

A DETERMINATION OF THE ATOMIC WEIGHT OF NITROGEN
OCCLUDED IN FERGUSONITE.

by

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Approved by:

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H. P. Cady
Head or Chairman of Department.

The privilege of thanking
Dr. H. P. Cady for the many valuable
suggestions and kindly assistance which
he gave during the course of this work
is taken at this point. The writer
wishes to make it clear that the idea
underlying this investigation was
Dr. Cady's.

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A DETERMINATION OF THE ATOMIC WEIGHT OF NITROGEN OCCLUDED IN FERGUSONITE.

In 1890 while working on the occurrence of nitrogen in uraninite Hillebrand¹ made complete analyses of many samples of the mineral. From the data furnished, it is interesting to calculate the strikingly constant ratio between nitrogen and uranium oxide (UO_2) in the various samples. That Hillebrand was aware of this constant ratio is made evident by a brief reference to it in the article cited; however, he attempted no explanation of it.

Calculations made on uraninite from Norway:

Place	% N	% UO_2	Ratio N/ UO_2
Annerød	1.23	48.25	.0255
Elvestad (a)	1.28	50.97	.0251
Elvestad (b)	1.28	50.83	.0252
Skroatorp	1.05	44.57	.0236
Huggenaskilen	1.08	43.56	.0248
Arendal	1.26	44.71	.0282

¹. U.S. Geo. Sur. Bull. 78, page 43, 1891.

Calculations were made on the ratio of nitrogen to uranium oxide (UO_2) in uraninite from North Carolina, Colorado, and Connecticut; but the ratio does not hold, beyond the statement that the greater the per cent of uranium oxide, the greater will be the per cent of nitrogen.

Because of the constancy of the ratio in the Norwegian varieties of uraninite, Dr. H. P. Cady suggested that there might be some relation between the origin of the nitrogen and the other elements present.

The periodic table was examined and it was observed that there was a possibility for a relationship between potassium and nitrogen, potassium undoubtedly being one of the radioactive elements.

Strong², on examining some old samples of potassium collected by Rowland, using the photographic method, found them to be radioactive; yet, potassium sulfite manufactured recently was not nearly so active. Using this same method, Levin and Ruler³ found that all the samples of potassium salts examined were active. Hoffman₄ made use of an exceedingly refined electrical method and found that the

². Amer. Chem. Jour. 42, 147 (1909)

³. Physik. Zeit. 10, 576 (1910)

⁴. Physik. Zeit. 24, 475 (1923)

activity of potassium salts is proportional to the potassium content. Harkins and Guy⁵ have lately come to the same conclusion.

So far none of the alkali metals have been found to emit α -particles. It may be that they are too slow for detection. At any rate, R. J. Strutt⁶ found that several beryls had a helium content far greater than that expected from the content of radium or thorium compounds. So it seems quite possible that the alkali earths may emit alpha particles which have not yet been detected.

Evidence for a possible relationship between potassium and nitrogen: There is a difference of twelve in their atomic numbers, which might indicate six alpha ray changes between the two, and a difference of approximately twenty-five in their atomic weights, while six alpha ray changes would call for a difference of only twenty-four in the atomic weights. The question which then came up was: might not this discrepancy in the atomic weights indicate the existence of an isotope of nitrogen which would have the atomic weight fifteen and be a decomposition product of potassium? It might be

⁵/ Proc. Nat. Acad. Sciences 11, 628 (1925).

