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THE ATOMIC WEIGHT OF ARSENIC.

BY W. CLARENCE EBAUGH.[1]

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INTRODUCTION.

IN the present state of our knowledge concerning the relative atomic weights of the elements, any additional evidence in regard to the generally accepted values will be welcomed. It is not enough to repeat old methods of determination and to follow out old lines of comparison. What is needed is the introduction of new analytical methods, new comparisons, and new ratios. In this way we can reenforce results obtained by earlier investigators or discover in them the existence of errors due to faulty methods of analysis or to impurities in the substances used in such investigations. It was with this guiding thought that the present redetermination of the atomic weight of arsenic was undertaken, and the result should be looked upon as a contribution to our knowledge of this constant. In no sense can it be regarded as conclusive, although in many respects it is certainly confirmatory.

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[1] From author's thesis for Ph.D. degree, University of Pennsylvania, 1901.

In an earlier study of the atomic weight of arsenic, Hibbs[1] applied a method that has frequently been used with success in other determinations; *viz.*, the conversion of sodium pyroarsenate into sodium chloride in a current of hydrogen chloride gas. Thus a new ratio (NaCl : As) as well as a new factor (Na) was introduced into the calculations. It seemed desirable to extend this method to other arsenic-containing substances; therefore silver arsenate, lead arsenate, barium arsenate, magnesium pyroarsenate, sodium sulpharsenate and sodium cacodylate were prepared with the intention of converting them into the halogen salts of their respective metals. If practicable these halides were to be reduced to metal by heating them in a current of hydrogen. Thus we would have the ratios

$$\mathrm{Me}_x\,\mathrm{Hal}_y : \mathrm{As}_z \text{ and } \mathrm{Me}_x : \mathrm{As}_z ,$$

where Me represents silver, lead, barium, magnesium and sodium, and Hal represents chlorine, bromine and iodine. As additional factors there would be introduced oxygen, sulphur, carbon and hydrogen.

Much of the work was disappointing, but it is believed that the data gathered from the experiments, when the preconceived ideas were capable of execution, will be of value as a contribution to our knowledge concerning the atomic weight of arsenic.

HISTORICAL.

The atomic weight of arsenic has been studied by six investigators. Seven methods of attacking the problem were used.

It is astonishing how closely the result of Berzelius' single experiment (75.02) accords with the means of the series of experiments which followed. Dumas' first value (74.985) is also remarkable in view of the complicated method of investigation employed by him. Kessler, in a paper published in 1861, seems to throw doubt upon his own results (75.175), since he finds that they are influenced by (*a*) the time of contact of his solutions with the air, and (*b*) the dilution of the solutions used. Why Wallace should have obtained results more than 0.8 of a unit (74.229) lower than his predecessors, is inexplicable.

The generalizations of Van der Plaats, Ostwald, Seubert, Rich-

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[1] Hibbs : Thesis, University of Pennsylvania, 1896.

ards, and Clarke, agree in assigning to arsenic the atomic weight 75, plus or minus a small probable error.

PREPARATION OF MATERIAL.

Silver Arsenate.—Silver nitrate was prepared from silver that had been subjected to the well-known purification method of Stas. Arsenious oxide was sublimed in an apparatus like that employed by Gattermann[1] in making aluminum chloride. The sublimed product was converted into arsenic acid by E. Kopp's method; *i. e.*, boiling 4 parts of arsenious oxide with 12 parts of nitric acid (sp. gr. 1.20) and 1 part of hydrochloric acid (sp. gr. 1.20). The arsenic acid was boiled down twice with an excess of nitric acid and then diluted to a definite volume. Ammonia water (sp. gr. 0.90) was boiled gently in a large flask, and the evolved ammonia led through an empty flask (which served as a condenser) into distilled water. The purified ammonium hydroxide and arsenic acid were then united in the proportions required to make triammonium arsenate. This solution was dropped gradually into a solution of silver nitrate; the precipitated silver arsenate was filtered out, washed thoroughly and dried at 150°-170° C.

