

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## A Revision of the Atomic Weight of Arsenic. I. The Analysis of Arsenic Tribromide. II. The Analysis of Arsenic Trichloride

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In a recent determination of the atomic weight of arsenic, Krepelka<sup>1</sup> has found the value 74.934 for this element by analysis of arsenic trichloride. In calculating the result, however, the atomic weight of chlorine is assumed to be 35.458. If the more probable value for chlorine, 35.457, is used, Krepelka's value is raised to 74.938.<sup>2</sup> Aston<sup>3</sup> from results with the mass-spectrograph finds arsenic to be a simple element with the packing fraction  $-8.8 \times 10^{-4}$  and the atomic weight 74.934. But this value has not been corrected from the physical scale,  $O^{16} = 16.0000$ , to the chemical scale. If the conversion factor of Babcock and of Naudé, 1.00012, is used the atomic weight of arsenic becomes 74.927, but with the equally possible one of Mecke and Childs, 1.00022, the atomic weight of arsenic is 74.919. The original exact agreement of Krepelka's and Aston's results thus disappears.

Recent success in the preparation and analysis of volatile inorganic halides in this<sup>4</sup> and other laboratories led us to use similar methods in the case of arsenic. The results of this work were satisfactory so far as can be told and yield an atomic weight of arsenic slightly less than 74.91.

### I. The Analysis of Arsenic Tribromide<sup>5</sup>

Two samples of arsenic tribromide were prepared, the first of which served only for preliminary analyses. The method of synthesis from the elements and purification by prolonged fractional distillation in exhausted all glass apparatus resembled closely that used in the investigations cited above.

In the preparation of Sample I, crystals of commercial metallic arsenic were placed in a glass bulb to which were attached two special all-glass valves (D, Figure 1), which could be opened by breaking at will, and the bulb was highly evacuated. In another glass bulb, attached to the first through one of the valves, was placed a slight deficiency of the purest bromine and, after the air had been flushed out of the bulb by boiling the bromine under reduced pressure, the glass tube leading to the pump was sealed. Then the valve between the bulbs was opened and the bromine vapor was allowed to act upon the arsenic at ordinary temperature. Occasional agitation was necessary during this operation in order to avoid accumulation of bromine in the bromide, which remained above the melting point owing to the heat of reaction. The bulb was allowed to stand

(1) Krepelka, *Coll. trav. Chim. Tchechoslov.*, **2**, 255 (1930).

(2) See first report of the International Committee on Atomic Weights for 1930, *THIS JOURNAL*, **53**, 1627 (1931).

(3) Aston, *Proc. Roy. Soc. (London)*, **A115**, 505 (1927).

(4) Baxter, Weatherill and Scripture, *Proc. Am. Acad.*, **58**, 245 (1923); Baxter and Scott, *ibid.*, **59**, 21 (1923); Baxter and Fertig, *THIS JOURNAL*, **45**, 1228 (1923); Baxter and Cooper, *Proc. Am. Acad.*, **59**, 235 (1924); **60**, 291 (1925); Baxter and Butler, *THIS JOURNAL*, **48**, 3117 (1926); **60**, 408 (1928).

(5) The purification and analysis of arsenic tribromide was carried out by W. E. Shaefer.

for some time until all evidence of uncombined bromine had disappeared. Preparatory to distillation the bulb containing the bromide was connected to a pump through a capillary and the bromide was boiled under reduced pressure to flush out gases, especially hydrogen bromide, before it was permanently sealed.

The bromine had been purified by a standard method used in this Laboratory, consisting in brief of the following steps: two successive distillations from solution in concentrated aqueous potassium bromide, the bromide in the second distillation having been made from a portion of the product of the first distillation; conversion to potassium bromide by means of potassium oxalate and fusion of the product with permanganate to eliminate organic matter; removal of iodine by liberation of a small proportion of the bromine with acid permanganate and boiling; liberation of about 80% of the remaining bromine with pure permanganate and sulfuric acid; drying with phosphorus pentoxide and distillation.

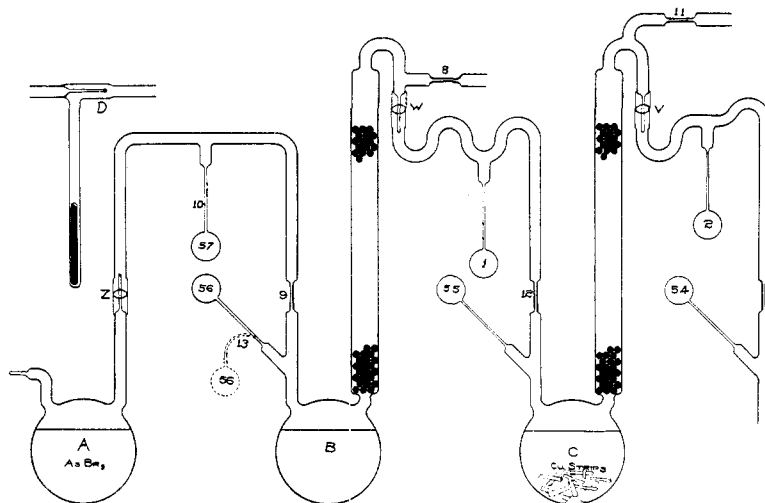


Fig. 1.

