

	Per cent.
Nickel found.....	43.79
Nickel calculated.....	43.60
Difference.....	0.19
Arsenic found.....	56.66
Arsenic calculated.....	56.40
Difference.....	0.26

Undoubtedly there is still a wide field open in regard to the behavior of hydrochloric acid gas upon mineral species. Smith and Hibbs¹ showed that mimetite lost its arsenic quantitatively, when heated in a stream of acid gas. In this laboratory others are being investigated with favorable indications. The direct employment of hydrochloric acid gas upon a powdered mineral would simplify many a tedious gravimetric process, leaving the separated elements in a desirable condition for further treatment.

In the case of a mineral such as niccolite, where it must first be decomposed with nitric acid and then transferred to a boat, the advantage is not so great. This, however, can be modified, so that the time factor is reduced and the advantage of the method still retained. Instead of using a boat, which has no advantage unless the non-volatile chlorides are to be weighed directly, a hard glass bulb can be substituted. The mineral is placed in the bulb, dissolved in nitric acid, and evaporated down by the aid of a current of air drawn through the bulb.

The residual oxides are then separated in a stream of hydrochloric acid gas as usual.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
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THE ATOMIC WEIGHTS OF NITROGEN AND ARSENIC.²

BY JOSEPH GILLINGHAM HIBBS.

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THE atomic weight of the metal molybdenum had been determined by expelling molybdic acid from sodium molybdate with hydrochloric acid gas, then weighing the residual sodium chloride.

¹ *Loc. cit.*

² From author's thesis presented to the Faculty of the University of Pennsylvania for the degree of Doctor of Philosophy. 1896.

Having found that nitric acid and arsenic acid were driven from their alkali salts with ease, leaving a chloride that was absolutely pure, and believing that the atomic masses of nitrogen and arsenic determined in this manner would afford a valuable contribution to the literature relating to these constants, a carefully conducted series of experiments was made with two nitrates and one arsenate. The results are given in detail in the following lines :

THE ATOMIC WEIGHT OF NITROGEN.

In the past, determinations of the atomic weight of nitrogen have been made from the density of the gas itself, from the ratio between ammonium chloride and silver, and from the decomposition of certain nitrates. The first method in particular has been frequently applied. Thomson, Dulong, Berzelius, and Lavoisier brought to light many new facts relating to the atomic weight of nitrogen; unfortunately, however, considerable that they have presented has been affected by complications that have introduced inaccuracies.

Dumas and Boussingault¹ found the mean density of nitrogen to be 0.972; for hydrogen they found a mean density of 0.0693, which would give nitrogen an atomic weight of 14.026. Regnault obtained a more concordant series of results, the mean being 0.97137, and a density for hydrogen of 0.0692, which makes the atomic weight of nitrogen equal to 14.0244.

Clarke gives in detail his computation of the means of the results obtained by Penny, Stas, and Marignac. Their work on the determination of the atomic weight of this particular element was mainly on the ratio of ammonium chloride and silver, and the decomposition of certain nitrates. A great degree of accuracy was maintained throughout the entire investigation; but the amount of work required to obtain a single result necessarily lays the method open to a serious error of manipulation.

In this connection a paragraph from Clarke's "A Recalculation of the Atomic Weights" may be cited: "The general method of working upon these ratios is due to Penny. Applied to the ratio between the chloride and nitrate of potassium, it is

¹ *Compt. rend.*, 1841—12. 1005.

as follows: A weighed quantity of the chloride is introduced into a flask which is placed upon its side and connected with a receiver. An excess of pure nitric acid is added, and the transformation is gradually brought about by the aid of heat, the nitrate being brought into a weighable form. The liquid in the receiver is also evaporated, and the trace of solid matter which has been mechanically carried over, is recovered and also taken into account."

The method indicated in this study, and actually applied with the results appended, is decidedly less objectionable. In this method there is no distillation, no precipitate, in fact, nothing that could involve serious error.

Clarke summarizes the results of Penny, Stas, and Marignac as follows:

1.	From specific gravity of N.....	N = 14.0244
2.	“ ammonium chloride.....	N = 14.0336
3.	“ ratio number four.....	N = 14.0330
4.	“ silver nitrate.....	N = 13.9840
5.	“ potassium nitrate.....	N = 13.9774
6.	“ sodium nitrate.....	N = 13.9906
	Mean of results for N	N = 14.0210

If oxygen is 16, this becomes 14.0291. Stas found the atomic weight of nitrogen to be 14.044. Dumas found 14 by experiments on the combustion of ammonia and cyanogen ($O = 16$). Pelouze found 14.014 by bringing a known weight of silver nitrate in contact with a known and slightly excessive weight of ammonium chloride, which excess was titrated. Anderson found 13.95 by the decomposition of the nitrate of lead, with just enough heat for decomposition (the same method that was used by Berzelius). Marignac found 14.02 by dissolving a known weight of silver in nitric acid and then melting and weighing the nitrate found.

