concentrations of mercuric ions in solutions of the various mercuric salts, it would appear probable that the p_H values at which precipitation with alkali actually occurs therefrom would also exhibit corresponding variations. Moreover, it would be expected that the p_H of the hydroxide precipitation from those salts which ionise in a complex manner, might be influenced by the presence in solution of alkali salts of the same acid. The present paper records glass-electrode titrations with sodium hydroxide of solutions of several mercuric salts, some of them also in the presence of the corresponding salt of an alkali metal.

EXPERIMENTAL.

The experiments included the titration of 100 c.c. of each of the mercuric salt solutions specified in Table I, which also gives the concn. of the titrating NaOH and the legend of the corresponding curve. All concns. are in mols./litre.

TABLE I.

Hg salt and concn.	Added acid and concn.	Added salt and concn.	NaOH, *N*.	Curve.
$HgCl_2$, 0·025	—	—	0·1019	$HgCl_2$
,, 0·010	—	KCl, 2·478	0·1000	250KCl
,, 0·010	—	,, 0·994	0·1000	100KCl
,, 0·010	—	,, 0·0994	0·1000	10KCl
$HgBr_2$, 0·00305	—	—	0·0100	$HgBr_2$ (upper)
,, 0·00526*	—	—	0·0200	$HgBr_2$ (lower)
$Hg(CN)_2$, 0·025	—	—	0·0992	$Hg(CN)_2$
$HgSO_4$, 0·0251	H_2SO_4, 0·0969	—	0·200	$HgSO_4$
$Hg(NO_3)_2$, 0·02446	HNO_3, 0·02296	—	0·0994	$Hg(NO_3)_2$
$Hg(ClO_4)_2$, 0·02576	$HClO_4$, 0·01337	—	0·0994	$Hg(ClO_4)_2$
$Hg(NO_3)_2$, 0·01023	HNO_3, 0·00196	$NaNO_2$, 0·02046	0·0992	$Hg(NO_2)_2$
,, 0·01023	,, 0·00196	,, 1·087	0·0992	$100NaNO_2$
$Hg(OAc)_2$, 0·00932	HOAc, 0·00040	—	0·0992	$Hg(OAc)_2$
,, 0·00466	—	NaOAc, 1·5	0·0992	320NaOAc

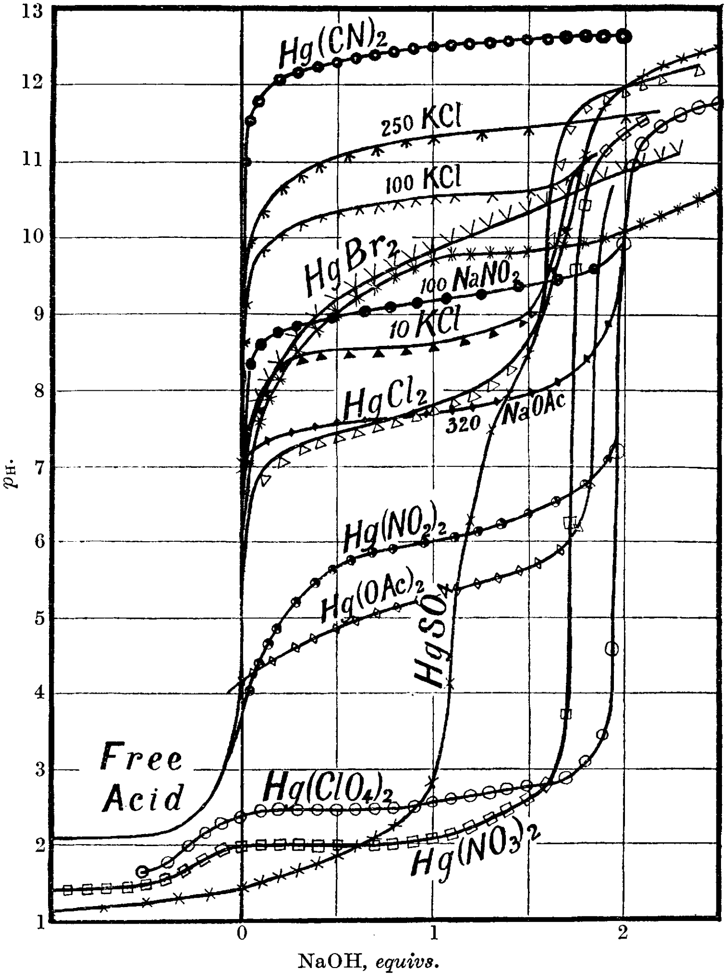
* Higher concns. of $HgBr_2$ could not be used owing to the sparing solubility of the salt.