The arsenic tribromide was distilled from the excess of arsenic into a second similar bulb connected to the first by a special valve and previously exhausted, and then was fractionally distilled in apparatus resembling that shown in Fig. 1. The Hempel column attached to the still was filled with glass beads and during the distillation was warmed with a flame sufficiently to prevent choking of the column. In each distillation the more volatile fraction was collected in small bulbs, 1, 2, beyond the column, while a residual fraction was either left in the still or collected in small attached bulbs, 55, 56. During the tenth distillation the apparatus was broken, and as the quantity of material remaining was small, it was discarded. A diagram of the distillation is shown in Fig. 2 in which the capital letters represent the main portions and numbers to the right represent more volatile and numbers to the left less volatile fractions. The sequence of numbers as a whole represents gradually decreasing volatility so far as any such difference actually existed.

The originally brown tribromide improved rapidly in appearance as the fractionation proceeded. After the first few distillations the liquid substance was pale yellow and the solidified nearly colorless; but even at the end the residue in the still always possessed a dark color. Three only of the head fractions were analyzed with the results indicated on the diagram and in Table I, Series 1.

Sample II was prepared from pure bromine and arsenic in essentially the same manner as Sample I. From the weights of arsenic and bromine used the weight of tribromide synthesized was calculated to be approximately 425 grams. Only minor modifications were made in the construction of the distillation apparatus as shown in Figure 1. The Hempel columns were suitably warmed by electrically heated sleeves.

In spite of the fact that an excess of arsenic was employed in the synthesis the most volatile fraction in the first distillation was red and appeared to contain free bromine. Possibly this was liberated at the temperature of the still ( $160^{\circ} \pm$ ) from a higher bromide (*e. g.*, ferric bromide), resulting from impurity of iron in the arsenic. The least volatile fraction was grayish white after solidification.

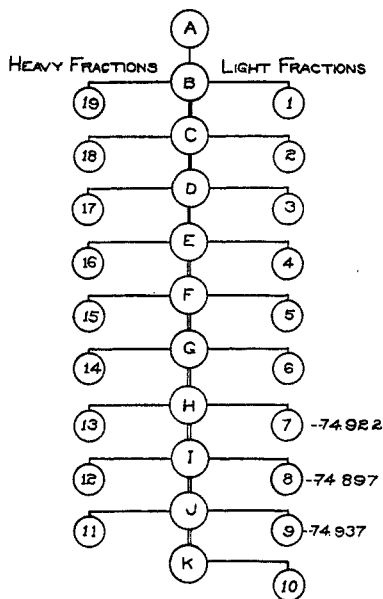


Fig. 2.—AsBr<sub>3</sub>, I.

In the second distillation, after removal of the light fraction, the tribromide was distilled upon copper strips, in order to eliminate free bromine if present. Reaction with the copper was evident for the color of the distillate disappeared and the copper became coated with a black substance, possibly AsBr<sub>3</sub>, 7 Cu<sup>6</sup> or metallic arsenic or both. In the third distillation from the copper the light fraction, 2 (Fig. 3), was nearly colorless when liquid and solidified to a white solid. The fourth and fifth fractionations also were from copper, but at that point its use was discontinued since no further effect was found. The heavy fraction 47 from the eleventh distillation was hydrolyzed with water and the product subjected to spectrographic examination in a graphite arc, with a Féry quartz spectrograph. No evidence of the presence of copper, tin or antimony could be detected. During the twelfth distillation the apparatus was opened to the air by the cracking of the Hempel column after three light fractions, 12, 13 and 14, had been removed.

Since over 200 grams of material remained it was poured into a new apparatus, the air was

flushed out by boiling the tribromide under reduced pressure and, after the system had been sealed, the fractionation was continued until only enough material remained to fill the six bulbs 28 to 33. An outline of the complete fractionation is shown in Fig. 3, with the atomic weights corresponding to the fractions analyzed.

The method of analysis was as follows. The exhausted sealed bulb containing the tribromide was weighed under water of known temperature by means of a tared platinum basket. Then it was cleaned, dried and weighed by substitution. At the same time the density of the air was found by weighing a standardized sealed glass globe.<sup>7</sup> Next the bulb was broken under 100–200 ml. of ammonia in a closed flask with a ground stopper, and after two to three hours the glass fragments were collected and weighed.

After a preliminary investigation the method of collecting the glass on a filter paper was given up because of the great difficulty in washing clean a filter through which the ammoniacal arsenite solution had been passed, even if the filter is subsequently washed with dilute nitric acid. On the other hand, platinum-sponge Gooch crucibles were found more satisfactory, for the excess in weight found when empty glass bulbs were

(6) Hilpert and Herrmann, *Ber.*, **46**, 2224 (1913).