Lead arsenate.—Disodium hydrogen arsenate (Merck) was recrystallized several times, dissolved in water and allowed to stand for some hours. Pure lead acetate of commerce was likewise subjected to three recrystallizations, dissolved in water and allowed to stand. The solution of lead acetate, filtered into a large beaker, was well diluted and treated with the filtered solution of disodium hydrogen arsenate. Constant agitation was maintained during the precipitation. The lead arsenate was allowed to subside and then washed by decantation until all soluble lead and alkali salts were removed. Drying at 150°-170° C. ensued.

Hydrogen Chloride Gas.—Concentrated sulphuric acid was dropped from a separatory funnel into hydrochloric acid (concentrated) contained in a 3-liter flask. The evolved hydrogen chloride gas was dried and purified by passing it through two sulphuric acid drying bottles and a calcium chloride tower.

Hydrogen Bromide Gas.—Two methods of preparation were tried. (*a*) Bromine was dropped slowly upon red phosphorus

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[1] Gattermann: "Practical Methods of Organic Chemistry," Trans. 1898, p. 324.

covered with water. To remove the excess of bromine the gas was passed through two U-tubes containing glass beads and red phosphorus. (*b*) Pure resublimed anthracene was substituted for the red phosphorus and water used in method *a*. Anthracene placed in U-tubes removed free bromine. All bromine used during this investigation was rectified by two distillations over manganese dioxide and sulphuric acid.

Hydrogen Gas.—Concentrated sulphuric acid (1 part) and water (3 parts) slightly colored by platinic chloride were allowed to act upon granulated zinc. The hydrogen was purified by its passage through a series of wash bottles containing (*a*) water or ammoniacal silver nitrate; (*b*) potassium permanganate; (*c*) alkaline lead nitrate;(*d*) and (*e*) sulphuric acid.

DESCRIPTION OF APPARATUS.

The gases prepared as described above were led through combustion tubes of hard glass in which were placed porcelain boats containing the material to be experimented upon. The exit end of the tube dipped either into a receiver containing water or into a U-tube containing sulphuric acid. The latter opened directly into a draft chamber. The combustion tube was heated over Bunsen burners provided with fish-tail attachments; an additional burner held in the hand served to supply extra heat when necessary.

A short arm Troemner balance, sensitive to the thirty-fifth of a milligram and a set of weights, carefully standardized were used for all weighings. In every instance the observed weight was reduced to the vacuum standard and the means of the series of determinations, the probable errors, etc., were calculated according to the formulas given by Clarke.[1]

All atomic weights used were taken from F. W. Clarke's annual report to the American Chemical Society for the current year.[2]

EXPERIMENTAL PART.

I. Conversion of Silver Arsenate into Silver Chloride.—It was shown by Moyer[3] that arsenic could be completely separated from

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[1] F. W. Clarke: "Recalculation of the Atomic Weights," p. 7.

[2] F. W. Clarke: This Journal, **23**, 94 (1901).

[3] Moyer: Thesis, University of Pennsylvania, 1896.

silver by heating silver arsenate in a current of hydrogen chloride gas. This fact was verified by the present author.

The method of procedure adopted was as follows: Dry silver arsenate was weighed out in a porcelain boat which was then placed in the combustion tube. A slow current of hydrogen chloride gas conducted through the tube gave rise to a vigorous reaction. Heat was evolved, the red-brown arsenate became yellowish white chloride and a deposit of water and arsenic trichloride appeared upon the inner walls of the tube. After half an hour a gentle heat was applied; when no further action could be observed the temperature was raised again, but not to such a degree as to cause the silver chloride to melt. At the close of the operation the silver chloride was barely fused, allowed to cool partially in the tube and then removed to a desiccator provided with anhydrous calcium chloride and soda lime. The desiccator and its contents were allowed to remain in the balance room for at least an hour before the boat was weighed. After weighing, the boat was reheated in a current of hydrogen chloride gas until the silver chloride was again fused. Cooling and weighing were carried out just as in the first instance. The analytical results follow:

