[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A Revision of the Atomic Weight of Indium

BY GREGORY P. BAXTER AND CHESTER M. ALTER

The International atomic weight of indium, 114.8, depends upon the investigations of Thiel[1] and Mathers[2] both of whom determined the ratios $InCl_3$:3AgCl and $InBr_3$: 3AgBr.

	$InCl_3$: 3AgCl	At. wt. In	$InBr_3$: 3AgBr	At. wt. In
Thiel	0.51473	114.97	0.62923	114.75
Mathers	.51442	114.83	.62932	114.80

In view of the fact that no attention was paid to the solubility of the silver halides in either determination it is not surprising that the chloride analyses give higher values for indium in both cases. In our experiments also the trichloride and tribromide were synthesized from the pure elements, and solutions of the halides were then compared with pure silver. The value found for the atomic weight of indium, 114.76, differs only slightly from the present International value.

Purification of Materials

Water and acids were purified by distillation. Nitrogen was prepared from air by the Wanklyn process, and the hydrogen produced catalytically from the excess of ammonia was oxidized by hot copper oxide. After the gas had been thoroughly dried, oxygen liberated from the copper oxide was removed by hot copper. In preparing indium tribromide, commercial compressed nitrogen was passed over a long section of heated copper gauze before passing through the purifying train. Hydrogen was generated in a galvanic cell consisting of platinum–hydrochloric acid–zinc amalgam, and was passed over fused potassium hydroxide and phosphorus pentoxide. All the apparatus for purifying gases was constructed of glass with fused or well ground joints.

Chlorine was drawn from a tank of liquefied gas. It was purified and dried by passing over dilute sodium hypochlorite, concentrated sulfuric acid and resublimed phosphorus pentoxide. Purified bromine remaining from the investigation of Baxter and Behrens[3] on lanthanum bromide was dried with phosphorus pentoxide and distilled. Pure silver was prepared by standard methods.[4] Two samples were employed, one of which had been purified by Dr. J. P. Marble and Mr. A. D. Bliss, the other by Messrs. W. M. MacNevin, J. S. Thomas and ourselves.

The starting point in the preparation of pure indium was a commercial sample, claimed to be 99.99% pure. Examination of the sample in a pure graphite arc with a Féry quartz spectrograph showed the chief impurities to be lead and tin, with traces of zinc, cadmium, antimony, arsenic, silver and copper. Electrolytic transport through an electrolyte made by dissolving a portion of the original material in hydrochloric acid, with the main mass of metal serving as anode, removed the greater part of the impurity. In this electrolysis the anode was contained in a sintered glass crucible so that anode dust was effectively prevented from mixing with the cathode deposit. In a spectrogram

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(1) Thiel, *Z. anorg. Chem.*, **40**, 280 (1904).

(2) Mathers, THIS JOURNAL, **29**, 485 (1907).

(3) Baxter and Behrens, *ibid.*, **54**, 591 (1932).

(4) Baxter and Ishimaru, *ibid.*, **51**, 1729 (1929).

made from a mixture of this anode dust and a small portion of the electrolyte, the lines of the impurities, especially lead and tin, were pronounced. This once electrolyzed material was used in preparing the earlier samples of indium trichloride.

A second similar electrolysis yielded a product in the spectrogram of which none of the lines of impurities could be detected, although the anode dust and electrolyte from this electrolysis proved to contain a small amount of lead and tin and the merest traces of some of the other impurities. Judging from past experience the twice electrolyzed metal contained less than 0.001% of total metallic impurity, probably much less.

After electrolysis the electrolytic crystals of indium were thoroughly washed and dried by centrifugal whirling, and then for each synthesis the necessary quantity, contained in a quartz boat inside a quartz tube, was fused in a current of pure hydrogen.

The Preparation of Indium Trichloride and Indium Tribromide

The halides were synthesized by heating metallic indium in a current of nitrogen and the corresponding halogen. The tube in which the synthesis was carried out was of hard glass in the first two experiments, but of quartz in all later ones. It was of about one centimeter internal diameter and was constricted at four points so as to produce compartments 30, 15, 15, 5 and 30 centimeters in length. The constrictions separating the fourth compartment in which the trihalide was finally collected were capillaries thick enough to seal without collapsing when under reduced pressure. At one end the tube was connected, by means of a carefully ground joint, with the apparatus for purifying chlorine and nitrogen. At the other end it was connected with a T-tube, both branches of which could be closed and one of which was connected with an efficient oil pump. The quartz boat containing the indium was placed in the first section of the tube and after the air had been displaced by nitrogen the indium was heated in a current of nitrogen and chlorine by means of a movable electrically heated sleeve. The reaction apparently took place stepwise, the monochloride and dichloride being formed at first. With the temperature around 600° the more volatile trichloride sublimed into the second compartment, very little material being carried beyond this point. A second sublimation from the second to the third compartment in a current of nitrogen and chlorine (1 to 1) followed. We could not detect any evidence of melting of the trichloride, although the mixed chlorides in the boat melted during the synthesis. In this second sublimation ordinarily but not invariably there was no residue. Finally the trichloride was sublimed into the fourth compartment, in nitrogen containing a small amount of chlorine, except in Analysis 4 where pure chlorine was used. No residue was ever left in the third sublimation. After the capillaries on either side of the fourth compartment had been cleared of sublimate by gentle heating, the tube was thoroughly swept out with nitrogen. In Analysis 7 the compartment containing the trichloride was heated to 200° during this sweeping. The capillary nearest the inlet of the tube was then sealed with a blow pipe, and after closing the exit stopcock the pressure was lowered to less than 0.1 mm. by operating the oil pump. In many instances the trichloride tube was warmed to 150° during the exhaustion to facilitate the escape of excess chlorine. Finally the second capillary of the tube was sealed with a blow pipe.