(7) Baxter, *THIS JOURNAL*, **43**, 1317 (1921).

broken under ammoniacal arsenite and the fragments, after being collected on a weighed crucible, washed with one per cent. nitric acid, was found to be 0.10 mg. as the average of six experiments varying from 0.16 to 0.04 mg. This observed excess in weight was applied as a correction in early analyses. In later analyses the glass was treated with hot 20% nitric acid, since it was found that glass so treated retained nothing from the arsenic solution, and no correction was applied. From the weight and volume of the bulb and the weight of the glass the weight of the tribromide in vacuum was found. Then a quantity of the purest silver<sup>8</sup> as nearly as possible equivalent to the tribromide was weighed out and dissolved slowly in nitric acid with especial pains to avoid loss by

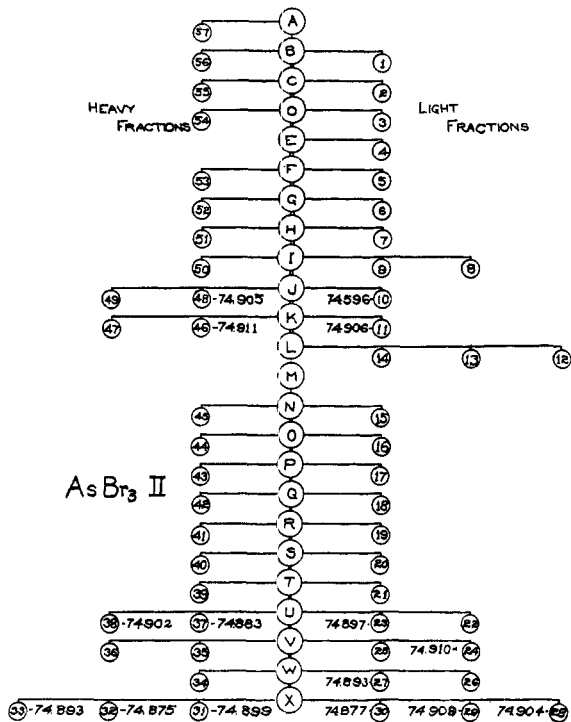


Fig. 3.--AsBr<sub>3</sub>, II.

spattering. After dilution until 0.08 to 0.1 normal the silver solution was quantitatively added to the bromide solution, which had been made acid with nitric acid and possessed approximately the same concentration as the silver nitrate. Occasional agitation for a period of a week followed and then portions of the solution were tested in a nephelometer for excess of bromide or silver. If a deficiency of either was found 0.01 normal solution was added and the nephelometric test repeated until the exact end-point had been reached. The process of testing the solutions in most cases extended over six to seven months so that occluded material so far as possible should have opportunity for extraction. In fact changes amounting to +0.1 mg. of silver on an average occurred between the second and the sixth month. This is in accord with the evidence secured in an investigation by Baxter and Greene<sup>9</sup> in this Laboratory in which it was found that in the

(8) For an outline of the method of purification see Baxter and Ishimaru, THIS JOURNAL, 51, 1730 (1929).

(9) Baxter and Greene, *ibid.*, 53, 611 (1931).

precipitation of ammonium bromide by silver nitrate a dilution of 0.03 normal was necessary to prevent occlusion of bromide although with ammonium chloride a concentration of 0.1 normal was apparently safe. How much effect this may have had in earlier work with bromides is difficult to determine.

Both the bulb and the silver were weighed by substituting weights for the carefully tared object. Weights were standardized by the Richards substitution method.<sup>10</sup> Vacuum corrections and the densities on which they were based are as follows:

	Density	Vacuum correction per gram
Air, 0° and 760 mm.	0.001293	
Weights	8.3	
Glass	2.50	+0.000335
Silver	10.49	-0.000031

TABLE I

ATOMIC WEIGHT OF ARSENIC							
Ag = 107.880 AsBr <sub>3</sub> .3Ag Br = 79.916							
Analy- sis	Fraction of AsBr <sub>3</sub>	AsBr <sub>3</sub> in vacuum, g.	Ag in vacuum, g.	Ag added or subtracted in soln., g.	Corr. wt. of Ag in vac., g.	Ratio AsBr <sub>3</sub> : 3Ag	At. wt. of arsenic
Series 1							
1	8	10.00486	10.28800	+0.00287	10.29087	0.972207	74.897
2	9	9.64625	9.91934	+ .00142	9.92076	.972330	74.937
3	7	13.92585	14.32125	+ .00155	14.32280	.972285	74.922
Average						.972272	74.919
Series 2							
1	10	5.73208	5.89407	-0.01120	5.88287	(0.974368)	(75.596)
2	48	6.63538	6.82552	- .00062	6.82490	.972231	74.905
3	11	8.10704	8.33965	- .00111	8.33856	.972235	74.906
4	46	8.02860	8.25943	- .00168	8.25775	.972250	74.911
5	23	5.04824	5.19142	+ .00112	5.19255	.972208	74.897
6	37	7.27190	7.47838	+ .00171	7.48011	.972165	74.883
7	38	7.70301	7.92164	+ .00145	7.92309	.972223	74.902
8	24	7.55491	7.76979	+ .00077	7.77056	.972248	74.910
9	29	6.49903	6.68397	+ .00062	6.68459	.972241	74.908
10	30	6.14542	6.31998	+ .00152	6.32150	.972146	74.877
11	31	6.74221	6.93428	+ .00062	6.93490	.972214	74.899
12	32	6.80346	6.99675	+ .00170	6.99845	.972138	74.875
13	33	5.84643	6.01332	+ .00030	6.01362	.972195	74.893
14	27	8.16037	8.39234	+ .00142	8.39376	.972195	74.893
15	28	7.54923	7.76450	+ .00038	7.76488	.972228	74.904
Average, omitting Analysis 1						.972208	74.897
Average, omitting Analyses 1, 10, 12						.972219	74.901

