

363. *Electrometric Studies of the Precipitation of Hydroxides. Part V. Tervalent Gold Chloride Solutions.*

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EVEN though hydrochloroauric acid and its salts are known in the crystalline form, there is a complete absence of physicochemical evidence of its behaviour in solutions as a monobasic acid. The only work recorded is the conductivity measurements of Kohlrausch (*Z. physikal. Chem.*, 1900, **33**, 272), from which he concluded that, not only did the molecule of hydrochloric acid contained in hydrochloroauric acid exist in solution as such, but the auric chloride underwent appreciable hydrolysis. Perhaps the fact that dilute hydrochloroauric acid solutions form no precipitate on addition of alkali has been considered as favouring the view of their acid nature. The present work, which consists of a detailed study of the reaction of sodium hydroxide with solutions of hydrochloroauric acid, confirms the conclusions of Kohlrausch and also provides further evidence of the amphoteric nature of auric oxide and of the formation of aurates, *e.g.*, NaAuO_2 , in solution.

Two samples of "gold chloride," were used, one agreeing with the formula $\text{HAuCl}_4 \cdot 3 \cdot 8\text{H}_2\text{O}$, and the other with $\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$. The different H_2O contents were due to deliquescence, and the Au was estimated by the method of Vanino and Seemann (*Ber.*, 1899, **32**, 1968). Conductivity and p_{H} measurements revealed no difference between solutions having the same concn. and prep. from the two products.

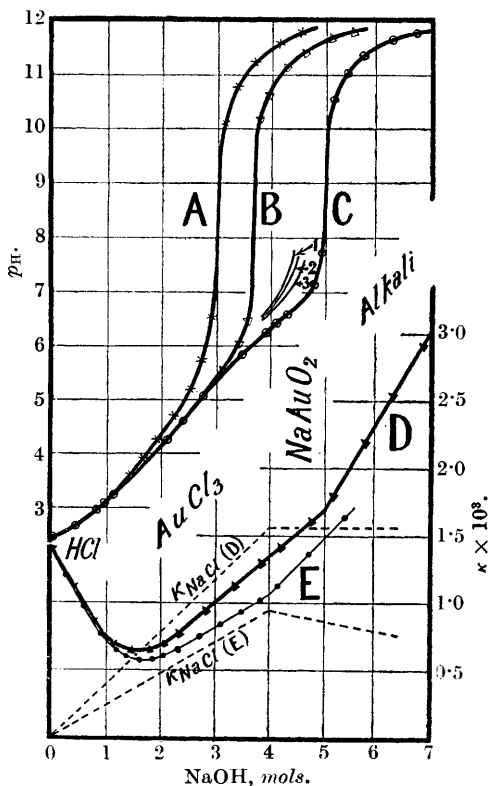
The glass electrode was used for the measurements of the p_{H} values (see Britton and Dodd, this vol., p. 1940). These were determined at 18° and the specific conductivities were measured at 25° . Preliminary glass-electrode titrations of HAuCl_4 solutions indicated that the p_{H} values set up on the addition of alkali were dependent on the length of time allowed before making observations. This was due, not to sluggishness of the glass electrode, but to the slowness of the attack of the alkali on the HAuCl_4 . Curves A and B (see fig.) are the titration curves of 50 c.c. of 0.004*M*- HAuCl_4 with 0.0392*N*- NaOH added in 2-c.c. portions, the potentials being measured, respectively, as rapidly as possible (within 1 min.) and 5 mins. after the addition. Neither of these two curves was reproducible. Curve C, however, which refers to a series of solutions of const. vol. that had stood until no further reaction occurred, as indicated by p_{H} changes, is reproducible. The time required was about 2 days. The solutions were prep. by adding the desired vols. of 0.0196*N*- NaOH to vols. of 10 c.c. of 0.02*M*- HAuCl_4 and then diluting each to 60 c.c.

The immediate titration curve, A, shows that the sudden increase in p_{H} caused by the presence of unattacked alkali occurred with 3 mols. of NaOH ; in the second curve, B, the inflexion was produced with appreciably less than 4 mols., whilst in the final curve, C, it was delayed until exactly 5 mols. had

been added. In none of the reactions was any ppt. formed, neither was any turbidity produced. The fact that 1 mol. of alkali had to be added in addition to the stoichiometrical amount, *viz.*, 4 mols., was evidently due to the formation of sodium aurate, NaAuO_2 , in the solution. The three curves coincide exactly during the addition of the first mol. of alkali, whilst B and C coincide during the reaction with yet another 2 mols. Curves 1, 2, and 3 give further evidence of the time required for the reaction of 4—4.5 mols. of alkali, since they represent respectively the reaction after $\frac{1}{2}$, 1, and 3 hrs.