The glass-electrode apparatus employed was similar to that described by Morton (*J. Sci. Inst.*, 1930, **7**, 187; see also Britton and Robinson, *loc. cit.*), the deflexions of a sensitive ballistic galvanometer being calibrated daily in terms of p_H values by one or more titrations of a universal buffer mixture.

In the $Hg(CN)_2$ titration, Fig. 1 shows that the p_H values set up immediately were those resulting from the added alkali alone; pptn., therefore, did not take place owing to lack of reaction. Lower p_H values, between 7 and 11, prevailed during the bromide titrations, but pptn. did not occur from the more dilute solution, and from the other, it occurred only after 1·05 equivs. of alkali had been added (p_H 9·80).

In the $HgCl_2$ titration, pptn. started at once (p_H 6·44), but occurred chiefly at p_H 7—8; it was complete with 1·6 equivs. of alkali, suggesting that $3HgO,HgCl_2$ had first separated and had subsequently undergone slight decomp. (Similar observations were made by Britton, *loc. cit.*, with oxygen electrodes.) Variations in the conc. of $HgCl_2$ (0·1—0·0025*M*) had but little effect on the [H˙] at comparable stages of the reaction.

Fig. 1.



Voit (*Annalen*, 1857, **104**, 351) noted that KCl prevented pptn. of HgO by alkali, but we find that at least 250 mols. of KCl per mol. of $HgCl_2$ are necessary to prevent immediate pptn. in 0·01*M*-$HgCl_2$ solution, and even then a little HgO separates on standing. Comparison of the curves for approx. 250, 100, and 10 mols. of KCl per mol. of $HgCl_2$ with that corresponding to pptn. from $HgCl_2$ alone shows that the effect of increasing KCl concn. is to raise the p_H at which pptn. occurs.

The p_H's obtained in NaOH titrations of solutions of $HgCl_2$ and varying amounts of KI showed that the complex ion, HgI_4'', was unattacked.

Both $Hg(NO_3)_2$ and $HgSO_4$ undergo appreciable hydrolysis in solution, basic salts being deposited; $Hg(ClO_4)_2$, however, yields an almost clear solution. For the purpose of titration, solutions of these salts were prepared by dissolving HgO in just sufficient acid to produce clear solutions; hence, in the $HgSO_4$ solution 97·0 c.c. of 0·2*N*-NaOH would be required to neutralise the free acid, and 25·1 c.c. more to form HgO. The fact that the p_H of the solution was lower than 1 indicates that even in the presence of an almost four-fold excess of free acid the $HgSO_4$ was much hydrolysed. The glass electrode is not entirely satisfactory in solutions of $p_H < 1·5$, so the p_H values are only approx. Cloudiness occurred with 11·0 c.c. and pptn. became complete with 110·8 c.c. of NaOH (p_H 4). The curve shows that the first sharp inflexion occurred at 1·1NaOH to 1·0$HgSO_4$; but after p_H 6 had been reached, the change of p_H became more gradual, indicating that the basic salt first pptd. was being decomposed. Cox (*Z. anorg. Chem.*, 1904, **40**, 146) has demonstrated by phase-rule methods that $HgSO_4$ forms only one basic sulphate, *viz.*, $2HgO,HgSO_4$, although Hoitsema (*Z. physikal. Chem.*, 1895, **17**, 655) states that $HgO,2HgSO_4$ also exists. The former would require 1·33 equivs. of alkali, and the latter 0·67 equiv. It is possible that the basic sulphate pptd. was Cox's salt, slightly contaminated with a less basic sulphate, possibly Hoitsema's.