Although the three specimens of tribromide used in Series 1 were consecutive light fractions, falling as they do in the latter part of the fractionation they may be considered to represent fairly the purest portion of the first preparation. This material was never as satisfactory as the second and in view of the small number of analyses and the somewhat less satisfactory concordance of results, the average of the series is chiefly valuable as a confirmation of the result of the second series.

(10) Richards, *THIS JOURNAL*, **22**, 144 (1900).

The analyses of the fractions of the second sample of tribromide, with the exception of the first, which seems to have been affected by some gross error, show no systematic variation. In some of the earlier analyses of this series it became evident that the interior wall of the flask in which the bulbs of tribromide were broken had been slightly scratched by the glass fragments, but since the analyses in which the scratched flask was used (2-9) were on the whole slightly higher than those carried out with a new flask (10-15), no appreciable error can be ascribed to this source. In Analyses 2-4 the samples used were collected immediately after the distillation from copper, but the results do not differ by a significant amount from those obtained with later fractions.

If the results are arranged in the order of decreasing volatility of material there is no apparent trend.

Fraction	Atomic weight	Fraction	Atomic weight
10	(75.596)	31	74.899
11	74.906	32	74.875
23	74.897	33	74.893
24	74.910	37	74.883
27	74.893	38	74.902
28	74.904	46	74.911
29	74.908	48	74.905
30	74.877		

The average value of all the results excluding that of Fraction 10, 74.897, differs by only 0.004 unit from the average obtained by excluding those of Fractions 30 and 32, 74.901. The apparent atomic weight of arsenic by this method therefore seems to be not far from 74.90.

### The Analysis of Arsenic Trichloride

Antedating the investigation upon arsenic tribromide described above, a preliminary series of experiments with arsenic trichloride had been completed. In fact it was the unexpected outcome of these earlier experiments which led to the later work. In this earlier work<sup>11</sup> arsenic trichloride was fractionally distilled in vacuum and various fractions were analyzed by comparison with silver.

The original material was synthesized by heating metallic arsenic in a hard glass tube in a current of chlorine drawn from a cylinder of liquid material. Although presumably dry at the outset, the chlorine was passed over concentrated sulfuric acid and phosphorus pentoxide. After standing for some time over metallic arsenic the product was twenty-five times distilled in exhausted glass apparatus without the use of fractionating columns. In every distillation both more and less volatile fractions were removed.

After the sixteenth distillation the apparatus was accidentally opened to the air. The material was thereupon poured into a new distilling bulb connected with a special valve and, after this had been exhausted and flushed by boiling, the distillation was continued.

(11) Begun by M. J. Dorcas and completed by E. W. Scripture.

In addition four (26-29) distillations with fractionating columns were carried out at the end, all of the residual material being finally collected in eight small bulbs.

The residue from the second distillation, Fraction 84, after hydrolysis was found by spectroscopic analysis to contain a trace of antimony but none could be detected in the residue from the third distillation (Fraction 82). The more volatile fraction from the first distillation (Fraction 1) was found to be apparently free from phosphorus. Residual impurities to be feared were therefore hydrogen chloride and oxychlorides or higher chlorides of arsenic. Since the first is more and the last two are less volatile than the trichloride, more or less rapid removal by fractionation is to be expected. An outline of the fractionation is given in Fig. 4.

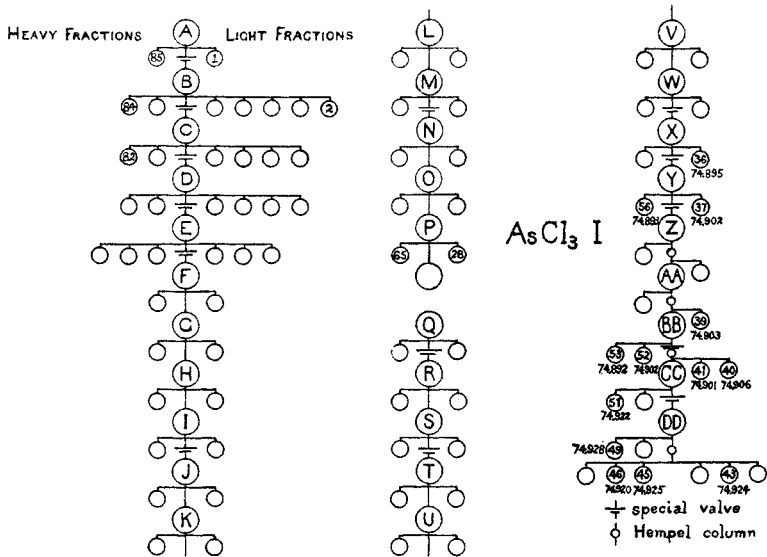


Fig. 4.