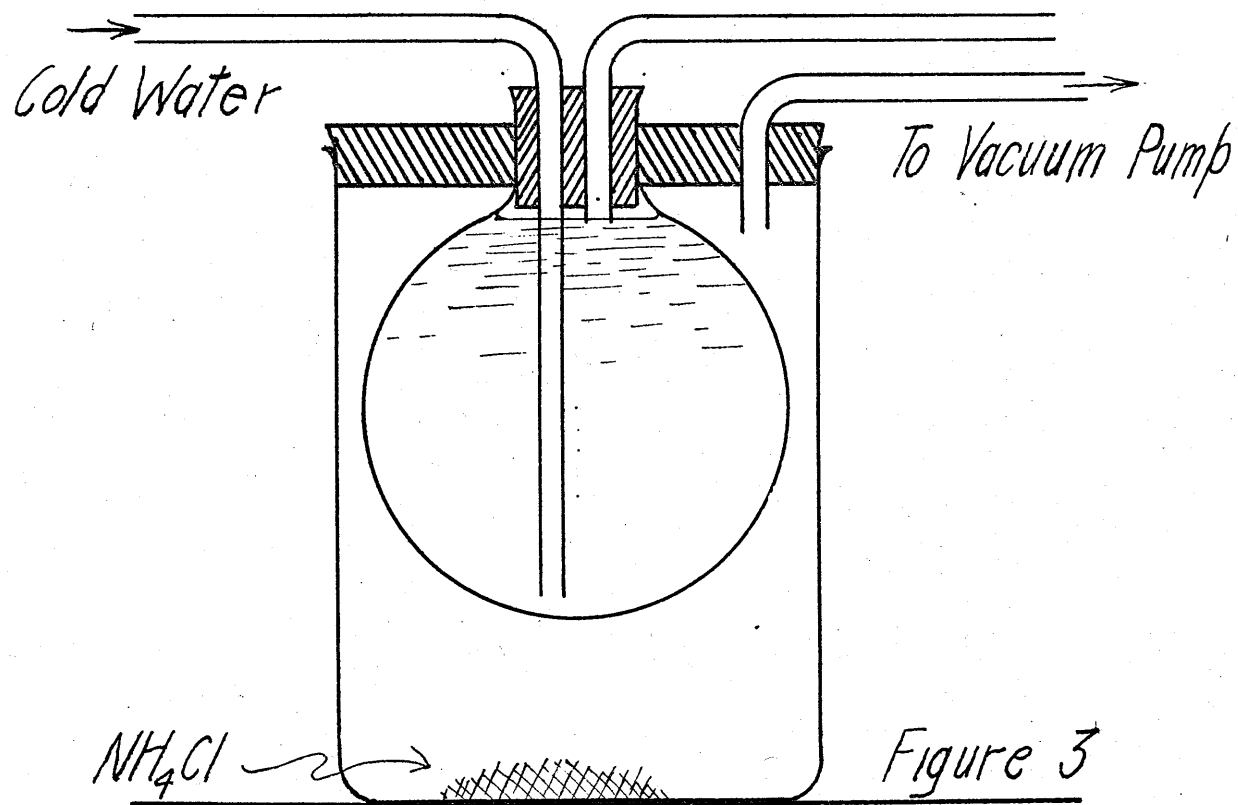
⁶. Proc. Roy. Soc. A, 80, 587 (1908).

argued that it is just as likely that nitrogen is a decomposition product of an isotope of potassium of atomic weight thirty-eight. The objection to this is that, so far, all indications of positive ray work show that the isotopes of potassium are above forty. Then there seems to be the possibility for the existence of isotopic nitrogen which is a decomposition product of potassium, six alpha ray changes having occurred between the two.

The search for nitrogen of a possible radioactive origin was then begun, and atomic weight determinations made.

Because of the availability of a sample of natural ammonium alum, an atomic weight determination was made on the nitrogen of that ammonia. Then samples of various nitrogen containing ores were obtained and the nitrogen extracted.

There is a difference of opinion as to how the nitrogen is contained in these ores. Some believe that it is contained in the mineral in a state of loose combination; yet simply heating it dry or with a non-oxidizing acid will serve to expel it, so it seems most likely that it is occluded in the ores in a free state.



