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THE POTENTIOMETRIC DETERMINATION OF INDIUM

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Introduction

An accurate and fairly rapid method of analysis of indium solutions has become desirable in order to facilitate further investigations on indium in this Laboratory. The two methods described in the literature are the electrodeposition[2,3,4] of the metal and the weighing of the indium oxide obtained by igniting the precipitated hydroxide.[5,6]

The electrodeposition of indium from a chloride solution, either in the presence of formic acid and ammonia or in the presence of Rochelle salt, as suggested by earlier authors, was found unsuitable for an accurate quantitative determination with chloride solutions. However, by using a sulfate solution, with a current density of 0.4 ampere per square decimeter and a potential of about 4 volts, very adherent deposits of indium with no platinum black were obtained with a rotating cathode. But the difficulty of precipitating the last few milligrams of indium from the solution, as observed by the present authors in over a dozen electroplating experiments, makes this an uncertain method of analysis. As mentioned by Dennis and Geer, the electrodeposition of indium was found to be an excellent method of purifying it from iron, since one deposition from a sulfuric acid solution of the crude oxide gave a metal which showed no test for iron with potassium thiocyanate.

Determinations as the oxide, In_2O_3, were made by essentially the method of Thiel and Koelsch as follows. The hydroxide was precipitated from the solution of the chloride by the addition of a slight excess of freshly filtered ammonium hydroxide. The white, flocculent precipitate was washed by decantation until free from chlorides with a 1% solution of ammonium nitrate and filtered into a Gooch crucible. In the first set of determinations the crucibles were heated over a blast-lamp for thirty minutes, cooled and weighed. This was repeated but a constant weight was not obtained. In the second set of determinations the crucibles were placed in an electric furnace and brought to about 850° for thirty minutes. This was repeated until the weight was constant to 0.2 mg. The crucibles

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[1] National Research Fellow in Chemistry.

[2] Kollock and Smith, THIS JOURNAL, **32**, 1248 (1910).

[3] Dennis and Geer, *ibid.*, **26**, 437 (1904).

[4] Mathers, *ibid.*, 29, 485 (1907).

[5] (a) Thiel and Koelsch, *Z. anorg. Chem.*, **66**, 288 (1910); (b) *ibid.*, **40**, 280 (1904).

[6] Dennis and Bridgman, THIS JOURNAL, **40**, 1531 (1918).

were then heated in the furnace at about 900° for about forty minutes, when a loss of weight of several milligrams occurred.

Both of these methods were thus found by the authors to be not well suited to the purpose at hand. A new method of analysis was therefore worked out. This consists in titrating the indium with potassium ferrocyanide and determining the end-point potentiometrically Since indium forms with potassium ferrocyanide a precipitate which is insoluble in nitric and sulfuric acids and in hydrochloric acid up to 4 *N*, and since it does not give an insoluble compound with potassium ferricyanide, the system lends itself to this method of electrotitration. The composition of the insoluble compound formed during the titration has been investigated in order to obtain a convenient method of standardizing the ferrocyanide solution.

Apparatus

The apparatus used consists of (1) a motor-driven stirrer; (2) a 1 *N* KCl-calomel reference half-cell; (3) an oxidation-reduction electrode made by fusing 1 cm. of small (0.05 cm. diameter) platinum wire through the end of a small glass tube; (4) a certified buret; and (5) a Leeds and Northrup "Type K" potentiometer with a high sensitivity galvanometer. A beaker containing the unknown solution diluted to about 300 cc. is a convenient size. For the inert metal electrode a short platinum wire rather than a foil electrode is used. For the reference electrode a 1 *N* calomel half-cell is satisfactory and consequently no attempt has been made to use a system of bimetallic electrodes.[7,8]

The Method of Titration

Preliminary experiments showed that solutions of indium chloride titrated potentiometrically give curves almost identical in form with those obtained by titrating zinc[9,10,11,12] in acid solution at 70° with potassium ferrocyanide. During the potentiometric titration, equilibrium is reached at the oxidation-reduction electrode in less than thirty seconds, except in the immediate vicinity of the end-point where the voltage is changing rapidly. The ratio of indium solution to ferrocyanide solution obtained by taking the mid-point of the vertical section of the curve as the end-point was found to be quite constant. Stock solutions of carefully purified indium chloride were prepared by dissolving well-washed precipitates of the hydroxide in a slight excess of a constant-boiling solution of hydrochloric acid and diluting to about 0.03 or 0.07 molal.

The effects of acid, neutral salts, concentration of indium salt and temperature on the ratio of the two solutions were studied. In all experiments the ferrocyanide was added to the indium solution from the buret,

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[7] Willard and Fenwick, THIS JOURNAL, **44**, 2504 (1922).

[8] Van Name and Fenwick, *ibid.*, **47**, 9 (1925).

