per atom in samarium metal. In view of the considerable stability of divalent samarium compounds a value slightly less than 3.0 for the number of valence electrons, V, in the metal might have been anticipated.

The Crystal Structure of Samarium Monoxide

The diffraction data in Table II show the presence of a cubic face-centered phase with $a = 5.026 \pm 0.002$ Å. in the heat treated sample of samarium metal. From the method of preparation this phase may be expected to be an oxide and it is reasonable to identify the phase with the grey coating formed on metal pieces on heat treatment. The phase has been observed in a number of samples. Indeed, one particular sample, resulting from an attempt to reduce samarium bromide with lithium metal, gave only the the diffraction lines of this cubic phase. The measurements of this pattern are listed in Table V.

TABLE V

DIFFRACTION DATA FOR SAMARIUM MONOXIDE

Radiation: CuKα

$\sin^2\theta$			Intensity	
Obsd.	Calcd.	ΣH_i^2	Obsd.	Calcd.
0.0710	0.0698	3	100	110
.0944	.0931	4	70	86
.1882	.1861	8	70	59
.2583	.2560	11	100	50
.2815	.2793	12	35	20
.3759	.3724	16	20	9
.4448	.4422	19	50	19
.4678	.4655	20	70	26
.5608	.5586	24	50	21
.6309	.6284	27	60	20
.7466	.7448	32	30	11
.8152	.8147	35	80	38
.8383	.8379	36	80	35
.9310	.9310	40	80	40

The reflections with even values of ΣH_i^2 are appreciably stronger relative to those with odd values of ΣH_i^2 than can be accounted for by the samarium atoms alone. One is led to conclude that the cubic phase is SmO with the sodium chloride type of structure. The last column of Table V gives the intensities calculated on this basis with the aid of the formula

$$I \propto |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

The unit-cell constant is observed to vary from sample to sample, the lowest observed value being $a = 5.015 \pm 0.002$ Å. and the highest $a = 5.050 \pm 0.002$ Å. It is not known whether the variation is caused by impurities or by deviations from the ideal composition SmO.

The interatomic distance of Sm–6O = 2.52 Å. is about 0.06 Å. smaller than calculated from the ionic radii.

The authors wish to thank Miss Marian Gibbs for measuring the diffraction films.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Stability of the Lower Oxidation States of Indium in Aqueous Solution

BY LOREN G. HEPLER, Z Z. HUGUS, JR., AND WENDELL M. LATIMER

RECEIVED JULY 2, 1953

The equilibria between In^{+3}(aq) and In(m) have been investigated. Equilibrium constants for the reactions: 2In(m) + In^{+3}(aq) = 3In^{+}(aq) and In(m) + 2In^{+3}(aq) = 3In^{+2}(aq) have been determined to be 2.4×10^{-11} and 1.9×10^{-8}, respectively. From these results the standard potentials are calculated: In(m) = In^{+}(aq) + e^{-}, $E^0 = 0.14$; In^{+}(aq) = In^{++}(aq) + e^{-}, $E^0 = 0.40$; In^{++}(aq) = In^{+3}(aq) + e^{-}, $E^0 = 0.49$.

Introduction

It has long been known that such compounds as InCl and $InCl_2$ or In_2Cl_4 exist. Thiel[1] has observed that if one reacts either of the lower oxidation state chlorides with water, one obtains a solution containing tripositive indium ions and a deposit of indium metal. All of this information leads one to expect such species as In^{+} and In^{++} may exist in aqueous solution at low concentration even though they are unstable at high concentrations with respect to disproportionation to the metal and the In^{+3}(aq) ion.

To account for the observations of Thiel, Latimer[2] has taken the approximate potentials for the various indium couples to be

$$In = In^{+} + e^{-} \qquad E^0 = ca.\ 0.25 \qquad (1)$$
$$In^{+} = In^{++} + e^{-} \qquad E^0 = ca.\ 0.35 \qquad (2)$$
$$In^{++} = In^{+3} + e^{-} \qquad E^0 = ca.\ 0.45 \qquad (3)$$

There are a number of reasons for choosing these approximate potentials. The sum of the three potentials must be 3 × 0.340 (where 0.340 is the In–In^{+3} potential). In order to account for the observed decompositions, the potential for couple 3 must be greater than that for couple 2 and similarly, the potential for couple 2 must be greater than that for couple 1.