Experimental

The sample of crude ammonium alum (Tschermitzite from Wyoming) was pulverized, placed in a liter distilling flask, and sodium hydroxide solution added through a dropping funnel. This was heated and the ammonia easily liberated. The ammonia was distilled off through a Pyrex glass condenser into a porcelain vessel containing redistilled c.p. hydrochloric acid. After an excess of ammonia had been passed into the acid solution, it was carefully evaporated down and then dried at a low temperature, preferably at about eighty degrees centigrade. It was necessary to make this drying slowly and carefully at a low temperature, otherwise sublimation, before complete drying, would take place, in which case decomposition would occur and the ammonia being more volatile would pass off, leaving an excess of hydrochloric acid which would invalidate completely the atomic weight determinations.

After the sample had been dried, the ammonium chloride was sublimed twice in a vacuum; see drawing. Chlorine determinations were then made, precipitating the chlorine as silver chloride. Gooch crucibles were used. All weights were corrected to weights in vacuo, and the atomic weights of the nitrogen calculated from the data.

using this method,

$$\frac{X_1 + 39.489}{A} = \frac{143.337}{B}$$

where

X_1 = atomic weight of nitrogen.

A = corrected weight of sample of ammonium chloride used.

B = corrected weight of silver chloride obtained.

A second sample of ammonium chloride was prepared from ordinary c.p. ammonium sulfate, in the same way, and used as a control, determinations being run in parallel with those of the "alum" ammonium chloride. In this way any constant errors were taken care of and possible errors which could have been removed only by a much more elaborate process of purification and analysis.

Results of determinations by the above method:

Atomic weight of nitrogen in Ordinary	Atomic weight of nitrogen in Alum
NH ₄ Cl	NH ₄ Cl
14.031 ⁺	14.012
14.032 ⁺	14.021
14.016	14.023
14.030	14.024
Average 14.027	Average 14.020

This gives a variation of .05%, well within the limits of experimental error. This disposes, then, of the possibility of an isotope of nitrogen being present in

*Sublimed once - all other samples sublimed twice.

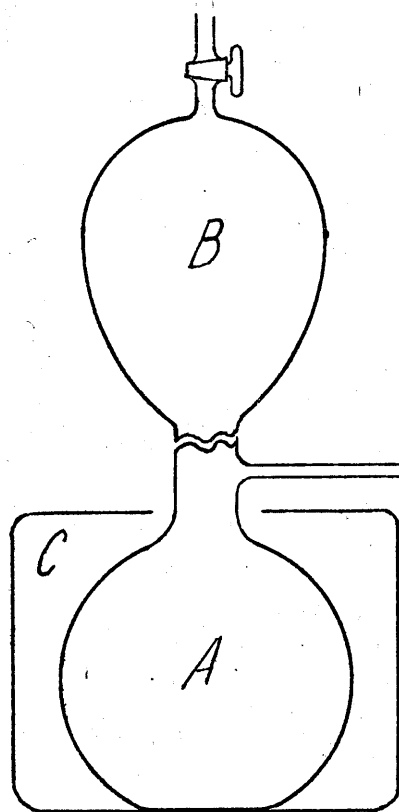
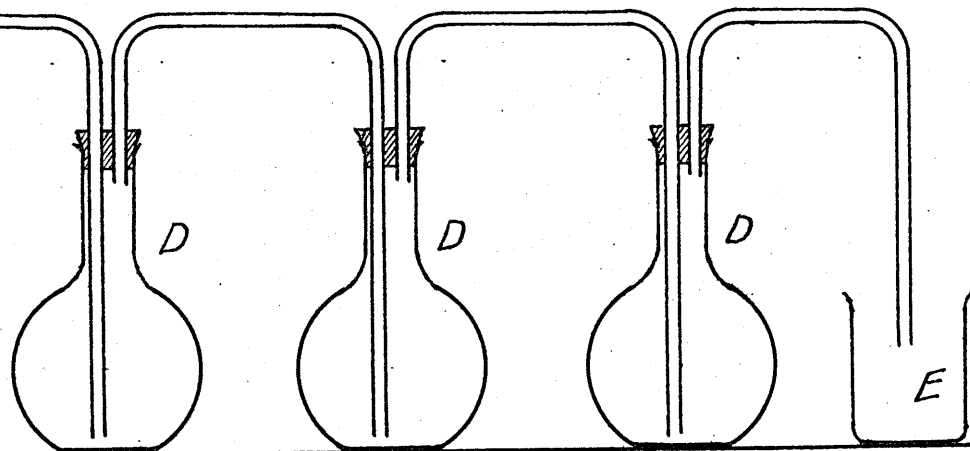


