The combination of the above results gives for the free energy of cyanogen gas, $F_{298.2} = 60{,}000$ calories.

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A Revision of the Atomic Weight of Arsenic. The Comparison of Arsenic Trichloride with Iodine Pentoxide

BY GREGORY PAUL BAXTER AND WILLIAM ERNEST SHAEFER

The atomic weight of arsenic has been under investigation in this Laboratory during a large part of the time during the past twenty years. Much of the earlier work was concerned with attempts to compare arsenic trioxide with the two oxidizing agents, iodine and iodine pentoxide. As the work progressed, however, it became evident that arsenic trioxide lacked the definiteness in composition indispensable for precise work, for its composition was found to vary with the oxygen concentration prevailing during the sublimation which constituted the final step in preparing the substance for weighing. The maximum reducing power was possessed by material which had been sublimed in an atmosphere containing a mere trace of oxygen. Even vacuum sublimed material possessed slightly less reducing power owing apparently to the fact observed that such material is slightly reduced to the metallic state, while sublimation in oxygen lowered the reducing power materially. The minimum atomic weight of arsenic found in this way was 74.95 (I = 126.917) while the maximum considerably exceeded 75. The minimum is appreciably higher than the one recently adopted by the International Committee on Atomic Weights, 74.93, which depends on Krepelka's analysis of arsenic trichloride, and still higher than the result of our own more recent analyses of arsenic halides,[1] 74.91. The chief outcome of the work with arsenic trioxide seems therefore to be that this compound is not suitable for use as an analytical standard of high precision.[2]

It seemed probable that arsenic trichloride, after solution, would furnish a far more reliable quantitative source of arsenious acid than arsenic trioxide. We therefore undertook a quantitative iodimetric analysis of arsenic trichloride. Because of convenience in handling, iodine pentoxide was first chosen as the oxidizing agent.

In outline, the procedure consisted in dissolving a weighed quantity of arsenic trichloride in sodium hydroxide, in a vacuum in order to avoid oxidation of the alkaline arsenite by the air. The solution was then neutralized,

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

(2) The investigations upon arsenic trioxide were carried out under the senior author's supervision by Professors G. W. Harris, P. C. Voter, L. A. Youtz and Drs. G. L. Wendt and E. W. Scripture.

and to it was added a very nearly equivalent quantity of iodic acid obtained by dissolving a weighed quantity of iodine pentoxide in water. If the acid developed in the reaction was not sufficient to ensure complete decomposition of the iodic acid, more was added. Ultimately the solution was neutralized with phosphate and the end-point found with very dilute iodine and arsenite solutions.

The quantitative reaction of arsenious acid with iodine has been considered in detail by Washburn[3] and the conclusions reached by him apply to the present case since at the end of the reaction all iodic acid had been destroyed and the equilibrium involved only iodide, arsenate and acid. Washburn has shown that in order that the reaction

$$H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI$$

shall proceed to completion within 0.001%, the hydrogen-ion concentration at the end must fall between the limits 10^{-4} and 10^{-9} with the geometrical mean 3×10^{-7}. This result was attained in our experiments by the use of mono- and di-sodium phosphates as suggested by him.

Purification of Reagents

The numerous reagents required in the analytical operation were purified as follows.

Hydrochloric acid of constant boiling composition was slowly distilled with rejection of the first two-thirds. This acid gave no immediate coloration when treated with potassium iodide and starch.

In order to prepare sodium hydroxide free from oxidizing and reducing impurities, especially iron, good commercial material was first dissolved and treated with a slight excess of pure barium hydroxide. After centrifugal settling of the precipitate of barium carbonate, which carried with it much of the iron, the solution was treated with a slight excess of sodium carbonate and again clarified centrifugally. Evaporation in platinum dishes followed until the monohydrate would crystallize on cooling. The crystals were freed from mother liquor by centrifugal whirling and were rinsed with a very small amount of water. The product was recrystallized in the same way. Although the mother liquor of the first crystallization was found to contain a trace of iron, none could be detected in the mother liquor of the second.

Monosodium phosphate was dissolved and, after the solution had been filtered, the salt was twice recrystallized with centrifugal drainage and rinsing. Iron could not be detected in either mother liquor.

Di-sodium phosphate was twice recrystallized with centrifugal drainage. The final crystals as well as the second mother liquor were found to be free from iron.

