at 0°.[13] Krypton and argon also form hydrates, but not so readily as xenon; the dissociation pressures of their hydrates are, respectively, 14.5 and nearly 100 atm. at 0°.[14] While the hydrates of neon and helium have not yet been found, the present work indicates either that 1000 atm. at 0° is not enough pressure for the formation of helium hydrate or that the critical decomposition point is below 0°. The relative ease of hydrate formation of the inert gases is in line with their respective polarizabilities. Helium shows the lowest polarizability and should therefore be expected to have the highest dissociation pressure at any corresponding temperature.

We wish to express thanks to Messrs. C. W. Seibel and W. M. Deaton for the very pure helium used in this work.

Summary

The solubility of helium was measured at 0, 25, 50 and 75° from 25 to 1000 atmospheres partial pressures.

The calculated Bunsen and Ostwald absorption coefficients showed excellent agreement with the best known values.

Like hydrogen and nitrogen, helium also shows a minimum of solubility, though at a lower temperature.

WASHINGTON, D. C. RECEIVED FEBRUARY 27, 1935

[13] De Forcrand, *Compt. rend.*, **181**, 15 (1925).

[14] De Forcrand, *ibid.*, **176**, 355 (1923).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RADCLIFFE COLLEGE]

A Revision of the Atomic Weight of Arsenic. The Ratio of Arsenic Trichloride to Iodine

BY GREGORY PAUL BAXTER AND LAURENCE DAVID FRIZZELL

In two recent investigations determinations of the ratios of arsenic trichloride and tribromide to silver[1] and of arsenic trichloride to iodine pentoxide have been described.[2] The atomic weight of arsenic derived from this work is 74.91. Below is described the determination of the ratio of arsenic trichloride to iodine.

The procedure in general followed that described for the determination of the ratio of arsenic trichloride to iodine pentoxide. Weighed amounts of arsenic trichloride after hydrolysis were allowed to react with nearly equivalent weighed amounts of iodine. The acid formed during the reactions was neutralized and the end-point found with very dilute standard solutions of arsenite and iodine.

Purification of Reagents

Water and hydrochloric acid were purified by distillation. Mono- and di-sodium phosphates, sodium and potassium iodides, di-sodium arsenate and potassium permanganate were subjected to several recrystallizations, with centrifugal drainage and rinsing of the crystals in a porcelain centrifuge. Pyrex vessels were employed and the solutions were initially clarified by filtration through sintered glass. The phosphates, large amounts of which were used in the analyses, were free from both reducing and oxidizing impurities such as iron.

The Preparation of Arsenic Trichloride

The method for preparing and purifying arsenic trichloride followed closely that described in the earlier papers.[1,2] The compound was synthesized from scrubbed and dried tank chlorine and commercial arsenic which had been freed from trioxide at a high temperature in a vacuum. After standing over arsenic crystals the trichloride was refluxed for some time in a column filled with arsenic crystals forming part of a previously exhausted glass system. It was then subjected to a series of twenty-three fractional distillations in previously exhausted systems. One or more light and heavy fractions were removed in each distillation. The apparatus employed resembled closely that used by Baxter and Shaefer and other investigators in similar work and is illustrated in Fig. 1. The bulb A containing the arsenic trichloride is connected with a Hempel column B filled with glass pearls and terminating in a special capillary valve C which could be opened at will by breaking the capillary with a magnetic hammer. Bulbs 3 and 39 served to collect light or heavy fractions after bending the capillaries through 180° and when filled were disconnected by sealing the capillaries. A receiving system of similar construction was attached through the capillary F and after exhaustion with a diffusion pump was connected to the still by breaking the special valve C. The earlier light and heavy fractions were rejected. Fractions analyzed are numbered in the order of decreasing volatility. Up to Fractions 14 and 15 the fractions collected were sealed off in bulbs as indicated in Fig. 1. Since the method of analysis precluded determination of the weight of the glass after the bulb was opened, the earlier fractions analyzed were transferred to bulbs the weights of which were known in advance by means of the system shown at E, Fig. 1. The bulb con-

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[1] Baxter, Shaefer, Dorcas and Scripture, THIS JOURNAL, **55**, 1054 (1933).