Figure 1



this ammonia alum.

The next step was the estimation of the quantity of occluded gas in several ores, in order to find which would be the most profitable to buy.

The apparatus used was essentially like that employed by Hillebrand,⁷ and almost identical with the large apparatus shown in the accompanying diagram, except that it was built on a much smaller scale, so small that three sets of apparatus could be included in one water-bath. A constant leveling device was used on the bath, the bath heated by an electric hot plate, and the whole placed on an asbestos covered, raised platform in order to minimize the danger of fire, and the determination allowed to run for as many days as was necessary to remove the most of the gas. Although the apparatus was allowed to run continuously for as long as twenty-two days, the evolution of gas never entirely ceased.

For brevity, only the large gas extraction apparatus will be described and the method of operating it, since it and its operation is identical to that of the smaller ones. The large apparatus is the one used to obtain a quantity of the gas on which the atomic weight determination of the nitrogen was made.

⁷. U. S. Geo. Sur. Bull. 78, 1891

A stop cock was sealed into the bottom of a Kjeldahl flask (800 c.c.) and the mouth of the Kjeldahl flask was sealed to that of a liter flask. A vent tube was sealed into the neck of the liter flask. The ore to be decomposed was added through this small tube. The decomposing solution was a one to six solution of sulfuric acid in freshly boiled distilled water.

The ore was crushed as finely as possible on a steel mill and finished with an agate mortar and pestle. After this ore had been pulverized and placed in the apparatus, a little distilled water was added and this was boiled for a few moments in order to remove any air which was adsorbed on the particles of ore. Then the stop cock on the Kjeldahl flask was connected to a suction pump and the acid solution drawn through the three traps shown in the diagram up into the Kjeldahl flask, filling it.

The results obtained from various sources are as follows: (At standard conditions, CO₂ removed).

<u>Mineral</u>	<u>Where from</u>	<u>Cubic cm. of gas per gm. of ore.</u>
Uraninite	Pribram, Bohemia	1.30
Fergusonite	Arendal, Norway	3.00
Samarskite	Mitchell Co. N. Carolina	3.68
Uraninite	Crabtree Creek, Yancy Co. N. Carolina	2.26

Fergusonite	Near Bluffton, Texas	3.44
Fergusonite	Madagascar	1.33
Uraninite	Saxony	1.38
Uraninite	Kristianiaford, Norway	3.32

It was decided to use the gas in the Fergusonite from Arendal, Norway. A helium determination was made on this. It was found to contain 12.67% of helium. 1800 c.c. of the gas were obtained.

