[Contribution from the Chemical Laboratory of the University of California at Los Angeles]

THE POTENTIOMETRIC DETERMINATION OF GALLIUM

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Introduction

The methods of determining gallium so far described in the literature are based on its precipitation as the hydroxide and the subsequent ignition to the oxide. Slightly different procedures for doing this have been described by Porter and Browning[1] and by Dennis and Bridgman.[2] To facilitate further study of the chemistry of gallium, an accurate volumetric method is desired.

Since gallium is known to form a slightly soluble ferrocyanide and a soluble ferricyanide, the system might be expected to lend itself to the method of electrometric titration which has been worked out for the related elements, zinc, cadmium, and more recently indium.[3,4]

The results of the investigation described in this paper show that the method is applicable to gallium. The composition of the insoluble ferrocyanide formed has been determined and the conditions for obtaining accurate results have been studied.

Description of the Apparatus

The apparatus used consisted of (1) a motor-driven stirrer; (2) a 1 *N* potassium chloride–calomel reference half-cell; (3) an oxidation-reduction electrode made by fusing 1 cm. of platinum wire, 0.05 cm. in diameter, into the end of a small glass tube; (4) a certified buret; and (5) a Leeds and Northrup student potentiometer with a Leeds and Northrup galvanometer of 2.84 megohms sensitivity. A 1-liter beaker was found to be a convenient titration vessel.

Preparation of the Materials

Metallic gallium obtained originally from the Bartlesville Zinc Company of Bartlesville, Oklahoma, was the substance used in the preparation of all solutions of gallium salts. The metal was dissolved in 12 *N* hydrochloric acid and to increase the rate of solution, which is slow, a piece of platinum foil was kept in contact with the metal. The resulting solution was diluted with about 250 cc. of water and the gallium precipitated as the hydroxide with a slight excess of ammonia. After heating the solution to boiling for a few minutes to coagulate the precipitate, the hydroxide was filtered off and washed free from all but a trace of chlorides. Later work showed that the gallium was not completely precipitated. Our results indicated that the hydroxide is much more

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[1] Porter and Browning, This Journal, **43**, 111 (1921); *ibid.*, **41**, 1491 (1919).

[2] Dennis and Bridgman, *ibid.*, **40**, 1531 (1918).

[3] Bray and Kirschman, *ibid.*, **49**, 2739 (1927).

[4] Müller and Gäbler, *Z. anal. Chem.*, **62**, 29 (1923).

soluble in dilute ammonia than would be inferred from the literature. The precipitate of hydroxide was then dissolved in a measured amount of c. p. 12 *N* hydrochloric acid and diluted to approximately 0.08 molal in gallium chloride.

The potassium ferrocyanide and potassium ferricyanide used were of the standard c. p. quality. The solutions of potassium ferrocyanide, containing 1 g. of ferricyanide per liter, were made up in brown, glass stoppered bottles and kept in the dark when not in use. The solutions were standardized against metallic zinc by the potentiometric method.[5]

The following series of values, 0.05589; 0.05581; 0.05583, obtained for the molality of one of the ferrocyanide solutions shows the reproducibility of the method.

Results of the Titration Experiments

Preliminary experiments showed that solutions of gallium chloride, titrated potentiometrically with potassium ferrocyanide, give curves similar in form to those obtained in the titration of zinc or indium.[3] The results of titrations under varying conditions are shown in Table I.

Table I

Results of Titrations of Gallium Chloride Solutions with Potassium Ferrocyanide

Expt.	Stock soln.	Wt. of $GaCl_3$ soln., g.	Vol. of $K_4Fe(CN)_6$, cc.	Ratio	Temp.	Total vol., cc.	Acidity, *N*
1	A	10.29	14.10	1.370	Room	450	0.025
2[a]		10.33	...	...	Room	450	.125
3		10.32	14.16	1.372	75°	400	.03
4		10.34	14.20	1.373	Room	400	.03
6		10.37	14.22	1.371	Room	325	.03
7[b]		10.44	...	...	Room	425	..
8		10.34	14.21	1.374	Room	425	.01
1	B	10.12	11.32	1.118	40°	350	.005
2		21.26	22.68	1.119	40°	800	.005
3		20.21	22.61	1.119	Room	800	.005
4		20.23	22.77	1.125	60°	800	.005
5		20.21	22.68	1.122	40°	400	.01
6		10.13	11.34	1.120	60°	800	.003
7[c]		20.24	...	...	75°	800	.005

[a] Five cc. of 12 *N* HCl was added.