[2] Baxter and Shaefer, *ibid.*, **55**, 1957 (1933).

taining the trichloride was contained in a breaking chamber connected with a ground joint one half of which together with the attached bulb had been carefully weighed. The joint was made tight by means of mercury in the cup. After the system had been completely exhausted and sealed by fusion, the bulb containing the trichloride was then broken by jarring and the trichloride was distilled into F. Then the capillary of F was sealed off and the weight of the half joint determined. The exterior volume of the filled bulb was found and after its weight had been found and corrected to vacuum, the weight of trichloride was obtained by subtracting the difference between the original weight of the bulb and joint and the portion sealed off, after correction to vacuum. In collecting samples after Fractions 14 and 15 the bulbs were connected to the fractionation system by ground joints as described above so that no subsequent transfer was necessary. This method has already been employed by Weatherill[3] and Baxter and Shaefer.[2]

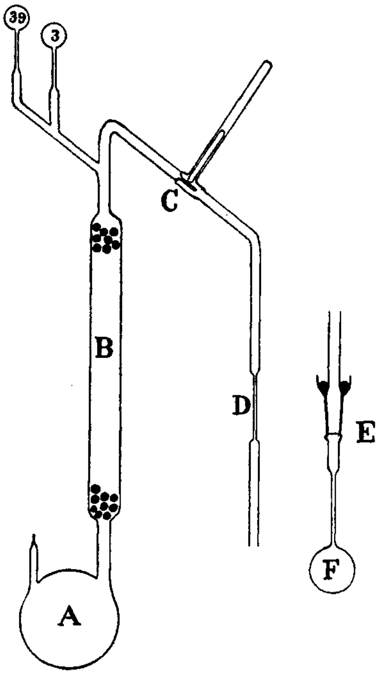

Fig. 1.

The Purification of Iodine

Iodine was dissolved in aqueous potassium iodide and then was distilled with steam. After thorough washing with water the product was converted to hydriodic acid by suspending in water and passing in thoroughly scrubbed hydrogen sulfide. The sulfur was coagulated by boiling and removed by filtration through sintered glass. Hydrocyanic acid if present was then eliminated by prolonged boiling. Nearly five-eighths of the iodine was next set free by means of potassium permanganate and collected by distillation. The processes of reduction with hydrogen sulfide and oxidation with permanganate were then repeated and the resulting iodine was redistilled with steam. Thus the iodine was three times distilled from iodide of increasing purity. This method has been described in detail by Baxter.[4] Two samples designated I and II were purified in the same way.

A third sample (Sample III) resulted from thermal decomposition of iodine pentoxide in an investigation by Baxter and Butler.[5] This material had been carefully preserved and was not further purified. The iodine pentoxide resulted from dehydration of recrystallized iodic acid, which in turn had been prepared from carefully purified iodine.

Samples I and II were freed from gross amounts of moisture by a preliminary sublimation in air. All three samples were finally subjected to a series of sublimations from one compartment to another of a quartz tube, through constrictions filled with platinum spirals and maintained at red heat, in a current of pure dry air. This treatment removes organic matter which is difficult to eliminate by simple sublimation.

Method of Analysis

In outline the method of analysis was as follows. Arsenic trichloride was first hydrolyzed by reaction with a solution of disodium phosphate in the proportion of one molecule of the former to eighteen of the latter. A nearly equivalent amount of iodine was then introduced and after reaction with the arsenite, excess or deficiency of iodine was found with dilute solutions of arsenite and iodine in the presence of starch as indicator.

The reactions involved may be approximately indicated as follows

$$\begin{array}{l}
AsCl_3 + 3H_2O = H_3AsO_3 + 3HCl \\
3HCl + 9Na_2HPO_4 = 3NaCl + 6Na_2HPO_4 + 3NaH_2PO_4 \\
H_3AsO_3 + 3Na_2HPO_4 = NaH_2AsO_3 + 2Na_2HPO_4 + NaH_2PO_4 \\
NaH_2AsO_3 + I_2 + H_2O = NaH_2AsO_4 + 2HI \\
2HI + 6Na_2HPO_4 = 2NaI + 4Na_2HPO_4 + 2NaH_2PO_4 \\
\hline
AsCl_3 + 18Na_2HPO_4 + 4H_2O + I_2 = NaH_2AsO_4 + 12Na_2HPO_4 + 6NaH_2PO_4 + 3NaCl + 2NaI
\end{array}$$

During the reaction of the arsenic trichloride with the disodium phosphate the resulting arsenite solution is never appreciably alkaline and the danger of oxidation, which proceeds at an appreciable rate in alkaline solution, is never serious. At the end of the reaction of the arsenite with the iodine the solution, which contains di- and mono-sodium phosphates in the ratio of two to one, is essentially neutral. Conditions favorable for the quantitative reaction of arsenite and iodine have been considered in detail by Washburn,[6] who has pointed out that in order that the reaction shall proceed to completion within 0.001%, the hydrogen ion concentration at

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(3) Weatherill, THIS JOURNAL, **46**, 2444 (1924); **54**, 3932 (1932).