Curve D gives the spec. conductivities at 25° of the mixtures (see above, Curve C) that had been allowed to stand for 2 days. It shows a rapid fall

in spec. conductivity during the reaction with the first 1.5 mols. of NaOH , then a uniform rise until 5 mols. had been added, after which the slope produced is that due to free alkali. The broken line, marked κ_{NaCl} (D), corresponds to the spec. conductivity that would have been caused by the NaCl alone if the NaOH added up to 4 mols. had been converted into an equiv. amount of NaCl . It is probable that the lower conductivities actually obtained during the addition of 1.7—4 mols. of NaOH must have been due to some of the NaOH being utilised in forming, not NaCl , but an apparently less conducting sodium aurate. The remaining curve, E, is that of a conductometric titration performed as quickly as possible, though owing to the time



required to bring the solution in the cell to 25° , 6—8 mins. elapsed before each new addition of 2 c.c. of alkali could be made. It corresponds to the titration of 60 c.c. of 0.0033*M*- HAuCl_4 with 0.0392*N*- NaOH . In this curve the final break occurs at 4 mols., and the slope thereafter, being exactly that which would be produced by free alkali, shows that in the time allowed the reaction had proceeded a little farther than in the comparable p_H titration shown by Curve B. Whilst the initial sections of D and E are similar, as would be expected from the corresponding portions of A, B, and C, that portion of E between 2 and 4 mols. of alkali lies above the theor. curve for NaCl .

Discussion.

From each of the curves shown, it is evident that the reaction which took place during the addition of the first mol. of alkali was the neutralisation of the hydrochloric acid present in hydrochloroauric acid. This is made clear in the table, which gives the data corresponding to the first section of curves C and D. The p_H data in col. 2, moreover, show that the concentrations of hydrogen ions of the solutions during the addition of 1.5 mols. of alkali were even greater than could be set up by the single mol. of hydrochloric acid, and consequently the remaining mol. of auric chloride must have been undergoing hydrolysis, the extent of which is given in col. 3. As the free hydrochloric acid was neutralised, the hydrolysis rapidly increased from 6.5 to 23.3%. Assuming that the first 1.5 mols. of alkali reacted to form sodium chloride, it is possible to calculate (i) p_H values at 18° and κ at 25° of 0.003333*M*-HAuCl₄ solutions containing various amounts of sodium hydroxide, (ii) the

NaOH HAuCl ₄ ' mols.	p_H .	Hydrolysis of AuCl ₃ , %.	$\kappa_{\text{obs.}}$ $\times 10^3$.	$\kappa \times 10^3$.		
				HCl.	NaCl (calc.).	Total.
0.00	2.45	6.45	1.40	1.48	0.00	1.48
0.25	2.56	7.70	1.22	1.14	0.10	1.24
0.50	2.71	8.52	1.07	0.83	0.20	1.03
0.75	2.90	12.90	0.90	0.54	0.31	0.85
1.00	3.11	23.30	0.75	0.33	0.42	0.75
1.25	3.37	—	0.67	0.18	0.50	0.68
1.50	3.63	—	0.66	0.09	0.58	0.67

specific conductivity established by the hydrochloric acid, from the p_H value and Λ_0 at 25°, and (iii) the contribution made by the sodium chloride. The last were read off from a concentration-specific conductivity curve of sodium chloride (Stearn, *J. Amer. Chem. Soc.*, 1922, **44**, 670). It will be seen that the sums of these items given in the last column are almost equal to the observed specific conductivities, and therefore the basic portion of the auric chloride could not have been appreciably ionised. Hence the first stage of the reaction may be represented as

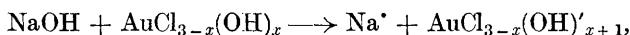


The lack of simple ionisation and the probable heterogeneous nature of the basic gold chloride would explain why the attack of alkali is a time reaction as shown by the direct electrometric titration curves. According to Hittorf and Salkovsky (*Z. physikal. Chem.*, 1899, **28**, 546), auric chloride exists in solution in the form



They showed that the gold existed in the complex anion. It is likely that in these titrations the initial effect of the alkali was to

react with the basic gold chloride to form a stable negatively charged complex, thus



which, as the result of the subsequent slow reaction, broke down to give sodium aurate and sodium chloride. The complex nature of the auric chloride solutions is also apparent from its reactions with silver nitrate and silver carbonate: Jacobsen (*Compt. rend.*, 1908, 146, 1213) states that the precipitate obtained with the former is $4\text{AgCl}, \text{Au}(\text{OH})_3$, whilst Hittorf and Salkovsky (*loc. cit.*) state that with the latter it is $\text{Ag}_2\text{AuOCl}_3$.

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