A.—ATOMIC WEIGHT OF NITROGEN BY ACTION OF HYDROGEN CHLORIDE UPON POTASSIUM NITRATE.

The purest salt obtainable was dissolved in water, filtered, and recrystallized six times, a solution of which was tested for chlorides, sulphates, etc., but no impurity was found. One more crystallization was made and the best crystals were

selected. These were washed with distilled water and dried at 210° C. for three hours, powdered, and again dried, and finally placed in a weighing bottle. This compound was dried before each experiment. It was also allowed to stand in a balance case one hour before weighing. The same degree of care was exercised in the preparation of the boat-for weighing.

The weighing bottle was placed on the scale pan and allowed to stand several minutes in order to regain its normal temperature. After weighing it was quickly opened and a portion of the salt removed to the boat and again closed and allowed to stand in the balance case for several hours before reweighing. The boat was then introduced into the combustion tube and the gas passed over it. The characteristic action took place. The only difference in the method of procedure adopted here and that described in the first section of this paper, was a longer time being given to complete the action, using a lower temperature, in order to do away with all possibility of fusion of the salt. It was then carefully removed to a vacuum desiccator and allowed to stand over night before weighing. It may be said also that experiments were only conducted on clear days to insure the non-entrance of moisture.

With potassium nitrate, no great variation of amount was taken.

Five determinations were made in this case :

No.	Potassium nitrate taken. Gram.	Potassium chloride obtained. Gram.	Correction for potassium nitrate. Gram.	Correction for potassium chloride. Gram.	Correction for weight of potassium nitrate Gram.	Correction for weight of potassium chloride. Gram.	Molecular weight of potassium nitrate obtained.	Atomic weight of nitrogen obtained.
1.	0.11084	0.08173	0.00006	0.00004	0.11090	0.08177	0.101121	14.011
2.	0.14864	0.09960	0.00007	0.00005	0.14871	0.10965	0.101120	14.010
3.	0.21056	0.15525	0.00011	0.00008	0.21067	0.15533	0.101123	14.013
4.	0.23248	0.17214	0.00012	0.00009	0.23360	0.17223	0.101121	14.011
5.	0.24271	0.17894	0.00013	0.00009	0.24284	0.17903	0.101124	14.014

Atomic weight of nitrogen = 14.0118 ± 0.000472 .

The atomic values used in these calculations were taken from "Table of Atomic Masses," revised by F. W. Clarke, in October, 1891.

The figures deduced from these values are, of course, subject to any change made by later revision of atomic weights. It is not so much the exact figure to which attention is called, as to the constancy of result brought forward by this method. The values used were :

Oxygen	16.00
Potassium.....	39.11
Chlorine	35.45
Specific gravity potassium nitrate.....	2.1
Specific gravity potassium chloride	1.99

B.—ATOMIC WEIGHT OF NITROGEN BY ACTION OF HYDROGEN CHLORIDE UPON SODIUM NITRATE.

The same degree of care and method of procedure were here observed as in Division A. The results are as follows :

No.	Potassium nitrate taken. Gram.	Sodium chloride obtained. Gram.	Correction for sodium nitrate. Gram.	Correction for sodium chloride. Gram.	Correction for sodium nitrate. Gram.	Correction for sodium chloride. Gram.	Molecular weight of sodium nitrate.	Atomic weight of nitrogen.
1.	0.01550	0.01064	0.01550	0.01066	85.061	14.011
2.	0.20967	0.14419	0.00009	0.00007	0.20976	0.14426	85.061	14.011
3.	6.26217	0.18029	0.00012	0.00009	0.26229	0.18038	85.064	14.014
4.	0.66610	0.46805	0.00035	0.00024	0.66645	0.45829	85.064	14.014
5.	0.93676	0.64422	0.00042	0.00034	0.93718	0.64456	85.058	14.008

Atomic weight of nitrogen = 14.0116 ± 0.000741.

Atomic values used were

Oxygen	16.00
Sodium	23.05
Chlorine	35.45
Specific gravity sodium chloride.....	2.16
Specific gravity sodium nitrate.....	2.26

When these results are compared with those obtained by Penny and Stas by treatment of potassium chloride with nitric acid, and the treatment of potassium nitrate with hydrochloric acid (likewise for sodium), a close comparison can be made.