The analysis of the trichloride fractions was carried out as in the description of the analysis of the tribromide (page 1056) except that in the first eight analyses the glass of the bulbs was collected on filter paper which was then carefully charred and burned in a weighed platinum crucible, while in the last six it was collected on a platinum-sponge crucible. Later, in the work with arsenic tribromide which has already been described, it was found that it is difficult if not impossible to wash a filter entirely free from the arsenite solution so that the weights of arsenic trichloride in the first eight analyses are slightly too small and the resulting atomic weight of arsenic slightly too low. Even when the glass is collected on a platinum sponge crucible and ultimately washed with 1% nitric acid, as in the last six analyses, a slight excess in weight of the glass of 0.04 mg. was found as an average in blank experiments with empty glass bulbs. A negative correction of this magnitude has therefore been applied to the weight of the glass in each analytical experiment. The following table contains the results of these analyses.

The second specimen of arsenic trichloride was prepared and fractionally distilled in vacuum by much the same method as that described for the tribromide.<sup>12</sup> Crystalline commercial arsenic was first freed from moisture and arsenic trioxide by heating it to 350° in an exhausted hard glass tube. Then the greater part of the arsenic was placed

(12) Carried out by W. E. Shaefer.

TABLE II

Analy- sis	Frac- tion	Ag = 107.880		AsCl <sub>3</sub> : 3Ag	Cl = 35.457		At. wt. of arsenic
		AsCl <sub>3</sub> in vacuum, g.	Ag in vacuum, g.	Ag added in solution, g.	Corr. wt. of Ag in vacuum, g.	Ratio AsCl <sub>3</sub> : 3 Ag	
Series 3							
1	36	5.58768	9.97046	0.00605	9.97651	0.560084	74.895
2	37	7.75110	13.83350	.00510	13.83860	.560107	74.902
3	56	9.14735	16.32589	.00640	16.33229	.560078	74.893
4	39	6.79634	12.13385	.00010	12.13395	.560109	74.903
5	40	6.07547	10.84693	-.00020	10.84673	.560120	74.906
6	41	5.07411	9.06125	-.00200	9.05925	.560103	74.901
7	53	6.33798	11.34328	-.02698	11.31630	.560075	74.892
8	52	6.90994	12.33893	-.00210	12.33683	.560107	74.902
Average						.560098	74.899
Series 4							
9	51	3.93552	7.02526	0.00035	7.02561	0.560168	74.922
10	49	5.41621	9.66859	.00000	9.66859	.560186	74.928
11	45	4.81464	8.59458	.00025	8.59483	.560179	74.925
12	43	4.66762	8.33241	.00000	8.33241	.560176	74.924
13	46	3.13878	5.60332	.00000	5.60332	.560164	74.920
Average						.560175	74.924

in a hard glass tube connected at one end with a supply of pure dry chlorine. The other end of the hard glass tube delivered into a glass bulb containing the remainder of the arsenic. The chlorine was prepared from manganese dioxide and concentrated hydrochloric acid and after being thoroughly scrubbed with water was dried with concentrated sulfuric acid and phosphorus pentoxide. All the apparatus was constructed of glass with fused or ground joints. During the passage of the chlorine the arsenic was heated hot enough to ensure complete reaction of the chlorine. About 900 g. of trichloride was prepared.

After the trichloride had been allowed to stand in contact with the arsenic in the bulb for several days until it was colorless, it was poured into a distilling bulb attached to a special valve. The bulb was next placed in a bath of hot water and exhausted with an efficient water pump. This caused the trichloride to boil vigorously and displace the greater part of the air and the hydrogen chloride formed by hydrolysis during contact with the air in the transference. The bulb was then permanently sealed by fusing a capillary in the lead to the pump.

Since it was possible that the unexpectedly low atomic weight of arsenic which had so far been obtained by analysis of the trihalides might be due to residual chlorine or higher chloride, especial effort was now made to make certain that these impurities, if present, were eliminated. This was done by repeated distillation over arsenic at increasingly higher temperatures. First the trichloride was many times distilled from one bulb to another, both of which contained crystals of arsenic which had been heated in a vacuum, through Hempel columns also filled with arsenic crystals instead of glass beads.

Fractional distillation was then undertaken in apparatus similar to that shown in Fig. 1. During a distillation the still was heated in a water-bath to 50-60° and the receiving bulb was cooled with ice water. Under these conditions very efficient refluxing without choking occurred in the Hempel columns. The sample bulbs were usually cooled with carbon dioxide snow and alcohol, but sometimes merely with ice and salt. After thirteen fractional distillations had been carried out, the remaining material (80



cc.) was set aside for subsequent examination. The course of this fractionation is shown on the left-hand side of Fig. 5.