The alkali required to neutralise the excess acid in the $Hg(NO_3)_2$ solution was 23·11 c.c., and that to decompose the $Hg(NO_3)_2$ was 49·2 c.c. Pptn. began with 17·5 c.c. (p_H 1·74) and ended with 65·5 c.c. (*i.e.*, 1·68 equivs.). Since the initial p_H was approx. 1·43, the $Hg(NO_3)_2$ was hydrolysed to the extent of about 29% even in presence of the acid. The appearance of the inflexion before the stoicheiometric end-point shows that the salt pptd. was somewhat more basic than $2HgO,Hg(NO_3)_2$.

In the $Hg(ClO_4)_2$ titration, the initial p_H (1·68) indicates that the $Hg(ClO_4)_2$ was 14·6% hydrolysed.

Solutions of $HgCl_2$, unlike the nitrate, sulphate and perchlorate, were only very slightly acidic ($p_H \approx 4$). Since the glass electrode, when calibrated over a wide p_H range, tends to give somewhat inaccurate results in unbuffered solutions such as those of $HgCl_2$, an electrode was calibrated between p_H 3 and 5 immediately before and after the measurements. This was used at 18° with two series of $HgCl_2$ solutions, (*a*) prep. at room temp., and (*b*) boiled and immediately cooled to 18°. The respective p_H values are recorded in cols. 2 and 4 of Table II. From these values the % hydrolysis was calc., both Cl radicals

TABLE II.

Dilution, l./g.-mol.	p_H (*a*).	Hydrolysis, % (*a*).	p_H (*b*).	Hydrolysis, % (*b*).	$\kappa_{25} \times 10^5$.	p_H, calc.	Hydrolysis, % (25°).
32	3·99	0·16	3·82	0·24	6·81	3·80	0·26
64	4·08	0·27	3·96	0·35	5·19	3·92	0·39
128	4·20	0·40	4·18	0·42	3·98	4·03	0·60
256	4·28	0·67	4·44	0·47	3·12	4·14	0·94
512	4·56	0·71	4·67	0·55	2·47	4·24	1·48

being assumed to participate in the hydrolytic reactions. The two sets of p_H data show that boiling had but little effect on the extent of the hydrolysis.

According to Sherrill (*Z. physikal. Chem.*, 1904, **47**, 103), Morse (*ibid.*, 1902, **41**, 709), and Luther (*ibid.*, 1904, **47**, 107), the concn. of $Hg^{\cdot\cdot}$ ions in $HgCl_2$ solutions is extremely small, Luther giving 10^{-8} in $0{\cdot}26M$-solution. Such a low ionisation could not be reflected in the conductivity measurements, and hence Ley's assumption (*Ber.*, 1897, **30**, 2192), that the conductivities of $HgCl_2$ solutions must have been caused by the hydrolysed acid, finds justification (see, however, Luther, *Z. physikal. Chem.*, 1901, **36**, 385). His values of the spec. conductivity (κ) at 25° are recorded in col. 6. By taking Λ_{0HCl} at 25° to be 427, the p_H values and % hydrolysis corresponding to Ley's data have been calculated (cols. 7 and 8). These are in satisfactory agreement with the direct measurements, although for the more dilute solutions they are probably a little too high.

