Rare Gases of the Atmosphere —A Classic of Science

Chemistry

THE RECENTLY DISCOVERED GASES AND THEIR RELATION TO THE PERIODIC LAW. By William Ramsay. An address delivered before the Deutschen chemischen Gesellschaft, December 19, 1898. Translated by "J. L. H." Printed in Science, February 24, 1899.

The end of the Nineteenth Century brought many surprises in the field of physics and chemistry. Several old theories went by the board, and the discovery of a set of new elements with absolutely no chemical properties threatened for a moment to jeopardize Mendeleeff's periodic law. Ramsay therefore watched with some anxiety the determination of atomic weight of his new gases, and was gratified to find them falling regularly into place among the older elements, bringing new harmony into the periodic table.

GENTLEMEN: It is well known to you all how the remarkable observation of Lord Rayleigh that nitrogen from the atmosphere possesses a greater density than that prepared from ammonia or nitrates led to the discovery of argon, a new constituent of the air. I need not say that had it not been for this observation the investigations of which I shall speak this evening would never have been carried out, at least not by me. You also, doubtless, will remember that the search for some compound of argon was rewarded, not by the attainment of the quest, but by the discovery, in cleveite and other rare uranium minerals, of helium, an element whose existence in the chromosphere of the sun had already been suspected. And, further, I hardly need to recall to your minds that the density of helium is in round numbers 2, and that of argon 20, and that the ratio of specific heats of both these gases, unlike that of most others, is 1.66.

From these figures it follows that the atomic weight of helium is 4 and that of argon 40. It is true that in many quarters this conclusion is not admitted, but I have always thought it better to recognize the validity of the theory of gases and accept the logical deduction than to deny the truth of the present theories. The only reason for not admitting the correctness of these atomic weights is that that of argon is greater than that of potassium, but this is no severer attack upon the validity of the periodic law than the accepted position of iodin after, instead of before. tellurium. As a matter of fact, all the more recent determinations of the atomic weight of tellurium give the figure 127.6, while that of iodin remains unchanged at 127.

Since these new elements form no compounds, it is not possible to decide the question by purely chemical methods. Were it only possible for us to prepare a single volatile compound of helium or of argon our problem would be solved. In spite of many attempts, I have not been able to confirm Berthelot's results with benzine or carbon bisulfid. I have, however, offered to place a liter of argon at the disposal of my distinguished colleague, that he may repeat his experiments on a larger scale. No one can doubt that it is exceedingly desirable that the question of these atomic weights should be finally decided, and that by chemical methods.

In order that the subject may not depend wholly on physical theories, I have considered it from another standpoint. If we assume, as from countless chemical facts we are fully justified in doing, that the periodic law is true, then, giving helium the atomic weight 2 and argon 20, there is no possible place for an element of their mean atomic weight; for, unless we absolutely overturn the accepted views, there is no vacancy in the table for such an element. This appears from the following portion of the tables:

H = 1 He = 2(?) Li = 7 Gl = 9.2 B = 11 C = 12 N = 14 O = 16 F = 19 A = 20(?)

It is true there is space enough between He = 2 and Li = 7, but it is highly improbable that an element belonging to the argon series could have so low an atomic weight. The difference between adjacent members of the same group of elements is generally from 16 to 18 units, but here such a difference is wholly excluded. If, on the other hand, we assume He = 4 and A = 40, it would be, in my opinion, by no means improbable that such an element could exist whose atomic weight would be somewhere about 16 units greater than that of helium, and consequently 20 units less than that of argon. The discovery of such an element would be, therefore, not only a proof of the correctness of 40 as the atomic weight of argon, but also a confirmation of the present views regarding the significance of the specific heats of gases for their molecular weight.

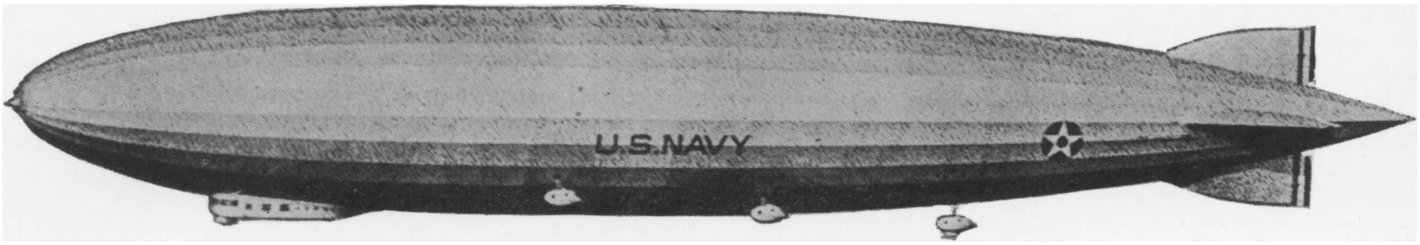
A glance at the periodic table will make these considerations clear, for in the latter case we have the following series:

He = 4, Li = 7, Gl = 9.2, B = 11, C = 12, N = 14, O = 16, F = 19, (?) = 20, Na = 23, Mg = 24.3, Al = 27, Si = 28, P = 31, S = 32, Cl = 35.5, A = 40.