Latimer[2] also has made an approximate calculation of the potential of couple 1. The entropy of InCl(c) was estimated to be 23.2 in comparison to 23.0 for AgCl. This leads to a value for the entropy of formation of InCl(c) which may be combined with the Bureau of Standards[3] value for the heat to

---

[1] A. Thiel, *Z. anorg. Chem.*, **39**, 119 (1904); **40**, 280 (1904).

[2] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Second Edition, Prentice–Hall Inc., New York, N. Y., 1952.

[3] National Bureau of Standards, Circular 500 (Feb., 1952), "Selected Values of Chemical Thermodynamic Properties."

give −39,200 cal./mole as the free energy of formation. The solubility of InCl cannot be measured, but one would expect from relations in this region of the periodic system that it should be more soluble than TlCl but probably less than one molal. This leads to an E° value that is in approximate agreement with that chosen above for the In–In$^+$ couple.

We have endeavored to determine experimentally the equilibrium constants for the various possible reactions between metallic indium and In^{+3} (aq). This has been done by equilibrating solutions of various concentrations of In^{+3}(aq) with In(m) and then determining the number of equivalents of reducing agent present at equilibrium in each of the solutions.

Experimental Procedures

Indium oxide, which contained iron as the most important impurity, was purified in the following manner. The oxide was dissolved in hydrochloric acid. Indium hydroxide was precipitated from this solution by the addition of an excess of ammonium hydroxide solution. The precipitate was washed with hot water and then dissolved in 6 *M* acetic acid. Hydrogen sulfide was bubbled through the solution to precipitate indium sulfide. The sulfide was filtered off, washed with acetic acid and then dissolved in nitric acid. Indium hydroxide was again precipitated by the addition of an excess of ammonium hydroxide solution. The precipitate was washed thoroughly with hot water and then dissolved in hydrochloric acid. Spongy indium was then plated out of this solution onto a platinum electrode. The spongy mass of indium was then used as anode in another plating solution.[4,5]

A stock solution of indium perchlorate was prepared by dissolving pure indium metal in perchloric acid. The solution was standardized by determining indium as In_2O_3.

An electrolytic method was devised for the preparation of finely divided indium. Pure indium metal was dissolved in a minimum quantity of hydrochloric acid. Spongy indium was then plated out of this solution onto a piece of 1.5 mm. platinum wire. A large tubular piece of platinum gauze served as anode. This choice of electrodes ensured a relatively high current density on the cathode. The resulting spongy deposit of indium was scraped off the platinum wire and washed with water. After the metal dried, it was passed through a set of standard wire mesh screens. In this way a good yield of 50–200 mesh indium metal was prepared.

Standard arsenite solutions were prepared by dissolving analytical reagent grade As_2O_3 in sodium hydroxide solution and then neutralizing the solution with sulfuric acid. Standard ceric solutions were prepared by diluting G. Frederick Smith Chemical Company reagent grade 0.5 *M* "perchloratoceric acid" to the desired concentration and titrating with a standard arsenite solution. Osmium tetroxide was used as a catalyst for the reaction and "ferroin" was used as indicator.[6]

A stock solution of cerous perchlorate, which was used to maintain constant ionic strength in the solutions to be equilibrated with indium metal, was prepared in the following manner. Ammonium hexanitrato cerate from the G. Frederick Smith Chemical Co. was dissolved in water. Ammonium hydroxide was then added to this solution to precipitate hydrous ceric oxide. The precipitate was removed by filtration and then very thoroughly washed with hot water. The precipitate was now dissolved in perchloric acid to which some hydrogen peroxide had been added. This solution was heated gently on a hot-plate until it became so concentrated that cerous perchlorate precipitated when the solution was cooled. The resulting crystals were filtered off on sintered glass and then dissolved in water to give a solution of cerous perchlorate which contained only a very little perchloric acid. This solution was standardized by oxidizing Ce^{+3} and then titrating the Ce^{+4} with arsenite solution. The acid content of the solution was determined by diluting an aliquot and measuring the *p*H of the resulting solution.