Besides being considerably hydrolysed, $Hg(NO_3)_2$ solutions give rise to a relatively large concn. of $Hg^{\cdot\cdot}$ ions (cf. Morse, *loc. cit.*). As shown by Fig. 1, it is not possible to estimate volumetrically the amount of free HNO_3 in the presence of $Hg(NO_3)_2$. The present results show, however, that if KCl is added in an amount at least sufficient to form $HgCl_2$ by metathesis, this salt is formed quantitatively and any excess of strong acid (HNO_3 or HCl) can then be accurately titrated by using methyl-orange. The curve in Fig. 1 commencing at p_H 2·1 refers to titration of 100 c.c. of $0{\cdot}025M$-$Hg(NO_3)_2$, $0{\cdot}015N$-HNO_3, and $0{\cdot}05M$-KCl with $0{\cdot}1N$-NaOH. The neutralisation of the free acid was complete at p_H 5·3; more alkali then caused pptn., and the p_H curve followed the same course as in the direct titration of $HgCl_2$.

The conductivity data of Ley and Kissell (*Ber.*, 1899, **32**, 1363) show that both the nitrite and the acetate are but slightly ionised, and Pick (*Z. anorg. Chem.*, 1906, **51**, 20) has found that, with excess of KNO_2, $Hg(NO_2)_2$ forms a complex anion of the type $Hg(NO_2)_4''$. In view of the small ionisation of $Hg(NO_2)_2$, it was considered that this salt would be formed in solution merely by allowing $Hg(NO_3)_2$ to react with the equiv. of an alkali nitrite. The curve $Hg(NO_2)_2$ shows the neutralisation of the small excess of HNO_3, and the portion corresponding to the decomp. of the $Hg(NO_2)_2$ formed lies between p_H 4 and 7. Pptn. was delayed until p_H 5·93 (0·68 equiv. of NaOH). The curve marked $100NaNO_2$ shows the effect of adding about 100 mols. of $NaNO_2$ to 1 mol. of $Hg(NO_2)_2$. In this case, the pptn. was partial and did not begin until p_H 10·7 was attained (2·23 equivs. NaOH). Using *ca.* 10 mols. of $NaNO_2$, no ppt. was formed until 1·05 equiv. of alkali was added (p_H 7·6) and pptn. occurred mainly between p_H 7·6 and 8·1.

With $Hg(OAc)_2$ pptn. began at p_H 5·37 (1·13 equivs. of NaOH). The p_H values during the attack of the alkali ranged between 4 and 6·7, *i.e.*, that prevailing when free HOAc is neutralised with alkali. Hence it was calc. that the $Hg(OAc)_2$ must be hydrolysed to the extents shown below for various stages of the titration, the method of calculation being that adopted by Britton and Meek, this vol., p. 183 :

NaOH,			Hydrolysis, %.	
c.c.	equiv.	p_H.	I.	II.
4	0·383	4·75	26·32	62·40
8	0·809	5·12	29·80	50·58
12	1·23	5·46	31·80	42·70
16	1·66	5·90	34·64	40·70

The $Hg^{\cdot\cdot}$ concn. of $Hg(OAc)_2$ solution is exceedingly small : the solubility product of $Hg(OH)_2$, 1×10^{-26}, was just exceeded at p_H 5·37, and therefore the $Hg^{\cdot\cdot}$ concn. was $10^{-8\cdot5}$. Hence the basic complex present in the solution during the first half of the titration is probably un-ionised, unless it dissociates in a complex manner and furnishes inappreciable amounts of $Hg^{\cdot\cdot}$ ions.

The addition of NaOAc to a $Hg(OAc)_2$ solution causes no pptn. in the cold or on boiling, but leads to solutions of gradually increasing p_H such as would occur if the Na salt were buffered by free HOAc. The p_H values of various solutions of the two salts are given below. They show that the NaOAc keeps the highly basic $Hg(OAc)_2$ in solution. Moreover, if sufficient NaOAc is added, NaOH produces no immediate ppt. even on boiling, but a very faint ppt. separates on standing. The original solution [320 mols. of NaOAc per mol. of $Hg(OAc)_2$] had p_H 7·33, which gradually increased to 9 on addition of 2 equivs. of NaOH. In the absence of $Hg(OAc)_2$, the NaOAc would have given a p_H of 8·5, so the lower values must be attributed to the existence of free HOAc hydrolysed from the Hg salt. The solution therefore resembles those, particularly that of Pb, investigated by Britton and Meek (*loc. cit.*), in which the heavy-metal hydroxide or basic salt is kept in solution by means of NaOAc.