To test the last three substances for reducing agents, fifteen gram portions of each were separately neutralized with pure hydrochloric acid or sodium hydroxide and after the addition of one gram of twice recrystallized potassium iodide and starch the solutions were titrated with very dilute iodine solution. Only a trace was necessary to produce the characteristic color.

Starch solution was prepared by pouring an emulsion of five grams in a small volume of cold water into a liter of boiling water and boiling for a few moments. After settling overnight the partially clarified solution was poured into small bottles, which were

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(3) Washburn, THIS JOURNAL, **31**, 201 (1909).

closed with sterilized stoppers after the solutions had been kept at the boiling point for two hours. These were opened as needed.

Purification of Arsenic Trichloride

Two preparations of arsenic trichloride were utilized. In the preparation and purification of material for earlier work[1] large fractions of the purest material were collected in exhausted bulbs provided with special joints through which the contents could be transferred to other bulbs in vacuum. These were utilized in part. The second preparation was a new one, purified as described in the investigation cited above. Fractions of purity corresponding to that of the first sample were employed.

In order that the weight of the sample of arsenic trichloride might be known before the bulb was broken, the empty bulb was weighed while sealed to one half of a small, very carefully ground joint. The system was then fitted to the other half of the joint and sealed by means of a mercury cup. Then the bulb was exhausted and after being connected with the supply of trichloride, was filled by distillation and sealed off. The remainder of the attached tube including one half the joint was cleaned and weighed, and after correction for air displacement the weight of glass in the bulb was obtained by difference. When the bulb itself had been weighed in air and under water the weight of trichloride in vacuum could be found. This method has been utilized by Weatherill.[4]

Iodine pentoxide was made from carefully purified iodic acid by dehydration. Three specimens of iodic acid were used. One had already been purified by Professor P. C. Voter for earlier work upon the comparison of arsenic trioxide and iodine pentoxide (Sample V). Another was prepared especially for our work (Sample S). A third (Sample B) was made by one of us for an investigation on the atomic weight of iodine.[5] In all three cases the method of preparation and purification was essentially like that recently described by Baxter and Butler,[6] so that only the outline will be given here. Iodine first was freed from other halogens by two distillations from potassium iodide solution. In the second distillation the iodide had been made from iodine obtained in the first distillation. After being dried the iodine was twice sublimed in a current of oxygen in a quartz tube through a constricted portion of the tube filled with platinum wire heated to redness. The product was next converted to potassium iodate by means of recrystallized potassium permanganate and the potassium iodate was purified by crystallization. The iodate was then precipitated as barium iodate with recrystallized barium hydroxide. After being thoroughly washed the barium iodate was converted to iodic acid by means of an equivalent quantity of distilled sulfuric acid, and the iodic acid solution was separated from the barium sulfate and evaporated to crystallization. Prolonged fractional crystallization followed. Only the purer fractions were used in the experiments to be described.

To convert the iodic acid into iodine pentoxide the former was powdered in an agate mortar together with a small quantity of the first phase formed in the dehydration, $HIO_3 \cdot I_2O_5$, and then, while contained in a weighed platinum boat, the mixture was heated at 80–100° in a current of pure air until the first stage in the dehydration was over. The temperature was then raised until the second stage in the dehydration took place (180°) and finally the product was kept at 240° for two hours. The weight of the pentoxide was then adjusted to very nearly the desired weight by removing material or adding pentoxide which had previously been similarly prepared and the whole was heated for an additional two hours preparatory to being weighed. This treatment has already been found by Baxter and Tilley[7] to yield a product of great uniformity, but

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[4] Weatherill, THIS JOURNAL, **46**, 2437 (1924); **54**, 3932 (1932).

[5] Baxter, *ibid.*, **32**, 1591 (1910).

[6] Baxter and Butler, *ibid.*, **53**, 969 (1931).

[7] Baxter and Tilley, *ibid.*, **31**, 203 (1909).

still containing 0.0023% of moisture. The boat was weighed while contained in a weighing bottle by substitution for a counterpose of similar weight and volume. During the heating of the pentoxide the boat was contained in a quartz tube which formed part of a Richards bottling apparatus so that the pentoxide was not exposed to moisture between the heating and the weighing.