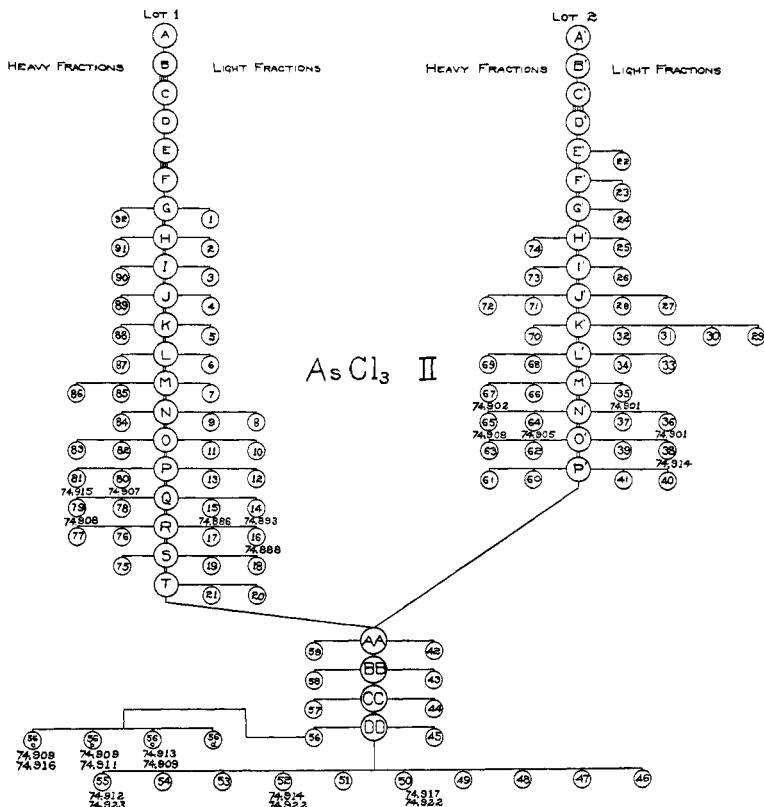


Fig. 5.

Since the analysis of the fractions obtained in this preparation (Table III, Series 5) still indicated a low value for the atomic weight of arsenic, the experiment was tried of passing the vapor of the trichloride through a tube filled with arsenic heated to a relatively high temperature. A new lot of trichloride was prepared exactly as before and after being boiled under low pressure to remove dissolved gases was distilled into an exhausted system consisting of two bulbs connected through a hard glass tube which terminated in ground glass joints and filled with arsenic which had been previously heated in vacuum. The ground joints fitted well but were not lubricated. Instead the joints were made vacuum tight by an outside layer of de Khotinsky cement. The trichloride was then five times distilled back and forth from one bulb to the other while the arsenic was heated to the temperature of sublimation. After transfer by distillation to a new exhausted system, fractionation of the product was carried on until twelve distillations had been made. The course of this fractionation is shown on the right-hand side of Fig. 5. The material remaining after the twelfth distillation (100 cc.) was then combined with the remainder from the previous preparation and the fractionation of the mixture continued as indicated in the lower part of Fig. 5. This treatment also failed to alter the composition of the trichloride (Table III, Series 6).

Three groups of analyses of these arsenic trichloride fractions were made, covering the first and second preparations as well as the mixture of the two. In the first group not only were light and heavy fractions compared, but also the effect of oxidizing the arsenite before precipitation of silver chloride was investigated, although there is no reason to expect reduction of silver salts. The oxidation was accomplished in two experiments by adding hydrogen peroxide in essentially the theoretical quantities to oxidize the arsenite; in two experiments potassium bichromate was used for the purpose. The oxidizing solution was added to the acidified solution of the arsenite through a funnel tube extending to the bottom of the solution. Although the bichromate was chloride free, the hydrogen peroxide contained a trace of chloride which was estimated quantitatively by means of a nephelometer and a corresponding correction applied.

The glass fragments were collected on a platinum sponge crucible as described on page 1056, and after the initial weighing were again twice washed with 5 normal nitric acid. The first washing usually produced a slight loss in weight, amounting on an average in eighteen experiments to 0.10 mg. The second washing was almost without effect, for the average of the very small change was 0.01 mg.

The precipitation of the silver chloride was carried out much as described on page 1057, but even greater pains were taken to prevent occlusion by the silver chloride by slow addition of the silver nitrate solution. That the silver chloride was really pure was shown by examining the arc spectrum of carefully washed material from two analyses in a Féry quartz spectrograph. No trace of arsenic could be detected.