The apparatus used in these experiments is pictured schematically in Fig. 1. All of the experiments were carried out at 25.0 ± 0.1°. A constant ionic strength of 0.83 was maintained in the solutions of indium perchlorate that were equilibrated with metallic indium. Cerous perchlorate served as the added electrolyte. All of the solutions were 0.1 *M* in perchloric acid.

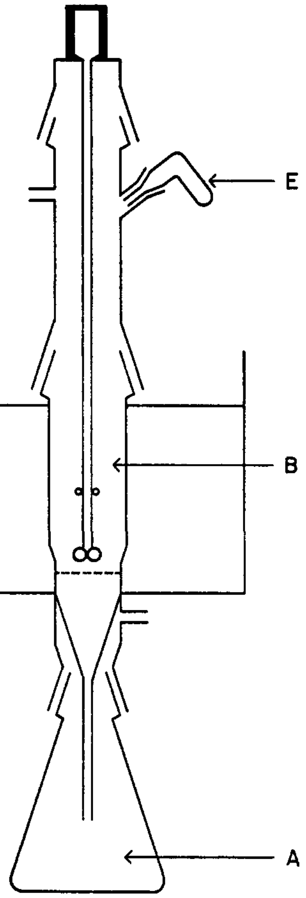

Fig. 1.—Apparatus employed to establish equilibrium between indium metal and In^{+++} solution.

An aliquot of standard ceric solution was pipetted into the flask A. Then an aliquot (from 100 to 200 cc.) of indium perchlorate solution was pipetted into B. In order to prevent the solution from passing through the sintered glass filter and to exclude oxygen from the system, nitrogen was bubbled through the filter. A weighed amount of metallic indium was put into the tube E. After allowing enough time for the nitrogen to sweep all of the oxygen out of the system, the metal was introduced into the solution by rotating the bent tube E. The solution was allowed to remain in contact with the metal for a measured length of time. Then the solution was rapidly drawn through the filter into the ceric solution. The flask containing the ceric solution was removed and the ceric solution titrated with arsenite. We were able to calculate the number of equivalents of reducing agent present in the solution in equilibrium with the metallic indium from the data obtained with this experiment. This quantity (expressed in equivalents/liter) we will designate as *R*.

Blank runs of several kinds were carried out. Water was equilibrated with metallic indium. *R* was found to be zero, which indicated that none of the indium metal was getting through the filter. A 0.1 *M* solution of perchloric acid was also equilibrated with metallic indium. Both *R* and the amount of indium that dissolved in 2 hours were found to be negligible. The time of equilibration was varied from 15 minutes to 5 hours. For a given concen-

---

[4] E. Hattox and T. DeVries, This Journal, 58, 2126 (1936).

[5] G. P. Baxter and C. M. Alter, *ibid.*, 55, 1943 (1933).

[6] I. Kolthoff and E. Sandell, "Textbook of Quantitative Analysis," Third Edition, The MacMillan Co., New York, N. Y., 1952.

tration of In^{+3} it was found that R increased as the time of equilibration increased until an equilibration time of one hour was reached. Variations in R with the amount of indium metal used were found to be extremely small.

Results and Interpretation

We have systematically interpreted our data on the assumption of the equilibria

$$2In + In^{+3} = 3In^{+} \qquad Q_1 \qquad (4)$$
$$In + 2In^{+3} = 3In^{+2} \qquad Q_2 \qquad (5)$$

We shall write the equilibrium quotients for these reactions in terms of concentrations (moles/liter) of the various species.

$$Q_1 = (In^{+})^3/(In^{+3}) \qquad (6)$$
$$Q_2 = (In^{+2})^3/(In^{+3})^2 \qquad (7)$$

The number of equivalents of reducing agent in a solution of these ions is equal to twice the number of moles of In^{+} plus the number of moles of In^{++} present. It is therefore seen that $R = 2(In^{+}) + (In^{++})$. We substitute in this equation from the equilibrium quotient expressions 6 and 7 for (In^{+}) and (In^{++}) to obtain 8.

$$R/(I^{+3})n^{1/3} = 2Q_1^{1/3} + Q_2^{1/3}(In^{+3})^{1/3} \qquad (8)$$

A plot of $R/(In^{+3})^{1/3}$ against $(In^{+3})^{1/3}$ gives a straight line of intercept $2Q_1^{1/3}$ and of slope $Q_2^{1/3}$. The data used for making such a plot are given in Table I.