As has been noted elsewhere the pentoxide occasionally developed a slight brownish color under the conditions outlined above. Although no connection between the amount of color and the composition was detected, a comparatively successful effort to prevent discoloration was made by introducing before the bottling apparatus in the air train, a quartz tube containing iodine pentoxide which was kept at 240° while the main portion of the material was being heated. Whether this eliminated from the air some undesirable constituent or the beneficial result was fortuitous is difficult to determine.

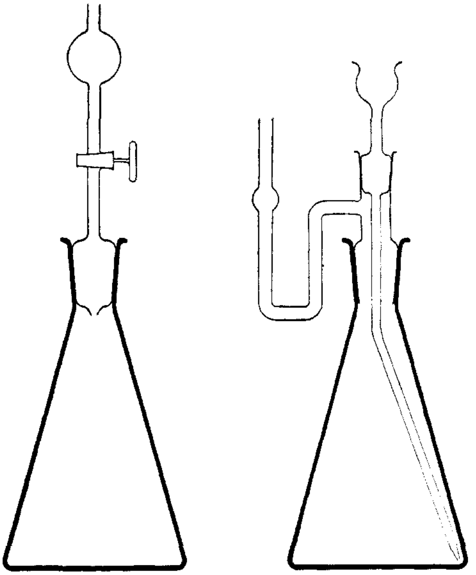

Fig. 1.

The weight of iodine pentoxide was corrected by subtracting 0.001% for adsorbed air as found by Mr. A. C. Titus in this Laboratory (investigation not yet published). Corrections for residual moisture of −0.0023% (see above) and for buoyancy of the air on the basis of the density 4.799 also were applied.

In carrying out the oxidation of the arsenic trichloride with the iodic acid it was necessary to add the reagents in a roughly quantitative fashion in order that the acidity of the solution might be accurately controlled. The first step in the process was the solution of the trichloride in an air-free sodium hydroxide solution in a vacuum, for past experience has shown that alkaline solutions of arsenite oxidize fairly rapidly in the air. This was done in the flask shown on the left in Fig. 1. In the early experiments a solution of five moles of alkali was boiled in the air and after cooling placed in the flask. The weighed bulb containing arsenic trichloride was then introduced and with the ground joint wet with water the flask was evacuated with a Geryk pump. Usually the sodium hydroxide solution boiled during the evacuation. The solution was then cooled with ice water and with the stopcock closed the flask was shaken violently enough to break the bulb containing the trichloride. Although as a rule the reaction immediately produced a clear solution of sodium chloride and arsenite, the flask was allowed to stand for some time in order to ensure the complete absorption of vapors and complete extraction of the arsenic trichloride from dead spaces in the bulb.

At the end of three hours a solution of 1.5 moles of monosodium phosphate which had been freshly boiled and cooled was admitted to the flask through the stopcock, and the contents of the flask thoroughly mixed. The solution was now very nearly neutral, since it was substantially buffered, so that exposure to the air was of no consequence. The course of the procedure up to this point may be roughly represented by the following equations

$$AsCl_3 + 4NaOH = 3NaCl + NaH_2AsO_3 + H_2O \qquad (1)$$

$$NaOH + 1^1/_2NaH_2PO_4 = Na_2HPO_4 + {}^1/_2NaH_2PO_4 + H_2O \qquad (2)$$

After air had been admitted to the flask, the stopper was loosened and both outside and inside of the stopper as well as the walls of the flask were thoroughly rinsed into the flask. The original stopper was then replaced by that represented on the right-hand side of Fig. 1.

In the meantime the iodine pentoxide, the weight of which had been adjusted as described on page 1959, was dissolved in pure water, and after the trap had been sealed with a measured amount of dilute standard arsenite solution, the iodic acid solution was slowly poured into the flask through the funnel tube extending to the bottom of the flask. The reaction proceeded with local liberation of iodine where the iodic acid first came into contact with the arsenite solution, but this iodine rapidly disappeared when the solution was mixed. Without regard to the actual steps in the process the ultimate reaction of the iodic acid with the arsenite corresponds to the reaction

$$NaH_2AsO_3 + {}^1/_3HIO_3 = NaH_2AsO_4 + {}^1/_3HI \qquad (3)$$

During the process the ground joints were sealed with water so that air expelled from the flask necessarily passed through the trap. Although there was no evidence that the solution ever contained an excess of free iodine, the arsenite in the trap would have absorbed any iodine which might have vaporized into the air. Since the solution was buffered, it was still approximately neutral and probably contained iodate. Therefore at this stage enough acid was added to complete the reaction of residual iodate with the iodide formed in the reduction. This was done in the form of 1.1 moles of diluted hydrochloric acid.