Concn., *M*.		$\frac{NaOAc}{Hg(OAc)_2}$.		Hydrolysis,%.	
$Hg(OAc)_2$.	NaOAc.		p_H.	I.	II.
0·00932	0·1	10·73	5·86	39·81	44·90
0·00932	0·2	21·46	6·13	42·66	45·99
0·00932	0·3	32·19	6·29	44·56	46·86
0·00932	0·4	42·92	6·42	43·61	45·97
0·00932	0·5	53·65	6·49	46·76	49·49

Discussion.

The curves given in Fig. 1 reveal that precipitation with alkali may take place at almost any p_H, depending on the nature of the mercuric salt and especially on the presence of certain alkali salts. Calculations show that the p_H range in which precipitation of basic mercuric salts or mercuric oxide occurs is determined mainly by the solubility product $[Hg^{\cdot\cdot}][OH']^2$. At 18° this is 1×10^{-26} (Britton, " Hydrogen Ions," 2nd edtn., 1932, p. 83 ; Labendzinsky, *Z. Elektrochem.*, 1904, **10**, 80 ; Allmand, *ibid.*, 1910, **16**, 263 ; Grossmann, *Z. anorg. Chem.*, 1905, **43**, 368).

Although mercuric nitrate, sulphate, and perchlorate are appreciably hydrolysed, there is evidence that they ionise fairly extensively : Morse (*Z. physikal. Chem.*, 1902, **41**, 709) found that a dilute solution of mercuric nitrate containing an equimolar amount of nitric acid was about 40% ionised. The ionic product, $[Hg^{\cdot\cdot}][OH']^2$, set up during the precipitation of basic mercuric nitrate can thus be roughly ascertained from the p_H value and the concentration of mercuric nitrate left in solution at any particular stage, the assumption being made that the basic nitrate indicated by the inflexion of the curve was precipitated from the beginning : the values thus found range from $0{\cdot}3 \times 10^{-26}$ to $0{\cdot}7 \times 10^{-26}$, which agree sufficiently with the accepted values to justify the belief that the solubility product of mercuric hydroxide determines the precipitation.

Precipitation from mercuric chloride solutions can be explained in terms of the equilibrium, $HgCl_2 \rightleftharpoons Hg^{\cdot\cdot} + 2Cl'$, which Luther (*Z. physikal. Chem.*, 1901, **36**, 385) and Morse (*loc. cit.*) have found may be represented by $K = [Hg^{\cdot\cdot}][Cl']^2/[HgCl_2]$. For K Luther gave $1{\cdot}5 \times 10^{-14}$ and $0{\cdot}18 \times 10^{-14}$, whilst Morse reported $1{\cdot}0 \times 10^{-14}$. Taking the last value, and assuming (*a*) that only the chloride-ion concentration originating from the sodium chloride formed during the precipitation with alkali was of sufficient magnitude to have any effect, (*b*) that the concentration of undissociated mercuric chloride was equal to that of the unattacked mercuric chloride, it was possible to calculate the mercuric-ion concentration at any stage of the precipitation. Hence, in conjunction with the p_H value, the following solubility products were calculated.

Titration of 100 *c.c. of* 0·025M-$HgCl_2$ *with* 0·1019N-NaOH.

NaOH, equivs.	0·2	0·4	0·6	0·8	1·0	1·2	1·4
p_{OH}	7·14	6·93	6·78	6·64	6·47	6·29	5·96
$[Hg^{\cdot\cdot}] \times 10^{13}$	58·7	13·2	5·1	2·4	1·3	0·6	0·2
$[Hg^{\cdot\cdot}][OH']^2 \times 10^{26}$	3·1	1·8	1·4	1·2	1·4	1·5	2·6

This solubility product was similarly determined from the data obtained by the addition of sodium hydroxide to mercuric bromide, Morse's value (*loc. cit.*) $[Hg^{\cdot\cdot}][Br']^2/[HgBr_2] = 2{\cdot}0 \times 10^{-18}$ being used.