Atomic weight of chlorine	35.45
Atomic weight of oxygen	16.00
Atomic weight of silver	107.92
Density of silver arsenate	5.77
Density of silver chloride	5.50

Silver arsenate. Grams.	Silver chloride. Grams.	Arsenic. Atomic weight.
0.23182	0.21547	74.987
0.47996	0.44615	74.944
0.52521	0.48820	74.956
0.80173	0.74517	74.996
0.94782	0.88083	75.061
1.02047	0.94830	75.083
1.03558	0.96258	74.974
1.05462	0.98014	75.033
Mean		75.004
Probable error		±0.012

II. Reduction of Silver Chloride to Metallic Silver.—The boat containing silver chloride, derived from silver arsenate as described in the previous section, was covered with a strip of platinum foil (to prevent possible loss by spirting) and placed in a combustion tube connected with the hydrogen supply. After the air contained in the apparatus was expelled by hydrogen a very gentle heat was applied. Gradually the temperature was raised until the tube was at a red heat. In this condition it was maintained for at least half an hour. If great care was not exercised during the first part of the operation, loss by spattering was sure to occur. Five to seven hours were required for a reduction. The boat, its contents and its cover were allowed to remain in the desiccator at the temperature of the balance room at least an hour before weighing. Reheating to redness, cooling and weighing ensured complete reduction. The silver obtained was arsenic-free and completely soluble in nitric acid. Results are given herewith:

Atomic weight of oxygen	16.00
Atomic weight of silver	107.92
Density of silver arsenate	5.77
Density of silver	10.57

Silver arsenate. Grams.	Silver. Grams.	Arsenic. Atomic weight.
0.23182	0.162175	75.027
0.47996	0.33583	74.950
0.52521	0.367525	74.907
0.80173	0.56099	74.936
0.94782	0.66318	74.959
1.02047	0.71400	74.964
1.05462	0.73771	75.082
Mean		74.975
Probable error		±0.015

III. Conversion of Silver Arsenate into Silver Bromide.—Silver arsenate was treated just as described under the first heading of the "Experimental Part" of this thesis, except that hydrogen bromide gas obtained from bromine and anthracene was substituted for hydrogen chloride gas. All due precautions against fusing were used, but it seemed that a little silver bromide always escaped when the last traces of arsenic were expelled. The weighing and other operations were conducted as outlined in previous sections. Variable results were obtained, most of them coming between 75.25 and 75.75. Two analyses yielded 74.984

and 74.967. The above determinations would serve well for ordinary quantitative analyses, but their lack of concordance bars them from use for atomic weight considerations. The silver bromide formed was arsenic-free.[1]

IV. Conversion of Lead Arsenate into Lead Chloride.—That arsenic could be completely eliminated from lead arsenate by the use of hydrogen chloride gas was proved by Hibbs[2]. In all of the following determinations, the lead chloride produced was examined for arsenic, but none was found.

Lead arsenate was weighed into porcelain boats. The boats and contents were heated to 150°-170° C. and again weighed. Hydrogen chloride gas was passed over the arsenate, at first in the cold, but afterwards at a gentle heat. A gradual increase in temperature was brought about and the current of gas was discontinued only after all action seemed to have ceased. In no case was the lead chloride fused. The usual precautions concerning cooling, weighing, reheating, etc., were followed out. The results obtained are:

Atomic weight of chlorine	35.45
Atomic weight of oxygen	16.00
Atomic weight of lead	206.92
Density of lead arsenate	6.29
Density of lead chloride	5.80

Lead arsenate. Grams.	Lead chloride. Grams.	Arsenic. Atomic weight.
0.38152	0.35381	74.988
0.436197	0.40449	75.016
0.57218	0.53065	74.964
0.60085	0.55717	75.020
0.74123	0.68736	75.010
0.77107	0.71494	75.067
0.88282	0.81858	75.054
0.97779	0.90674	75.054
	Mean	75.022
	Probable error	±0.009

Attempts were made to reduce lead chloride to metallic lead, by heating it in a current of hydrogen, but failed to give the desired

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[1] Throughout the course of experiments it was found that the reactions in which hydrogen bromide was used gave more trouble than did those where hydrogen chloride was employed. Hydrogen iodide was more unsatisfactory than either of the preceding acids.