In the last six analyses, as soon as the exact end-point had been found the silver chloride was determined gravimetrically. To do this, first an excess of about one gram of silver nitrate was added to the flask containing the analysis and after the solution had

TABLE III  
ATOMIC WEIGHT OF ARSENIC  
Ag = 107.880 AsCl<sub>3</sub>:3Ag Cl = 35.457

Analy- sis	Fraction of AsCl <sub>3</sub>	Oxidizing agent	AsCl <sub>3</sub> in vacuum, g.	Ag in vacuum, g	Ag added or subtracted in soln., g.	Corr. wt. of Ag in vacuum, g.	Ratio AsCl <sub>3</sub> : 3Ag	At. wt. of arsenic
Series 5								
1	80	None used	4.19732	7.49207	+0.00150	7.49357	0.560123	74.907
2	81	H <sub>2</sub> O <sub>2</sub>	4.98056	8.89089	+ .00065	8.89154	.560146	74.915
3	14	None used	4.73909	8.45956	+ .00190	8.46146	.560079	74.893
4	15	H <sub>2</sub> O <sub>2</sub>	4.15568	7.41843	+ .00166	7.42009	.560058	74.886
5	79	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5.15747	9.20840	- .00070	9.20770	.560126	74.908
6	16	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	5.29708	9.45821	- .00020	9.45801	.560063	74.888
							Average .560099	74.900
Series 6								
7	35		4.94345	8.82603	- 0.00010	8.82593	0.560105	74.901
8	36		4.82524	8.61471	+ .00020	8.61491	.560103	74.901
9	64		3.84375	6.86270	- .00030	6.86240	.560117	74.905
10	65		4.28593	7.65215	- .00040	7.65175	.560124	74.908
11	38		4.62010	8.24886	- .00080	8.24806	.560144	74.914
12	67		4.01638	7.17093	- .00020	7.17073	.560108	74.902
							Average .560117	74.905
Series 7								
13	50		5.10281	9.11017	- 0.00050	9.10967	0.560153	74.917
14	52		5.06855	9.04884	- .00020	9.04864	.560145	74.914
15	55		5.29138	9.44726	- .00070	9.44656	.560138	74.912
16	56a		5.67514	10.13242	- .00060	10.13182	.560130	74.909
17	56b		5.14259	9.18160	- .00050	9.18110	.560128	74.909
18	56c		5.82250	10.39523	- .00050	10.39473	.560140	74.913
							Average .560139	74.912
							Average of Series 5, 6 and 7 .560118	74.906
							Average of Series 6 and 7 .560128	74.909

TABLE IV  
 ATOMIC WEIGHT OF ARSENIC  
 $\text{Ag} = 107.880$   $\text{AsCl}_3:3\text{AgCl}$   $\text{Cl} = 35.457$

Analy- sis	Fraction of $\text{AsCl}_3$	$\text{AsCl}_3$ in vacuum, g.	$\text{AgCl}$ in vacuum, g.	Loss in wt. on fusion, g.	Dissolved $\text{AgCl}$ , g.	Corr. wt. of $\text{AgCl}$ in vac., g.	Ratio $\text{AsCl}_3$ : 3 $\text{AgCl}$	At. wt. of arsenic
Series 8								
19	50	5.10281	12.10317	0.00047	0.00069	12.10339	0.421602	74.922
20	52	5.06855	12.02154	.00031	.00090	12.02213	.421602	74.922
21	55	5.29138	12.55012	.00034	.00083	12.55061	.421603	74.923
22	56a	5.67514	13.46109	.00042	.00073	13.46140	.421586	74.916
23	56b	5.14259	12.19805	.00031	.00074	12.19848	.421576	74.911
24	56c	5.82250	13.81091	.00024	.00077	13.81144	.421571	74.909
Average							.421590	74.917

been vigorously shaken, it was cooled in an ice-bath. The precipitate was then washed thoroughly by decantation with an ice-cold 0.0003 normal solution of silver nitrate, and was transferred to a weighed platinum-sponge Gooch crucible by means of ice cold water. After being dried at 300° for twenty hours the precipitate was weighed. The bulk of the precipitate was next transferred to a porcelain crucible and the moisture lost by fusion determined.

The precipitating flask was rinsed with dilute ammonia and the rinsings were added to the water used in the transfer of the silver chloride. By nephelometric comparison with standard chloride solutions the chloride content of this solution was found, and applied as a positive correction to the weight of silver chloride. The solubility of silver chloride in the chilled silver nitrate washings was assumed to be 0.02 mg. per liter. Since no opalescence whatever could be produced in the original supernatant solution by further addition of silver nitrate the solubility of the silver chloride in this solution was neglected. In Table III a vacuum correction of +0.000071 per gram has been applied to the observed weights of silver chloride. This is based on the density 5.56.

In Table V the results of Series 5 are grouped according to volatility of the fractions

Light fraction	Oxidizing agent	Atomic wt. arsenic
14	None	74.893
15	$\text{H}_2\text{O}_2$	74.886
16	$\text{K}_2\text{Cr}_2\text{O}_7$	74.888
Average		74.889
Heavy fraction		
79	$\text{K}_2\text{Cr}_2\text{O}_7$	74.908
80	None	74.907
81	$\text{H}_2\text{O}_2$	74.915
Average		74.910

Apparently the use of an oxidizing agent is without influence. The light fractions however yield a somewhat lower value than the heavy fractions, and this difference might lead to the conclusion that the purification of the trichloride was not complete at the stage when these fractions were removed. A similar comparison of the results of Series 6 which represent fractions removed at a similar stage in the purification of the second lot of trichloride, shows no indication of any difference between light and heavy fractions, nor between these and fractions obtained in a still later stage in the fractionation (Table III, Series 7).