(4) Baxter, *ibid.*, **26**, 1577 (1904).

(5) Baxter and Butler, *ibid.*, **53**, 968 (1931).

(6) Washburn, *ibid.*, **30**, 36 (1908).

the end must fall between the limits 10^{-4} and 10^{-9} with the geometrical mean 3×10^{-7}. That the final solution in our experiments was actually as well as theoretically nearly neutral was shown by the fact that in every case it was alkaline to methyl red and acid to phenolphthalein.

The solution of disodium phosphate was first boiled in a thick-walled Pyrex Erlenmeyer flask. After the solution had cooled the bulb containing the weighed arsenic trichloride was introduced and the flask was exhausted with an oil pump through its well ground stopper. The stopper of the flask was provided with a stopcock surmounted by a bulb. Joints were made tight with water only. By shaking the flask the bulb of arsenic trichloride was broken, and after some time the inside and outside of the stopper were rinsed into the flask. In the meantime a slight excess of pure iodine had been sublimed into a weighing tube which could be closed at both ends with ground caps, and the weight adjusted very nearly to equivalence by removal of iodine crystals. The weighing tube was cautiously placed in the arsenite solution, and the caps removed. Solution of the iodine, most of which had been fused, was slow and was hastened by occasional agitation. Excess or deficiency of iodine was finally found with hundredth normal iodine and arsenite solutions, with the use of weight burets, in the presence of starch.

The standard iodine solution was prepared by dissolving a weighed quantity of iodine in concentrated potassium iodide and diluting to a determined weight of solution; the arsenite solution by breaking a bulb containing a weighed amount of arsenic trichloride in a solution of nine molecules of disodium phosphate. The solutions were then compared with starch as indicator. The relative concentration of one pair of solutions, which was used throughout the greater part of the work, changed by less than 0.5% in seven months. Washburn has already shown that carefully prepared iodine and arsenite solutions remain constant in concentration for long periods.[2,6]

Starch indicator was prepared by adding starch (grains) to boiling water and, after partial clarification by settling, transferring the solution to small bottles which were stoppered, sterilized and sealed with paraffin.

Since the final volume of the analytical solution was several hundred milliliters it was necessary to determine the excess of iodine necessary to produce the color adopted for the end-point. In order to do this solutions were prepared containing sodium chloride, sodium iodide, sodium arsenate and mono- and di-sodium phosphates in the proportions existing at the end of the reaction (see above) and, with starch as indicator, iodine solution was added until the necessary color was produced. For the color selected as the end-point the average correction per ml. of solution was found in this way to be 0.00057 mg.

The limiting factor in point of time was the slow rate of solution of the iodine. In the course of the first few analyses a mechanical shaking device was developed which duplicated the swirling produced when a flask is rotated by hand with the neck in a fixed position. This diminished very materially the time required for the main reaction without increasing any of the risks.

The tube in which the iodine was weighed was of quartz in Experiments 1, 5 and 7 and of Pyrex in Experiments 2, 3, 6, 8 and 10. Both tubes were tested for resistance to iodine by filling them with iodine in the usual way and then removing the iodine by sublimation. This treatment did not alter the weights of the tubes perceptibly. The weight of the tube was determined by substitution using a very similar counterpoise.

In Experiments 6 and 7 the breaking flask was filled with pure carbon dioxide before the iodine was introduced and this atmosphere was maintained during the solution of the iodine.

In Experiment 8, in order to discover whether hypoiodite had been formed during the solution of the iodine, before starch was added a sufficient quantity of constant boiling hydrochloric acid partially to reverse the main reaction was introduced, and this was then neutralized with disodium phosphate.

None of the variations in procedure seemed to have a perceptible effect on the results. In the earlier experiments the greatest uncertainty seemed to lie in the weight of the iodine which heretofore had been weighed in a container of considerable volume (30 ml.). In the later experiments therefore the iodine was weighed in a sealed glass bulb. This was accomplished by collecting a slight excess of iodine in a weighed glass bulb attached by a capillary to a slightly flared tube and after adjustment of the weight of iodine by removal of a portion by sublimation, sealing off the capillary with a small flame. The portion detached was weighed and the weight of the sealed bulb corrected to vacuum by determining its exterior volume and the air density at the time of weighing. The interior of the bulb was adjusted so that the volume of air contained was never more than 0.2 ml.