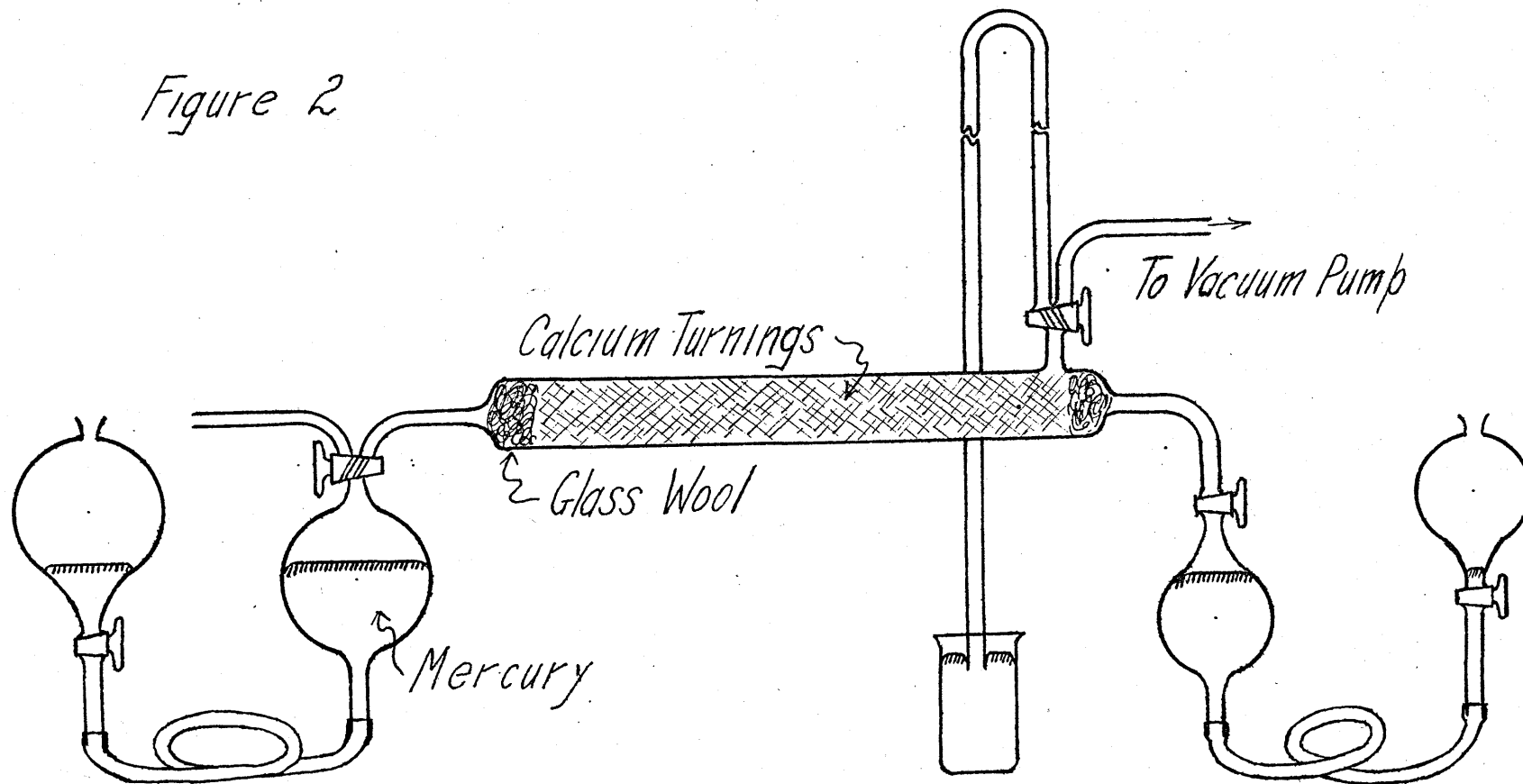
The method of fixing the nitrogen in the gas was essentially like that described by Maquenne⁸, in that hot metallic calcium was used to absorb the nitrogen, forming calcium nitride, Ca_3N_2 .

A thirty centimeter Pyrex tube, the combustion chamber, had a mercury gas pump sealed to each end. At one end was placed a three way stop cock, sealed into the chamber, one tube of which led to a vacuum pump, the other to a mercury manometer.

Maquenne suggests that pure calcium oxide with three-fifths its weight of metallic magnesium be placed in the combustion chamber, the tube being heated with a wide burner. As soon as the hot calcium is liberated, it will

⁸. Comptes Rendus 121, 1147 (1895).