The tribromide was synthesized in a nearly identical manner in a current of nitrogen charged with bromine by bubbling through liquid bromine at a somewhat elevated temperature.

Method of Analysis

The bulb of trihalide was weighed first in air and then under water of known temperature in order to determine its exterior volume. It was then cleaned and weighed more carefully in air, the density of which was found by weighing a sealed standardized globe.[5] From this weight together with the volume of the bulb and the density of the air the weight of the bulb in vacuum was found.

The bulb was next broken in 300–400 ml. of pure water which contained a very small amount of nitric acid to prevent hydrolysis, and after standing for some time the glass or quartz was washed first with water, then with a few ml. of nitric acid and again with water, and was collected on a weighed platinum sponge crucible. The crucible and contents were dried at 400° and weighed. Further washing with nitric acid failed to alter the weight of the crucible and quartz in a few cases where this was done. The weight of the glass or quartz was corrected to vacuum with the use of the air density determined at the time of weighing and the density of hard glass as determined (2.52) or that of fused quartz (2.203), and the weight of indium trihalide was found by difference. The halide solutions were precipitated at room temperature with a solution of weighed, very nearly equivalent amount of the purest silver and the end-point of the comparison found with the aid of a nephelometer. The chloride solutions were about 0.1 normal during precipitation. In Analysis 9 the solutions were about 0.04 normal; in Analyses 10–13 about 0.03 normal. The silver solution was added to the halide solution in every case except Analysis 10 where the reverse method was employed.

THE ATOMIC WEIGHT OF INDIUM

$InCl_3 : 3Ag$

Ag = 107.880 Cl = 35.457

Analysis	Material of bulb	No. of elect. of indium	$InCl_3$ in vac., g.	Ag in vac., g.	Ag added, g.	Corr. wt. of Ag in vac., g.	Ratio $InCl_3 : 3Ag$	At. wt. of indium
1	Hard glass	1	5.64316	8.25789	−0.00030	8.25759	0.683391	114.802
2	Hard glass	1	8.35611	12.22754	.00000	12.22754	.683384	114.799
						Average	.683388	114.801
3	Quartz	1	9.65967	14.13592	−0.00010	14.13582	.683347	114.787
4	Quartz	1	12.04518	17.62730	.00000	17.62730	.683325	114.780
5	Quartz	1	12.18165	17.82677	− .00010	17.82667	.683339	114.785
						Average	.683337	114.784
6	Quartz	2	5.78802	8.47132	0.00000	8.47132	.683249	114.756
7	Quartz	2	5.80139	8.49039	+ .00040	8.49079	.683257	114.758
8	Quartz	2	5.58558	8.17510	− .00040	8.17470	.683276	114.764
						Average	.683261	114.759

$InBr_3 : 3Ag$

Br = 79.916

Analysis	Material of bulb	No. of elect.	$InBr_3$ in vac., g.	Ag in vac., g.	Ag added, g.	Corr. wt. of Ag in vac., g.	Ratio $InBr_3 : 3Ag$	At. wt. of indium
9	Quartz	2	6.38915	5.83279	+0.00020	5.83299	1.09535	114.750
10	Quartz	2	9.07794	8.28729	− .00030	8.28699	1.09544	114.782
11	Quartz	2	8.91416	8.13810	.00000	8.13810	1.09536	114.755
12	Quartz	2	9.24920	8.44390	+ .00030	8.44420	1.09533	114.745
13	Quartz	2	6.22482	5.68270	− .00020	5.68250	1.09544	114.779
						Average	1.09538	114.762
						Average of Analyses 6 to 13		114.761

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[5] Baxter, THIS JOURNAL, **43**, 1317 (1921).

The final end-points of the titrations were found only after the lapse of several weeks although only minor changes were observed after the first week or two.

The bulb and the silver were weighed by substituting carefully calibrated weights. The crucibles with the quartz were weighed by substituting a similar tare crucible and the necessary weights.

Two analyses subject to known errors of uncertain magnitude are omitted from the foregoing table. Analyses 1 and 2 are subject to uncertainty owing to the use of glass during the synthesis and collecting of the trichloride. Analyses 3–5 yield a definitely higher value than those of Analyses 6 to 13, presumably owing to the lesser purity of the indium which served for the synthesis. The averages of Analyses 6 to 8 of the trichloride and Analyses 9 to 13 of the tribromide are nearly identical, although the concordance of the bromide analyses is less satisfactory. The average atomic weight of indium found in Analyses 6 to 13, 114.76, represents fairly the outcome of our work.

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The Second Dissociation Constant of Phosphoric Acid from 20 to 50°

BY LESLIE FREDERICK NIMS

The author has determined the second dissociation constant of phosphoric acid, by using the method employed by Harned and Ehlers[1] in their investigation of acetic acid. The research was undertaken in order to obtain accurate values of the dissociation constant at room and blood temperatures, and to test the applicability of the method to other than uni-univalent electrolytes.

Discussion of the Method

The essence of the method employed is that the dissociation constant is obtained from electromotive force measurements upon cells without liquid junctions, containing appropriate buffer mixtures. No extrathermodynamical methods are employed other than the use of the Debye–Hückel limiting function for the activity coefficients of the ions involved. The cells

$$H_2/NaH_2PO_4(m_1),\ Na_2HPO_4(m_2),\ NaCl(m_3)/AgCl/Ag\ +$$
$$H_2/KH_2PO_4(m_1),\ Na_2HPO_4(m_2),\ NaCl(m_3)/AgCl/Ag\ +$$

were employed. The electromotive force of either is given by the equation

$$E = E_0 - \frac{RT}{F} \ln \gamma_H \gamma_{Cl} m_H m_{Cl} \qquad (1)$$

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[1] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932).