Shortly after the discovery of helium I began the search for this suspected element at atomic weight of about 20, at first in connection with Doctor Collie, my former assistant, and later with my present assistant Doctor Travers. . . .

[*A large number of experiments were performed trying to extract gases from minerals with no result.—Ed.*]

OUR patience was now well-nigh exhausted. There seemed, however, to be a single ray of hope left, in an observation which had been made by Dr. Collie and myself. You will recall that the atomic weight of argon was apparently too high; at all events it would be more in harmony with the periodic law if the density of argon were 19 instead of 20, and hence its atomic weight 38 instead of 40. Hence, after some fruitless attempts to separate argon into more than one constituent by means of solution in water, we undertook a systematic diffusion of argon. We did not, however, carry this procedure very far, for, at that time, we believed that helium was a more probable source of the desired gas; nevertheless, we found a slight difference in density between the gas which diffused first and that which remained undiffused. We, therefore, decided to prepare a large quantity of argon,



The airship "Los Angeles" is inflated with Helium, one of the rare gases, discovered by Lockyer in the sun and by Ramsay on earth. Of the other rare gases, argon fills electric light bulbs, neon glows rosily in electric bulbs for televison apparatus, and all the gases contribute the colors of their spectra to the brilliant new advertising signs which decorate our streets.

and, after liquefying it, to investigate carefully the different fractions on distillation.

Such an operation demands much time. In the first place, the necessary apparatus is not to be found in any ordinary chemical laboratory; the preparation can not be carried out in glass tubes in an ordinary furnace, but requires iron tubes of large size and an especial furnace; in the second place, the operation must be repeated several times, for it is not convenient to work with an excessively large quantity of magnesium. As before, we removed the oxygen from the air by means of copper at a red heat; the atmospheric nitrogen remaining was collected in a large gasometer holding about 200 liters; after drying over concentrated sulphuric acid and phosphorous pentoxid, the gas was passed through an iron tube of 5 centimeters diameter filled with magnesium filings; the gas was then passed through a second copper oxid tube to remove the hydrogen; it then entered a galvanized iron gasometer, which was constructed like an ordinary illuminating gas gasometer, in order that the argon should come in contact with as little water as possible, since argon is quite appreciably soluble in water, and, had the ordinary form of gasometer been used, much would have been lost in this way. Again, the gas had to be led over hot magnesium to reduce still further the quantity of nitrogen; and, at last, it was circulated between the gasometers, passing on its way through a mixture of thoroughly heated lime and magnesia at a red heat. This is a means of absorption, recommended by Maquenne, to remove the last of nitrogen. Since, however, it is not possible to dry the lime absolutely. hydrogen is taken up by the gas, and this must again be removed by copper oxid, in order that all the hydrogen may be burned, after which the water must again be removed by drying tubes.

These operations required several months and were chiefly directed by Dr. Travers. . . .

[*After proving that the gases under investigation formed no compounds with any of the chemicals used in this purification process, the most hopeful line of investigation seemed to be refrigeration of the argon residue with liquid air.—Ed.*]

DR. HAMPSON, the inventor of a very simple and practical machine for the preparation of liquid air, which is based upon the same principle as that of Herr Linde, was so kind as to place large quantities of liquid air at my disposal. In order to become acquainted with the art of working with so unusual a material, I asked Dr. Hampson for a liter; with this Dr. Travers and I practiced and made different little experiments to prepare ourselves for the great experiment of liquefying argon.

It seemed to me a pity to boil away all the air without collecting the last residue; for, though it seemed improbable that the looked-for element could be here, yet it was, indeed, possible that a heavier gas might accompany the argon. This suspicion was confirmed. The residue from the liquid air consisted chiefly of oxygen and argon, and, after removing the oxygen and nitrogen, beside the spectrum of argon were two brilliant lines, one in the yellow, which was not identical with D_3 of helium, and one in the green. This gas was decidedly heavier than argon; its density was 22.5 instead of the 20 of argon. We had, therefore, discovered a new body, which was an element, for the ratio between the specific heats was 1.66. To this element we gave the name "krypton." Up to this time we have not followed further the study of this element; we have, however, collected and preserved many residues which are rich in krypton. It was, however, our first intention to examine the lightest part of the argon. In many, however, we remarked, in passing, that the wave-length of the green line of krypton is exceedingly close to that of the northern lights, being 5,570, while the latter is 5,571.