Figure 2



combine with any nitrogen to form calcium nitride.

Pure calcium oxide was obtained, and as an additional precaution was heated for nine hours at almost a white hot temperature in a muffle furnace, in order to free it from any traces of water or carbonate. The magnesium was washed with ether in order to free it from grease with which it was found to be contaminated. In spite of all these precautions, however, rather great pressures were, for some unknown reason, generated, and this method was found to be unsuitable.

Metallic calcium was sealed directly in the combustion tube with excellent results; the nitrogen was absorbed quietly, the absorption being easily followed by the rise of mercury in the manometer.

The apparatus was operated in this way: The system was almost completely evacuated with a pump and then "washed" with some of the gas to be fixed, in order to remove any traces of atmospheric nitrogen. The dried gas to be fixed was allowed to enter the left mercury pump. The stop cock between it and the combustion chamber was opened very slightly and the chamber allowed to fill about half full of gas (from observation of manometer). This was heated, and expansion of the gas took place until the calcium reached a sufficiently high temperature for the reaction between it and the nitrogen to take place. In order to prevent the deforming of the hot combustion chamber, the

pressure was kept about the same inside as out by admitting more gas as absorption took place. This was done by raising the level of the mercury in the left pump.

Practically all of the nitrogen is taken out by one passage over the hot calcium; but by using both pumps, circulation and consequently complete removal can be obtained, and the residual inert gases caught in the right pump.

After the early explosive experiences it seemed wiser to wear goggles throughout the process of fixation; although there was no apparent necessity for doing so after metallic calcium had been substituted for the mixture of calcium and magnesium in the combustion chamber.

At the completion of the reaction, the tube containing the calcium nitride was cut open and the nitride placed in a dry distilling flask which was sealed to a Pyrex condenser leading into a porcelain vessel which contained c.p. hydrochloric acid. Through a dropping funnel water was added, a few drops at a time, and in a short time all of the nitrogen had been hydrolyzed off, and, passing into the hydrochloric acid, formed ammonium chloride.

The ammonia was redistilled into a little less than the calculated amount of hydrochloric acid, in order to insure that there be no excess of hydrochloric acid present. Because of the losses attendant on sublimation, it was decided to let these two distillations serve in purification.

The chloride was slowly dried in an oven at 80°C. The reason for this slow, careful drying has already been pointed out.

One and one-half grams of the pure ammonium chloride were obtained.

Nitrogen for a control sample was prepared by passing vapors from liquid ammonia mixed with air over a mixture of hot copper oxide and metallic copper. This nitrogen was fixed and purified as described above.

Because of the smallness of the sample of "Norwegian" ammonium chloride, it was necessary to recover the ammonia from the filtrates off of the silver chloride, repurify, and reanalyze it.

The analysis of the ammonium chloride was carried out as described for the "alum" ammonium chloride.

The following results were obtained:

Atomic Weight of Nitrogen
from Control NH_4Cl

1. 13.983
2. 13.994
3. 13.981
4. 13.974

Average 13.984

Atomic Weight of Nitrogen
from "Norwegian" NH_4Cl

5. 13.987
6. 13.983
7. 13.991
8. 13.953⁺

Average 13.987

The "Norwegian" ammonium chloride gave an atomic weight of the nitrogen only .02% greater than that of the Control. Since this is well within the limits of experimental error, the possibility of the existence of an isotope of nitrogen here is disposed of.

CONCLUSION.

Although no indication of an isotope was found in the samples of nitrogen examined, it is not granted that the possibility for the existence of an isotope of nitrogen is completely disposed of, and it is hoped that determinations of atomic weight of nitrogen from other sources can soon be made.

- +. Analysis number 8 was not included in the average because it was run a day later than the others, the last of the sample in the weighing bottle, and had come into contact with some very damp air. It was feared that it had taken up moisture, which the result would indicate.