TABLE VI

Light fraction	Atomic weight	Heavy fraction	Atomic weight
35	74.901	64	74.905
36	74.901	65	74.908
38	74.914	67	74.902
Average 74.905		Average 74.905	

On the other hand, the gravimetric determination of the silver chloride leads to a slightly higher value for the atomic weight of arsenic, which indicates that less silver chloride was obtained than corresponds to the quantity of silver used in the comparison. The last two are compared in the following table.

TABLE VII

Analyses	Fraction	Ratio Ag:AgCl
13 and 19	50	0.752654
14 and 20	52	.752665
15 and 21	55	.752677
16 and 22	56a	.752657
17 and 23	56b	.752643
18 and 24	56c	.752617
		Average .752652

Theoretical (Ag = 107.880; Cl = 35.457) 0.752627

The deficiency of silver chloride amounts to 0.003% or 0.4 mg. in the quantities obtained in the above experiments.

The following table summarizes our work on arsenic trihalides by comparison with silver and silver chloride.

TABLE VIII

Series 1	AsBr <sub>3</sub> :3Ag	74.919
Series 2	AsBr <sub>3</sub> :3Ag	74.897
Series 3	AsCl <sub>3</sub> :3Ag	74.899
Series 4	AsCl <sub>3</sub> :3Ag	74.924
Series 5	AsCl <sub>3</sub> :3Ag	74.900
Series 6	AsCl <sub>3</sub> :3Ag	74.905
Series 7	AsCl <sub>3</sub> :3Ag	74.912
Series 8	AsCl <sub>3</sub> :3AgCl	74.917
		Average 74.909

Average weighted according to number of analyses 74.906

Although the third decimal place in the averages must beyond question be very uncertain, the evidence presented above points to a value not far from 74.91, 0.02 unit lower than the present International value.

While the reason for the discrepancy between Krepelka's and our results is not apparent, representing as they do work of a very similar character, certainly there is little question that the old value for arsenic, 74.96, adopted in the national and international tables until 1931 is too high. The bearing of Aston's results on this problem is not particularly decisive. The present accuracy claimed for the mass spectrograph is 1/10,000 and the

uncertainty of the conversion factor is fully as large. Therefore it is doubtful whether the atomic weight of arsenic could at present be determined with the mass spectrograph within 0.01 unit aside from the possibility that arsenic may contain small amounts of undiscovered isotopes.

### Summary

1. The preparation of pure arsenic trichloride and tribromide is described.
2. By analysis of the trihalides the atomic weight of arsenic is found to be 74.91.

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## Reactions of Ethylene Oxide. I. The Action of Ethylene Oxide on Diethylamine

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### Introduction

Previous to the recent paper of Horne and Shriner<sup>1</sup> the literature contained no satisfactory directions for the preparation of diethylaminoethanols from ethylene oxide and diethylamine. Simultaneously with Horne and Shriner, the present authors, using a different method of preparation, obtained products whose physical properties do not agree with those obtained by the above workers. The authors do not agree with Horne and Shriner's statement that ethylene oxide does not react with their solvent, methyl alcohol, an appreciable reaction being easily obtained at 55°. By successive additions of ethylene oxide to diethylamine and the resulting products the following compounds were prepared and will be referred to hereafter by the Roman numeral assigned to each.

I	$(C_2H_5)_2NCH_2CH_2OH$	II	$(C_2H_5)_2NCH_2CH_2OCH_2CH_2OH$
III	$(C_2H_5)_2N(CH_2CH_2O)_2CH_2CH_2OH$	IV	$(C_2H_5)_2N(CH_2CH_2O)_3CH_2CH_2OH$
V	$(C_2H_5)_2N(CH_2CH_2O)_4CH_2CH_2OH$	VI	$(C_2H_5)_2N(CH_2CH_2O)_5CH_2CH_2OH$
VII	$(C_2H_5)_2N(CH_2CH_2O)_6CH_2CH_2OH$		

### Experimental

**Preparation of Diethylaminoethanol.**—38.3 grams of diethylamine (b. p. 55–57°) and 23.5 g. of ethylene oxide were caused to react in a copper autoclave of 500-ml. capacity at 100°. The reaction was complete within one hour; 49.6 g. of (I) was obtained, a yield of 81%. The reaction could be completed in two to ten minutes in the presence of small quantities of water, but this greatly increased the difficulties of separating the products. The reaction was also carried out in the presence of ether and alcohol as solvents but with a decrease in the rate of the reaction. Diethylaminoethanol

(1) Horne and Shriner, *THIS JOURNAL*, **54**, 2925 (1932).