[9] Bichowsky, *J. Ind. Eng. Chem.*, **9**, 668 (1917).

[10] Müller, *Z. anorg. Chem.*, **128**, 126 (1923).

[11] Treadwell and Chevert, *Helv. Chim. Acta*, **5**, 633 (1922); (b) **6**, **550**, 559 (1923).

[12] Verzijl and Kolthoff, *Rec. trav. chim.*, **43**, 380 (1924).

no attempt being made to study the effect of adding the indium to the ferrocyanide, since satisfactory results were obtained by the easier method. Voltages were read to one millivolt as soon as equilibrium was substantially established 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, because the final curve was found to be independent of the rate of addition. The first part of the curve is of little or no importance and depends to a considerable extent on the previous treatment of the platinum wire electrode. The voltage gradually rises with the addition of the ferrocyanide solution to about 0.62 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. are made, and finally of 0.1 cc. as the end-point is more closely approached. Curve A of Fig. 1 is typical of the behavior at room temperature.

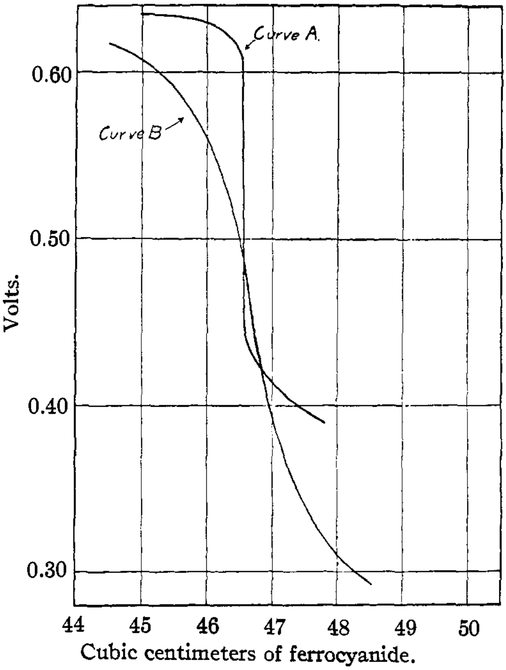

Fig. 1.

The effect of acid more concentrated than 0.05 N in the final solution is both to decrease the drop in potential at the end-point and to make the decrease take place gradually instead of suddenly. The effect of neutral salt is essentially the same as that of acid; thus, several titrations made with solutions to which both hydrochloric acid and potassium acetate had been added gave curves similar to those obtained by using dilute acid with a corresponding amount of potassium chloride. When the decrease in voltage takes place gradually, as in solutions of high ionic strength, it is very difficult to obtain an accurate end-point. The curves obtained in these cases were similar to Curve B in Fig. 1.

Titrations were made at room temperature (about 25 ± 2°), at 45° and at 85°. The best curves were obtained at room temperature. At 45° the curve is still fairly good but at 85° the drop in voltage is too gradual. The end-points were in general determined independently by the two authors from the titration data and seldom differed by more than 0.02 cc. The standard ferrocyanide solutions were kept in black lacquered bottles under an atmosphere of nitrogen.

In Table I are given the results of a number of titrations of two stock solutions, A and B, of indium chloride with the ferrocyanide solution. They show the accuracy with which the end-point can be determined under different conditions. The indium chloride solution was always about 0.02 *N* in hydrochloric acid.

TABLE I

TITRATIONS OF INDIUM CHLORIDE SOLUTIONS WITH POTASSIUM FERROCYANIDE

Stock sol.	$InCl_3$ solution, g.	$K_4Fe(CN)_6$ solution, cc.	Ratio	Temp., °C.	Volume of solution
A	20.06	20.38	1.016	Room	350
	20.07	20.38	1.016	Room	350
	40.69	41.30	1.015	Room	350
	20.00	20.24	1.012	Room	700
	20.14	20.48	1.017	45°	350
B	10.36	23.80	0.07321	Room	350
	15.80	36.32	.07326	Room	350

Composition of the Compound between Indium and Potassium Ferrocyanide

While the reproducibility of the ratios of indium solution to ferrocyanide solution shows the end-point to be sharp, it is desirable to know the ratio of indium to ferrocyanide in the precipitated compound, in order not to have to rely upon a pure indium preparation as the means of standardizing the ferrocyanide solution. To establish the composition of this compound, it was first necessary to determine the actual molality of the ferrocyanide in the solution used. This was done as follows. A solution of potassium ferrocyanide was made 0.05 normal as closely as possible by weighing out selected crystals of the trihydrate, adding 0.5 g. of potassium ferricyanide, dissolving in water and diluting to exactly one liter. This 0.05 formal solution was then titrated electrometrically against two very carefully standardized zinc solutions which one of the authors had prepared for electromotive force measurements on zinc sulfate.[13] Assuming the molality of the potassium ferrocyanide to be 0.05 in correspondence with the weight of crystals taken, the ratio of zinc to ferrocyanide in the titration was found to be 1.505 and 1.508 for the two separate zinc solutions. This is in agreement with Treadwell and Chevert,[14] who have

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[13] U. B. Bray, THIS JOURNAL, 49, 2372 (1927). The method of standardizing these zinc solutions was the potentiometric method, using another ferrocyanide solution. The basis of the standardization was Kahlbaum's "zur Analyse" zinc sticks and anhydrous zinc sulfate. All titrations were made under similar conditions of concentration, temperature and acidity.