Penny.	Hydrogen chloride method.
For potassium nitrate.....13.9774	For potassium nitrate.....14.0118
" sodium nitrate.....13.9906	" sodium nitrate.....14.0116

Showing a difference of

0.0344 for potassium salt,
0.0210 for sodium salt.

When a mean of the above results is taken, the atomic weight of nitrogen equals

13.9996 for potassium salt,
14.0011 for sodium salt.

Taking now a mean of these values, the atomic weight of nitrogen would be 14.0003.

C.—THE ATOMIC WEIGHT OF ARSENIC.

The atomic weight of arsenic has been obtained from the chloride (AsCl_3), the bromide (AsBr_3), and the trioxide (As_2O_3).

Pelouze, in 1845,¹ and Dumas, in 1859, determined it by the titration with known quantities of pure silver in the analysis of arsenic trichloride. The mean of their results, as computed by Clarke, gives the atomic weight of arsenic, 74.829. Wallace² makes the same titration with silver in the analysis of arsenic tribromide. His value is 74.046. Kessler made a set of determinations by estimating the amount of potassium bichromate required to oxidize 100 parts of arsenic trioxide to arsenic pentoxide. He obtained a mean value of 75.002.

A mean of these results gives the following :

From AsCl_3	74.829
“ AsBr_3	74.046
“ As_2O_3	75.002
General mean	74.918

If oxygen = 16, then the atomic weight of arsenic will equal 75.090.

Berzelius, in 1826, heated sulphur and arsenic trioxide together in such a way that sulphur dioxide alone escaped; this method gave 74.840 as the atomic weight of arsenic. But one experiment was made, so that it does not possess much value. In the above method there seems to be a wide variation in the results obtained, the difference between the extreme values is but little less than one unit.

By the hydrogen chloride method, we have but the weighing of the material used in the determination—which must necessarily enter every estimation or analysis—and a single weighing after the action of the acid gas. As in the case of nitrogen, the method seems to be as short and concise as possible.

¹ *Compt. rend.*, 10, 1047.

² *Phil. Mag.* (4), 18, 279.

The methods and *modus operandi* were exactly the same as those used in the determination of the atomic weight of nitrogen.

The sodium chloride obtained was perfectly white in color. In no instance was it fused. After weighing the salt residue it showed no traces of arsenic, and was readily soluble in cold water without residue. The same conditions of atmosphere were observed.

As the specific gravity of sodium pyroarsenate could not be obtained, it was determined by means of the specific gravity bottle, against chloroform, and was found to be 2.205, while the specific gravity of sodium chloride was taken as 2.16. The atomic values used were :

Oxygen	16.00
Sodium	23.05
Chlorine	35.45

The results here obtained, besides being to a great degree constant, compare favorably with those obtained by Pelouze (74.829) and Kessler (75.002).

A coincidence may here be shown by the fact that the mean of these values gives 74.9155, while the hydrogen chloride method gives 74.9158.

In order to give the method a thorough trial, the amounts taken cover a wide range. The smallest amount used was 0.02176 gram of sodium pyroarsenate, and the largest 3.22485 grams. It will also be noticed that the variation in result is but 0.027 for ten determinations.

No.	Sodium pyroarsenate taken Gram.	Sodium chloride obtained. Gram.	Correction for sodium pyroarsenate. Gram.	Correction for sodium chloride. Gram.	Correction for sodium pyroarsenate. Gram.	Correction for sodium chloride. Gram.	Molecular weight of sodium pyroarsenate.	Atomic weight of arsenic.
1.	0.02176	0.01439	0.00001	0.00000	0.02177	0.01439	354.008	74.904
2.	0.04711	0.03114	0.00002	0.00001	0.04713	0.03115	354.042	74.921
3.	0.05792	0.03828	0.00003	0.00002	0.05795	0.03830	354.054	74.927
4.	0.40780	0.26970	0.00021	0.00011	0.40801	0.26981	354.002	74.901
5.	0.50440	0.33028	0.00026	0.00017	0.50466	0.33045	354.033	74.916
6.	0.77497	0.51222	0.00041	0.00027	0.77538	0.51249	354.034	74.917
7.	0.82853	0.54762	0.00044	0.00029	0.82897	0.54791	354.034	74.917
8.	1.19068	0.78690	0.00056	0.00041	1.19124	0.78731	354.053	74.926
9.	1.67464	1.10681	0.00081	0.00051	1.67545	1.10732	354.057	74.928
10.	3.22485	2.13168	0.00152	0.00099	3.22637	2.13267	354.002	74.901
					Atomic weight of arsenic = 74.9158 ± 0.00222.			