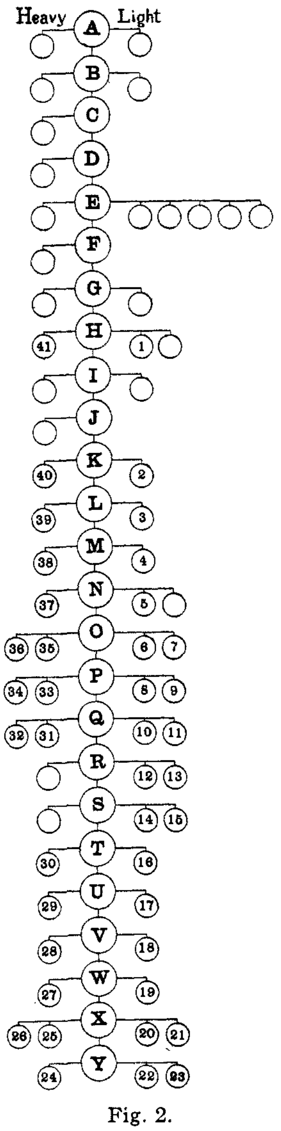

Fig. 2.

In an analysis both bulbs were placed in the phosphate solution and broken in the exhausted flask. In Analyses 12–15 the adjustment of the end-point was effected in the absence of air by admitting the adjusting solutions to the exhausted flask through the stopcock. Minor uncertainties affected all the analyses carried out in this way, Analyses 11–15.

In all subsequent experiments the iodine was collected in a bulb as above, but the bulb was exhausted by connecting it to a pump by means of a loosely fitting glass connection sealed with melted iodine. The weight of iodine was determined as above.

In Analysis 19 the bulbs and phosphate solution were contained in an exhausted and *sealed* flask, which was cracked open for adjustment of the end-point.

As a further variation and as a check on hypoiodite formation, in Analyses 22–25 the bulbs were broken in a solution of only three-fifths the necessary amount of di-sodium phosphate, the remaining two-fifths being added prior to the adjustment of the end-point. Since in three of these experiments the heavier iodine bulb broke first in the slightly alkaline di-sodium phosphate solution without producing any important effect, it seems unlikely that hypoiodite formation had any influence on the final results.

It is hardly necessary to add that all the precautions necessary and usual in the most precise work were observed. Limitations of space prevent these being given in detail.

The following densities were employed in computing vacuum corrections. Air density was observed at the time of weighing.

Air (0° and 760 mm.)	1.293
Weights	8.3
Iodine	4.93
Glass	2.5

THE ATOMIC WEIGHT OF ARSENIC

$AsCl_3:I_2$

Cl = 35.457 I = 126.916

Series 1

Analysis	Fraction of $AsCl_3$	Sample of I_2	$AsCl_3$ in vac., g.	I_2 in vac., g.	Iodine added, g.	Corr. wt. of I_2 in vac., g.	Ratio $AsCl_3:I_2$	At. wt. arsenic
1	3	I	10.33337	14.46807	0.00000	14.46807	0.714219	74.921
2	10	III	12.03069	16.84514	+ .00008	16.84522	.714190	74.913
3	32	III	11.90242	16.66543	− .00112	16.66431	.714246	74.927
4	31	III	11.76237	16.46924	− .00073	16.46851	.714234	74.924
5	11	III	11.50761	16.11273	− .00088	16.11185	.714233	74.924
6	12	III	10.86983	15.21944	− .00029	15.21915	.714221	74.921
7	13	III	10.43957	14.61762	− .00021	14.61741	.714187	74.913
8	14	III	10.52815	14.74083	− .00032	14.74051	.714232	74.924
9	16	II	9.23191	12.92588	− .00010	12.92578	.714225	74.922
10	15	II	9.75285	13.65529	.00000	13.65529	.714218	74.920
						Average	.714221	74.921

Series 2

Analysis	Fraction of $AsCl_3$	Sample of I_2	$AsCl_3$ in vac., g.	I_2 in vac., g.	Iodine added, g.	Corr. wt. of I_2 in vac., g.	Ratio $AsCl_3:I_2$	At. wt. arsenic
11	4	I	11.07602	15.50922	−0.00138	15.50784	0.714221	74.921
12	5	II	11.02523	15.43813	− .00093	15.43720	.714199	74.916
13	6	II	10.81172	15.13873	+ .00049	15.13922	.714153	74.904
14	9	III	11.03085	15.44515	− .00011	15.44504	.714200	74.916
15	7	III	11.41153	15.97914	+ .00026	15.97940	.714140	74.901
						Average	.714183	74.912