Titration of 100 *c.c. of* 0·005264M-$HgBr_2$ *with* 0·020N-NaOH.

NaOH, equivs.	0·8	1·0	1·2	1·4	1·6	1·8
p_{OH}	—	4·62	4·55	4·53	4·47	4·41
$[Hg^{\cdot\cdot}] \times 10^{17}$	—	24·0	13·9	8·0	4·2	1·7
$[Hg^{\cdot\cdot}][OH']^2 \times 10^{26}$	—	13·8	11·1	6·9	4·8	2·6

In presence of much alkali chloride mercuric salts are converted into complex salts in which the mercury exists in the anion, $HgCl_4''$. Abegg and Sherrill (*Z. Elektrochem.*, 1903, **9**, 549) found that ionisation of this anion, $HgCl_4'' = Hg^{\cdot\cdot} + 4Cl'$, was governed by $[Hg^{\cdot\cdot}][Cl']^4/[HgCl_4''] = K$, for which $p_K = 15{\cdot}95$. Pick (*Z. anorg. Chem.*, 1906, **51**, 20) obtained 16·30 for p_K. By assuming also that the ionic product $[Hg^{\cdot\cdot}][OH']^2$ during the precipitation from solutions of mercuric chloride in the presence of large amounts of potassium chloride had the value 1×10^{-26}, it was possible to calculate $[Hg^{\cdot\cdot}]$, and, if all the mercuric chloride is converted into $HgCl_4''$ ions, $[HgCl_4'']$ and $[Cl']$ could be found and p_K evaluated. The degrees of ionisation, α, in the 10KCl and 100KCl titrations were taken as 0·848 and 0·772 respectively. The typical values of p_K, given in Table III, are of the same order as those previously obtained.

TABLE III.

Titration of 100 *c.c. of* 0·01M-$HgCl_2$ (+0·09944N-KCl) *with* 0·111N-NaOH.

NaOH, equivs.	p_{H}.	$p_{Hg^{\cdot\cdot}}$.	$p_{HgCl_4''}$.	$p_{Cl'}$.	p_K.
0·4	8·50	14·6	2·14	1·14	17·0
0·7	8·54	14·6	2·27	1·12	16·8
1·0	8·67	14·9	2·45	1·10	16·8
1·3	8·83	15·2	2·73	1·08	16·8

Titration of 100 *c.c. of* 0·01M-$HgCl_2$ (+0·9944N-KCl) *with* 0·1N-NaOH.

NaOH, equivs.	p_{H}.	$p_{Hg^{\cdot\cdot}}$.	$p_{HgCl_4''}$.	$p_{Cl'}$.	p_K.
0·7	10·47	18·5	2·22	0·15	16·9
1·0	10·56	18·7	2·34	0·16	17·0
1·3	10·61	18·8	2·51	0·17	16·9
1·6	10·73	19·0	2·76	0·17	17·0

Since it was just possible that the mercuric-ion concentration of mercuric nitrite solutions would be established by equilibrium, $Hg(NO_2)_2 \rightleftharpoons Hg^{\cdot\cdot} + 2NO_2'$, values of $K = [Hg^{\cdot\cdot}][NO_2']^2/[Hg(NO_2)_2]$ were calculated by taking 1×10^{26} as the solubility product of mercuric hydroxide and assuming that the nitrite ions were produced by the sodium nitrite formed. The values obtained varied from 2·3 to $6·8 \times 10^{-12}$.

Pick (*loc. cit.*) has shown that, in the presence of an excess of alkali nitrite, mercuric nitrite enters into a complex anion, for which $[Hg^{\cdot\cdot}][NO_2']^4/[Hg(NO_2)_4''] = 10^{-13·54}$. Calculations based on an alkali titration of the $10NaNO_2 : 1Hg(NO_2)_2$ solution give remarkably constant values throughout the whole course of precipitation, *viz.*, $p_K = 14·8—15·0$.

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