[2] Hibbs: *loc. cit.*

result. The temperature at which the chloride is reduced is so near that at which it is volatilized that the method is valueless. Careful heating for eight hours did not reduce all the lead chloride; some of it was found sublimed into the upper part of the boat. More lead chloride, mixed with black crystals of lead, was found adhering to the platinum cover placed over the boat.

V. Conversion of Lead Arsenate into Lead Bromide.—Preliminary experiments showed that the usual apparatus could be modified to advantage by inserting a stop-cock, through which air could be admitted to the combustion tube, in the neck of the U-tube preceding the combustion tube. By opening this cock the acid vapor could be diluted with air and thus the violence of the reaction was diminished. A filtering flask and suction pump attached to the exit receiver were also used.

The method employed in previous determinations was inapplicable here because the arsenic tribromide collecting in the boat was not readily expelled without loss due to spattering. The reaction took place violently in the cold, and bromine, water, and arsenic tribromide separated in large amounts.

As there were occasionally violent explosions when hydrogen bromide prepared from phosphorus, water and bromine was used,[1] and as phosphorus was found in the receiver, the method was abandoned for that employing anthracene and bromine. From this time no explosions occurred. Evidently the cause of the disturbance is to be looked for in the phosphorus used in the generator, hydrides of phosphorus being formed, rather than in the halide of arsenic, as was supposed by Meyer.[2]

The boat containing lead arsenate was placed in the combustion tube and heated to 200° C. Air mixed with hydrogen bromide was drawn through the apparatus and after all apparent action had ceased the heat was increased, but not to a point where fusion or volatilization of lead bromide could result. Cooling and weighing, reheating, cooling and weighing were carried out as usual. This manner of working prevented spattering, for the arsenic tribromide was removed as fast as it formed. The lead bromide was gray-white in color and contained no arsenic. Results follow:

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[1] Chronologically this work preceded that described in Section III.

[2] Meyer: This Journal, **17**, 735 (1895).

Atomic weight of bromine	79.95
Atomic weight of lead	206.92
Atomic weight of oxygen	16.00
Density of lead arsenate	6.29
Density of lead bromide	6.61

Lead arsenate. Grams.	Lead bromide. Grams.	Arsenic. Atomic weight.
0.59704	0.73092	75.066
0.61712	0.75567	74.967
0.65799	0.80569	74.980
	Mean	75.004
	Probable error	±0.021

The lead bromide could not be reduced quantitatively for reasons analogous to those given for the non-reduction of lead chloride (see Section IV).

Many attempts were made to convert barium arsenate into barium chloride, magnesium pyroarsenate into magnesium chloride and sodium sulpharsenate and sodium cacodylate into sodium chloride, but the results were of such a nature as to be useless in fixing the atomic value under discussion and may well be omitted here.

A summary of the results obtained during the course of this investigation follows:

	Arsenic. Atomic weight.	Probable error.
Ag_3AsO_4——$AgCl$	75.004	±0.012
Ag_3AsO_4——Ag	74.975	±0.015
$Pb_3(AsO_4)_2$——$PbCl_2$	75.022	±0.009
$Pb_3(AsO_4)_2$——$PbBr_2$	75.004	±0.021
Mean	75.008	
Probable error	±0.006	

This mean result, drawn from 26 determinations, affords another confirmation of the generally accepted atomic weight of arsenic. It may be interesting to note that 14 of the results lie below the general mean, while 12 of them lie above this value.

UNIVERSITY OF PENNSYLVANIA.