TABLE I

(In^{+++})	$R \times 10^3$	(In^{+++})	$R \times 10^3$
0.000926	0.71	0.04628	3.24
.004628	1.25	.09256	4.12
.01000	1.90	.1215	5.24
.02314	2.30		

We calculate from the slope and the intercept of the line in Fig. 2 that $Q_1 = 3.3 \times 10^{-11}$ and that $Q_2 = 1.9 \times 10^{-8}$. It is possible to estimate the activity coefficients that are needed to calculate true equilibrium constants for these reactions from their respective Q's. We have used the experimental activity coefficients of such salts as $LaCl_3$, $La(NO_3)_3$, $NaCl$, $NaClO_4$, $AgNO_3$, $BaCl_2$, $ZnCl_2$ and $Cd(NO_3)_3$ as a basis for estimating the mean activity coefficients for In^{+}, In^{++} and In^{+3}. The γ's are taken to be 0.6, 0.45 and 0.3 for the three indium species at an ionic strength of 0.83. We calculate from these activity coefficients and the experimental values for Q_1 and Q_2 the values for K_1 and K_2

$$K_1 = 2.4 \times 10^{-11};\ K_2 = 1.9 \times 10^{-8}$$

It is seen that the activity corrections are small and that any errors in estimating these quantities will tend to cancel one another.

The above values for the two equilibrium constants have been used to calculate the free energies of formation of $In^{+}(aq)$ and $In^{++}(aq)$ and also to calculate the potentials for couples 1, 2 and 3. Results of these calculations are given in Table II.

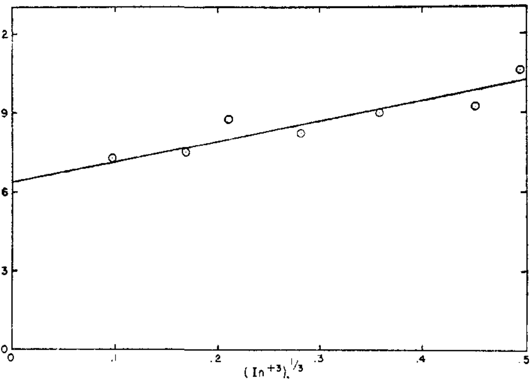

Fig. 2.—Plot showing relationship between reducing equivalents of the solution and concentration of In^{+++}.

TABLE II

Ion	ΔF^0_{298}, cal./mole	Couple	E^0
In^{+}	−3100	$In = In^{+} + e^{-}$	0.14
In^{++}	−12,300	$In^{+} = In^{++} + e^{-}$	.40
In^{+++}	−23,700[2]	$In^{++} = In^{+++} + e^{-}$	.49

There has been considerable speculation in the literature with regard to the possible existence of the In^{++} ion. The solid compound which has the stoichiometric composition $InCl_2$ has been found to be diamagnetic. This observation has led some authors to conclude that the dipositive indium ion must be a double ion. On the other hand, some authors have suggested that the compound in question is of the type $[In^{+}][(InCl_4^{-})]$.

In view of this uncertainty about the existence of the dipositive indium species in the solid phase, we have attempted to interpret our data by assuming that In^{+} is the only lower oxidation state species in aqueous solution. If this assumption were valid, the line in the graph in Fig. 2 would be horizontal. Thus our data definitely indicate the existence of some other lower oxidation state species in aqueous solution.

One may derive an expression similar to 8 in terms of In^{+} and In_2^{+4} which may then be used as a basis for a plot similar to that in Fig. 2. The experimental data are not sufficiently accurate to enable one to decide definitely which of these dipositive species is the more important in aqueous solution. However, we have concluded that our data may be best interpreted by taking In^{++} to be more important than In_2^{+4}.

BERKELEY 4, CALIFORNIA