Because the arsenite–iodine reaction is incomplete in acid solution, the solution at this stage frequently contained a small quantity of free iodine. The necessary neutralization was accomplished in some cases by adding 4.3 moles of disodium phosphate, of which one mole is necessary to neutralize $^1/_3$ mole hydriodic acid formed in the oxidation–reduction reaction and 3.3 moles to react with the hydrochloric acid added. In other experiments after the addition of the hydrochloric acid one mole of disodium phosphate was added, then, if the solution contained free iodine, a slight excess of dilute standard arsenite and 1.1 moles of sodium hydroxide.

Finally 5 ml. of starch solution was added and the end-point found by adding from weight burets hundredth normal arsenite and iodine solutions. During the adjustment of the end-point the solution was contained in a flask of colorless glass placed on a white background.

In blank experiments with solutions containing corresponding amounts of purified arsenate, iodide and phosphate, it was found that an excess of 35×10^{-8} g. of iodine per ml. of final solution was necessary to produce the starch–iodine color which was adopted as the end-point. A negative correction of this magnitude was applied in all experiments. The volume of the final solution was not far from 800 ml. in every case.

After the end-point had been found the solution was always tested with indicators for neutrality. It was always acid to phenolphthalein and alkaline to methyl red, and therefore the hydrogen-ion concentration must have lain between 10^{-6} and 10^{-8}.

The solutions used in finding the exact end-point were very nearly hundredth normal. The arsenite solution was prepared as recommended by Washburn[3] by dissolving purified and sublimed arsenic trioxide in sodium hydroxide and neutralizing with monosodium phosphate. The iodine solution was made by dissolving a weighed quantity of iodine in a concentrated solution of three times its weight of pure potassium iodide and diluting to known volume. Comparisons of these solutions, using weight burets, were made after each analysis, and, during the course of the work, with other determinate iodine solutions. The observed variations in composition amounted to less than 0.2%, an uncertainty of no consequence since the total volume of solution used in an analysis was very small.

After eleven analyses had been made the amount of sodium hydroxide used in the hydrolysis of the arsenic trichloride was reduced to 4 moles, followed by the addition of one mole of monosodium phosphate before the introduction of the iodic acid. This modification was without effect on the results.

Since the weight of iodine pentoxide is less than one-third as great as that of an equivalent amount of arsenic trichloride, the samples of trichloride were considerably increased in size as soon as the procedure had become familiar.

In Analysis 5 hydrochloric acid was used to neutralize the alkaline solution of the arsenic trichloride. This caused the precipitation of a part of the arsenic as arsenious acid, and this precipitate never entirely disappeared. In Analysis 9 air leaked into the solution flask before the alkaline solution had been neutralized. Although this resulted in incipient oxidation of the arsenite, the analysis was completed for sake of comparison. In Analysis 16 a small amount of arsenious acid was found in the stopper of the solution flask, and although the attempt was made to remove this there was no certainty that the attempt was successful. In Analysis 17 the reaction mixture seemed slightly turbid after the addition of the monosodium phosphate. The results of these four analyses are therefore unreliable. Aside from the fact that with experience the analytical procedure of the later analyses was carried out with more certainty and confidence, the remaining analyses were successful.