[b] Ammonia added till neutral.

[c] Decomposition observed.

These three runs gave curves from which the end-points could not be satisfactorily determined.

During the titration, equilibrium is substantially attained in from 3 to 5 minutes except in the immediate vicinity of the end-point, where the voltage is changing most rapidly. The volume of ferrocyanide solution used was obtained by determining the inflection point of the curve which resulted on plotting voltage against cc. of ferrocyanide solution added.

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[5] Bichowsky, *J. Ind. and Eng. Chem.*, **9**, 668 (1917); Müller, *Z. anorg. Chem.*, **128**, 126 (1923); Treadwell and Chevert, *Helv. Chim. Acta*, **6**, 550 (1923); Verzijl and Kolthoff, *Rec. trav. chim.*, **43**, 389 (1924).

The end-points were determined independently by the two authors from the titration data and differed on the average by 0.018 cc. in the 11 observations given in Table I.

In all experiments the ferrocyanide was added to the gallium chloride solution. Voltages were read to one millivolt as soon as equilibrium was substantially attained after each addition. At the beginning of the titration and up to within two or three cubic centimeters of the end-point, the ferrocyanide was allowed to run from the buret fairly rapidly. The voltage gradually rises with the addition of the ferrocyanide solution to about 0.60 volt and then remains practically constant until within a few cubic centimeters of the end-point after which a gradual decrease of potential occurs. Thereafter additions of 0.5 cc. were made and finally of 0.10 cc. as the end-point was more closely approached.

The shape of the titration curves obtained is indicative of the suitability of experimental conditions. An increase in concentration of hydrochloric acid was found to decrease the drop in potential at the end-point making this drop more gradual and therefore the inflection point less accurately determinable. The solutions of gallium chloride having the lowest acid concentration gave the most satisfactory curves. The effect of neutral salts was essentially the same as that of acid.

The curves resulting from the experiments at room temperature, 40 and 60° were similar and the corresponding ratios are the same as shown in Col. 5 of Table I. At 75° appreciable decomposition occurred, as evidenced by the blue color which developed during the titration, and the curves obtained were less satisfactory. Since equilibrium was not attained as rapidly at room temperature as at the higher temperatures, 40° was selected for subsequent titrations. It was found desirable to maintain the temperature within two degrees of that adopted because of the large temperature coefficient of the cell.

Three determinations employing an approximately 0.05 molal potassium ferrocyanide were made. Weighed amounts of the ferricyanide were added to the titration vessel. A sixteen-fold variation in the amount of ferricyanide present at the end-point produced no marked change in the type of curve obtained. We conclude that the amount of added ferricyanide can vary within rather wide limits, and since the presence of ferricyanide has been shown to prevent the decomposition of the ferrocyanide[6] it is preferable to add it with the ferrocyanide.

Composition of the Precipitate

The ratio of the gallium to the ferrocyanide in the precipitate obtained was determined by two independent methods, one employing metallic gallium as a reference substance and the other employing the oxide.

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[6] Kolthoff, *Rec. trav. chim.*, **43**, 380 (1924).

The gallium was prepared by electrodeposition[7] on a rotating platinum cathode from a solution of gallium sulfate to which sufficient ammonia had been added to produce a slight permanent precipitate of the hydroxide. The cathode coated with the gallium metal was washed, dried in an oven at 110° and weighed. The sample taken for a titration was obtained by treating the electrode with 1–2 cc. of 12 *N* hydrochloric acid, washing it, drying and weighing again. The gallium dissolves less readily than does indium and the solution was heated to hasten the reaction. This solution was diluted to 800 cc. and the titration carried out at 40°. The results of these titrations are shown in Table II.