[14] Ref. 11. Although Verzijl and Kolthoff (ref. 12) report an error of a few tenths of a per cent. from the theoretical potentiometric end-point in ferrocyanide precipita-

shown that the insoluble compound formed between potassium ferrocyanide and zinc is $Zn_3K_2(Fe(CN)_6)_2$. The exact molality of ferrocyanide solutions may therefore be determined by titrating against metallic zinc or standard zinc solutions and then making use of the ratio $3Zn:2Fe(CN)_6$.

The next step in the determination of the composition of the indium ferrocyanide precipitate was to prepare pure indium by electrolysis on a rotating platinum cathode from a carefully purified solution of indium sulfate. The cathode coated with indium metal was washed, dried in an atmosphere of hydrogen 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. This indium chloride solution was diluted to approximately 300 cc. and titrated as usual. The results of these titrations of solutions of weighed quantities of indium metal are given in Table II.

TABLE II

TITRATION OF METALLIC INDIUM AGAINST POTASSIUM FERROCYANIDE OF KNOWN MOLALITY

Milli-atoms of indium	Milli-moles of $K_4Fe(CN)_6$	Ratio In: $Fe(CN)_6$
1.234	0.9874	1.250
1.203	.9634	1.245
3.067	2.437	1.258
0.8328	0.6653	1.252
1.486	1.187	1.251
1.670	1.335	1.254
	Average	1.252

The ratio of indium to ferrocyanide is clearly 1.25 or $5In:4Fe(CN)_6$. Since the only other positive ions in the solution are potassium and hydrogen, the formula for the precipitated compound is presumably $In_5K(Fe(CN)_6)_4$. The determination of this definite ratio of indium to ferrocyanide in combination with the 3 to 2 ratio of zinc to ferrocyanide found by Treadwell and Chevert makes it possible to standardize with metallic zinc the ferrocyanide solutions that are to be used for indium titrations. The availability of pure zinc metal as compared with indium metal makes this method of standardization convenient.

Summary

A method of analyzing indium solutions by titrating with potassium ferrocyanide and determining the end-point potentiometrically has been described. The accuracy of the end-point is estimated at one or two-tenths of a per cent.

The precipitate formed between potassium ferrocyanide and indium solutions has been shown to be definite under the conditions described

tion titrations depending upon the electrolyte present, any such small errors would tend to cancel out with the subsequent indium titration.

and to contain indium and ferrocyanide in the ratio $5In:4Fe(CN)_6$ (within 0.2%). The formula of the precipitate is therefore presumably $In_5K(Fe(CN)_6)_4$. The determination of the ratio of indium to ferrocyanide in this compound permits using metallic zinc for standardizing the ferrocyanide solution, since the composition of the zinc ferrocyanide precipitate has been determined.

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THE HIGH-TEMPERATURE EQUILIBRIUM BETWEEN THORIUM OXIDE AND CARBON

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Plan of the Investigation

The present work is a continuation of a program of research in the field of high-temperature equilibria, using the same general methods and apparatus that have been more completely described in an article on zirconium oxide and carbon.[1] Many facilities have been added to increase the precision and improve the physical conditions of the work. The equilibrium measurements have been carried on up to a temperature of 2500°K. As a result of the higher temperatures now employed many new sources of difficulty and error have been encountered, necessitating a complete study of the temperature corrections for the deviations in behavior of the carbon furnace from that of an ideal black body. It has not been possible to make the carbon elements strictly reproducible but, in spite of the elevated temperature, results have been obtained comparable in precision to the previous work under more moderate conditions.

Previous work on the reduction of thorium oxide by carbon is that of Troost[2] and of Moissan and Étard.[3] Impure thorium metal can be obtained, but with excess of carbon the carbide, ThC_2, is formed. This is a yellow, crystalline compound that yields a wide variety of hydrocarbons on hydrolysis with water. These have been studied in detail by Lebeau and Damiens.[4]

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[1] C. H. Prescott, Jr., THIS JOURNAL, **48**, 2534 (1926).

[2] Troost, *Compt. rend.*, **116**, 1229 (1893).

[3] Moissan and Étard, *ibid.*, **122**, 576 (1896).

[4] Lebeau and Damiens, *Compt. rend.*, **156**, 1987 (1913).