Series 3

Analysis	Fraction of $AsCl_3$	Sample of I_2	$AsCl_3$ in vac., g.	I_2 in vac., g.	Iodine added, g.	Corr. wt. of I_2 in vac., g.	Ratio $AsCl_3:I_2$	At. wt. arsenic
16	33	III	14.50315	20.30782	+0.00024	20.30806	0.714157	74.905
17	34	III	16.22008	22.71053	+ .00109	22.71162	.714175	74.909
18	30	III	9.63062	13.48529	− .00059	13.48470	.714189	74.913
19	17	III	10.11654	14.16510	− .00025	14.16485	.714200	74.916
20	29	III	10.05286	14.07616	− .00033	14.07583	.714193	74.914
21	28	III	10.60621	14.85029	+ .00039	14.85068	.714190	74.913
22	19	III	11.13389	15.59023	− .00104	15.58919	.714206	74.917
23	27	III	10.93869	15.31664	− .00081	15.31583	.714208	74.918
24	20	III	9.78401	13.69953	+ .00006	13.69959	.714183	74.911
25	26	III	9.85690	13.80122	.00000	13.80122	.714205	74.917
26	25	III	9.62562	13.47809	− .00068	13.47741	.714204	74.917
27	21	II	10.24867	14.34987	+ .00010	14.34997	.714195	74.915
28	22	III	9.97953	13.97262	+ .00062	13.97324	.714189	74.913
						Average	.714192	74.914
						Average of all	.714200	74.916

In computing the atomic weight of arsenic the atomic weight of iodine is assumed to be 126.916. Although Hönigschmid and Striebel[7]

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[7] Hönigschmid and Striebel, *Z. anorg. allgem. Chem.*, **208,** 53 (1932).

in their second paper give 126.917 as their final value, the data in their Experiment 15 do not correspond to the result calculated. If this experiment is omitted their average is lowered by 0.001 unit.

If the results are arranged in the order of decreasing volatility of the arsenic trichloride fractions no trend is apparent.

Fraction	At. wt.	Fraction	At. wt.
3	74.921	19	74.917
4	74.921	20	74.911
5	74.916	21	74.915
6	74.904	22	74.913
7	74.901	25	74.917
9	74.916	26	74.917
10	74.913	27	74.918
11	74.924	28	74.912
12	74.921	29	74.914
13	74.913	30	74.913
14	74.924	31	74.924
15	74.920	32	74.927
16	74.922	33	74.905
17	74.916	34	74.909

Nevertheless the fractions used in Series 3 represent the middle and possibly purer portions of the material.

The different samples of iodine, too, give no evidence of dissimilarity.

	Average
Sample I (2 experiments)	74.921
Sample II (5 experiments)	74.915
Sample III (21 experiments)	74.915

The three series of results involve three methods of collecting and weighing iodine. The first one, in which an open weighing tube was used, is apparently less accurate than the others although loss of iodine vapor between the weighing and the introduction into the arsenite solution would have *lowered* the result. As stated on page 853 many of the experiments of Series 2 were subject to slight uncertainties. In Series 3 the iodine was weighed in an exhausted sealed bulb, and the reaction was completed in a closed vessel. The results of this series seem to us to be on the whole the most reliable. The average of this series, however, is not very different from the average of all the experiments.

Baxter, Shaefer, Dorcas and Scripture found 74.909 by comparison of arsenic trichloride and tribromide with silver, while Baxter and Shaefer found 74.910 (calculated with I = 126.916) by oxidation of arsenic trichloride with iodine pentoxide. The conclusion of these authors that the atomic weight of arsenic is not far from 74.91 is supported by our work.

Baxter and Shaefer found $6AsCl_3/I_2O_5$ = 3.25818 as the average of all reliable experiments, while from Series 3 of our experiments $AsCl_3/I_2$ = 0.714191. By combining these values I_2/I_2O_5 = 0.760343, and I = 126.905, but in this indirect method of computing iodine experimental error is multiplied four times; *e. g.*, if the first ratio were 0.001% too low and the second 0.001% too high, the computed atomic weight of iodine would be 126.915.

Summary

In experiments involving the oxidation of arsenic trichloride with iodine the ratio $AsCl_3:I_2$ is found to be 0.714191 and the atomic weight of arsenic to be 74.91 (I = 126.916).

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