TABLE II

TITRATION OF METALLIC GALLIUM AGAINST POTASSIUM FERROCYANIDE

Gallium metal, mg.	Milliatoms of gallium	$K_4Fe(CN)_6$, ml.	Millimoles of $K_4Fe(CN)_6$	Ratio $Ga:Fe(CN)_6$
33.0	0.473	6.28	0.351	1.348
42.9	.615	8.45	.472	1.304
113.3	1.625	21.71	1.212	1.340
57.9	0.830	11.19	0.625	1.329
81.8	1.173	16.04	.896	1.310
68.3	0.980	13.18	.736	1.331
			Average	1.327

The procedure adopted in the precipitation of the gallium as hydroxide and its subsequent ignition to the oxide was essentially that recommended by Porter and Browning.[1] Ammonium acid sulfite was used as the precipitating agent in a neutral or slightly acid solution. A test was made for complete precipitation by evaporating the filtrate to approximately 50 cc., adding 10 cc. more of the ammonium acid sulfite solution and boiling for a few minutes. No precipitate was formed and only a very faint turbidity was observed on the addition of potassium ferrocyanide to the resulting solution.

The weights of oxide obtained from two equal portions (10.10 g.) of the gallium chloride solution were 0.0804 g. and 0.0809 g. The weights remained constant even after four hours' heating at a temperature of approximately 800°. In this respect it differs from indium oxide which has been found to lose weight when heated to this temperature.[3] The gallium oxide was not markedly hygroscopic after this treatment.[2] The average weight of oxide, 0.08065 g., corresponds to 0.8605 milliatom of gallium. The number of millimoles of ferrocyanide corresponding to 10.10 g. of the stock solution as calculated from the average of four titrations was 0.6432. From these data the ratio of gallium to the ferrocyanide in the precipitate is seen to be 1.337.

From these results the ratio of gallium to ferrocyanide is clearly 1.333,

[7] Fogg and James, THIS JOURNAL, **41**, 947 (1919); Richards and Boyer, *ibid.*, **41**, 133 (1919); Dennis and Bridgman, *ibid.*, **40**, 1537 (1918).

which corresponds to the formula $Ga_4(Fe(CN)_6)_3$ for the precipitate. The precipitate is not of a complex nature and therefore differs from the ferrocyanide of zinc and indium. The determination of this ratio makes it possible to use ferrocyanide solutions, standardized against metallic zinc, for the determination of gallium.

Summary

A method of analyzing gallium chloride solutions by titrating with standard potassium ferrocyanide solution in the presence of ferricyanide and determining the end-point potentiometrically has been described. The accuracy is estimated at two or three tenths of one per cent.

The ferrocyanide precipitate formed under the conditions described has been shown by two independent methods to have the formula $Ga_4(Fe(CN)_6)_3$.

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SOAPS AS COLLOIDAL ELECTROLYTES

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It is well known that members of the large class of substances exemplified by the family of soaps exhibit in solution only moderate osmotic effect or activity, whereas their conductivity is excellent. So much is this the case, that often the whole activity seems to be ascribable to the concentration of one simple ion as measured by any of the ordinary methods leaving the carrier of the opposite charges to be explained as highly conducting colloidal particles or ionic micelles.[1] It is clear that this interpretation necessitates a broader interpretation of the electrolytic dissociation theory than that which is currently being attempted for electrolytes in aqueous solution. Linderstrøm-Lang[2] has tried to fit the data for soap solutions to the Procustes' bed of the 100% ionization theory on the assumption that soap solutions are completely dissociated into ordinary sodium or potassium ions and simple univalent fatty ions. It is the object of this note to point out that this cannot be done without deliberately ignoring too many facts.

It is perfectly possible, by means of *ad hoc* assumptions, to regard almost any substance, whose solution conducts, from the standpoint of 100%

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[1] References to previous papers from the Bristol and Stanford Laboratories may be found in the following: McBain and Buckingham, *J. Chem. Soc.*, **1927**, 2679–2689; McBain, Willavoys and Heighington, *ibid.*, **1927**, 2689–2699; McBain, Chap. 16, pp. 410–429 of "Colloidal Behaviour," Vol. I by Bogue; see also Salmon, THIS JOURNAL, **42**, 426–460 (1920); other similar references in Linderstrøm-Lang, ref. 2.

[2] Linderstrøm-Lang, *Compt. rend. Lab. Carlsberg*, **16**, No. 6, 1–47 (1926).