THE ATOMIC WEIGHT OF ARSENIC

$6AsCl_3:I_2O_5$

Cl = 35.457 I = 126.917 O = 16.000

Number of analysis	Sample of I_2O_5	$AsCl_3$ in vacuum, g.	I_2O_5 in vacuum, g.	I_2O_5 added, g.	Corr. wt. of I_2O_5, g.	Ratio $6AsCl_3$: I_2O_5	Atomic weight of arsenic
1	V	7.21705	2.21258	0.00249	2.21507	3.25816	74.910
2	V	9.15444	2.80857	.00074	2.80921	3.25872	74.941
3	V	10.21968	3.13708	− .00077	3.13631	3.25850	74.929
4	V	9.66130	2.96232	.00289	2.96521	3.25822	74.913
5	V	17.39861	5.34196	− .00271	5.33925	(3.25862)	(74.935)
6	V	17.77941	5.45795	− .00119	5.45676	3.25824	74.914
7	V	20.40160	6.26226	− .00088	6.26138	3.25832	74.919
8	V	17.17037	5.27103	− .00067	5.27036	3.25791	74.896
9	S	21.97776	6.74454	.00052	6.74506	3.25835	74.920
10	S	21.44152	6.58189	− .00660	6.57529	(3.26092)	(75.063)
11	S	22.11839	6.78910	− .00009	6.78901	3.25797	74.899
12	S	21.15293	6.49277	− .00059	6.49218	3.25822	74.913
13	S	17.66650	5.42285	− .00095	5.42190	3.25836	74.921
14	S	18.35205	5.63217	.00036	5.63253	3.25822	74.913
15	S	14.63971	4.49278	.00020	4.49298	3.25835	74.920
16	S	20.48010	6.28582	− .00111	6.28471	(3.25872)	(74.941)
17	S	13.53616	4.15442	− .00078	4.15364	(3.25887)	(74.949)
18	S	17.51544	5.37535	.00067	5.37602	3.25807	74.905
19	S	17.32860	5.31837	.00037	5.31874	3.25803	74.903
20	B	18.18162	5.58001	.00032	5.58033	3.25816	74.910
21	S	18.05460	5.54012	.00134	5.54146	3.25809	74.906
			Average excluding Analyses 5, 10, 16, 17			3.25823	74.914
			Average excluding Analyses 1–5, 10, 16, 17			3.25818	74.911
			Average of last four analyses			3.25809	74.906

Sample V of iodic acid was used in the first eight analyses. In twelve of the remaining thirteen the material prepared especially for this investigation was used (Sample S). In analysis 20 Sample B was used. The average ratios of arsenic trichloride to iodine for the three specimens are. respectively, 3.25827, 3.25818 and 3.25816.

The average ratio in the first eleven analyses where the trichloride was dissolved in five molecules of sodium hydroxide is 3.25827, while the average in the remaining experiments where four molecules were used is 3.25815. The first four experiments give the average result 3.25840, while in the last thirteen where the quantity of material used was more than twice as large, the average is 3.25819, but two of the first four experiments give results essentially identical with the average of the last thirteen.

In the last four experiments the air current was passed over heated iodine pentoxide before entering the bottling apparatus, and as has been stated in these experiments the iodine pentoxide prepared for the analysis remained colorless. The average ratio found in these experiments is however only slightly lower than the average of all.

If the atomic weight of iodine is assumed to be 126.917, as recently determined by Hönigschmid,[8] the atomic weight of arsenic calculated from the average ratio obtained in all the reliable experiments is 74.916. If the first four, which may be looked upon as preliminary, are omitted, the result is 74.911, while the last four experiments yield 74.906.

This work confirms the conclusion recently reached by Baxter, Shaefer, Dorcas and Scripture[1] from analyses of arsenic trichloride and tribromide that the atomic weight of arsenic is not far from 74.91, and makes improbable the recent suggestion of Baxter and Butler[6] that iodine pentoxide does not possess normal composition.

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[8] Hönigschmid and Striebel, *Z. physik. Chem.*, Bodenstein Festband, 283 (1931); *Z. anorg. Chem.*, **208**, 53 (1932).

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Anhydrous Hydrazine. VI.[1,2] Hydrazine Trinitride Monohydrazinate, $N_2H_5N_3 \cdot N_2H_4$

BY A. L. DRESSER AND A. W. BROWNE WITH MICROSCOPICAL STUDIES BY C. W. MASON

Of all the chemical elements, no other two display in their binary compounds with each other so wide a range of chemical character as do nitrogen and hydrogen in their limited series of combinations. The compounds thus far isolated may be classified as (1) basic, (2) acidic, (3) saline, and (4) solvated saline hydronitrogens. In the first of these groups

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[1] For the earlier articles of this series see (a) Hale and Shetterly, THIS JOURNAL, **33**, 1071 (1911); (b) Welsh, *ibid.*, **37**, 497–508 (1915); (c) Welsh and Broderson, *ibid.*, **37**, 816 (1915); (d) Welsh and Broderson, *ibid.*, **37**, 825 (1915); (e) Dresser and Browne, *ibid.*, **53**, 4235 (1931).

[2] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article No. 2 under Heckscher Grant No. 158. For references to earlier articles published under Heckscher Grants No. 4 and No. 60 see THIS JOURNAL, **52**, 2799 (1930), footnote 1; 2806 (1930), footnote 2. Original manuscript received April 23, 1932.