Our whole supply of argon was now liquefied in the following manner: The gasometer containing the argon was connected with a series of tubes in which the gas passed over respectively hot copper oxid, concentrated sulphuric acid, and phosphorous pentoxid; it then passed by a two-way cock into a small flask, holding about 30 cubic centimeters, which was enclosed in a Dewar tube. By means of the other opening of the cock, the flask was connected with a mercury gasometer. By means of a U-shaped capillary and mercury trough, it was also possible, through a three-way cock, to collect the gas at will in glass tubes. About 50 cubic centimeters of liquid air were poured into the double walled tube, and, by means of a Fleuss air pump kept constantly in action, the liquid air boiled at 10 to 15 millimeters pressure. The argon liquefied rapidly as soon as subjected to this low temperature, and in the course of half an hour it was completely condensed. Altogether there were about 25 cubic centimeters of a clear, limpid, colorless liquid, in which floated white flakes of a solid substance. By stopping the pump the pressure over the liquid air was now increased, and the argon boiled quietly. the first portions of the gas being collected in the mercury gasometer. Changing now the three-way cock, the largest portion of the argon passed back into the iron gasometer; after nearly all the liquid had boiled away and only the solid substance was left in the flask, the last portions of the gas were collected separately. The solid substance remained persistently in the flask; it was slowly volatilized by means of a Töpler pump, which stood in connection with the apparatus.

WE first directed our attention to the lighter fractions, for these had for us the greatest interest. The density of this gas was found to be 14.67; the ratio between the specific heats was as usual 1.66, and the spectrum showed, beside the well-known groupings of argon, a large number of red, orange, and yellow lines of varying intensity. Evidently we had before us a new element, which was contaminated with argon.

This gas was then liquefied in a similar apparatus to that first used, but constructed on a smaller scale; a portion, however, remained uncondensed. Even by raising the reservoir of the mercury gasometer until an overpressure of an atmosphere was reached, it was impossible to convert all the gas into a liquid, although the temperature of the boiling air was reduced as low as possible by rapid pumping. By repeated raising and lowering of the reservoir we finally passed all the gas through the cooled space, in order to free it, as far as possible, from argon. The uncondensible gas was collected by itself, and the remainder was evaporated into another gasometer.

You can well imagine how eager we were to know what the density of this purified gas would prove to be. It was immediately weighed. Our satisfaction can well be realized when we found that its density was 9.76. Since, however, its spectrum at low pressure still showed argon lines, though weak, we were compelled to admit that this number was certainly too high. It was impossible that this gas should not contain argon, since at the temperature used argon possessed a measurable vapor pressure.

We have, therefore, estimated that the density of the pure gas is 9.65. Here our work for the time was ended by the beginning of the summer holidays.

Neon, the New Gas

On our return we resumed the study of this gas, which we will hereafter designate by its name of "neon." Its spectrum was photographed by Mr. Baly, one of my assistants, by means of a spectrometer which we had constructed during the vacation. To our astonishment, the lines of helium were easily recognized. A comparison photograph showed this beyond all question. Hence the density of the gas was in all probability too low, owing to the presence of the helium. Since now the temperature used was insufficient to liquify the neon, and since the argon had been removed as far as possible, we had to face the problem of how one could free neon from its accompanying impurities. A means was found in its solubility. It is well-known that the solubility of those gases which do not react chemically with the solvent follows in general the same order as their condensibility. According to this helium should have a lesser solubility than neon, and neon than argon. The solubility of these gases in water is, however, too slight to be available for their separation. We have, therefore, used liquid oxygen as a solvent. This mixes with all three gases and boils at a temperature not far from the boiling point of argon. We therefore mixed the gas with sufficient oxygen to be almost wholly condensed at the temperature attained by boiling air at the lowest pressure. The uncondensed portion, about one-fifth of the whole, was separated and collected as that richest in helium; the middle portion we considered as purified neon, while the remainder consisted of a mixture of argon and neon; naturally, all these portions contained oxygen in larger or smaller quantities.

After the removal of the oxygen, which was accomplished by passage over hot copper filings, we determined the density and refractivity of the middle portion. The density in two determinations was 10.04 and 10.19; the second figure was obtained after passing the electric spark through the gas mixed with oxygen in the presence of caustic potash and subsequent removal of the oxygen by phosphorus. The entire quantity weighed was only 30 cubic centimeters at a pressure of 250 millimeters. The weight was 0.0095 gram. I mention these figures in order to show with what an exceedingly small quantity of gas it is possible to carry out a very satisfactory density determination.

The refractivity of this portion with reference to the air as unity was 0.338. This portion still showed the spectra of argon and helium, and was, therefore, submitted to a second purification, in which the heavier part was more completely removed than the lighter. Even this purification, however, did not remove all the argon, but its quantity was decidedly diminished. The density was somewhat diminished, and helium was stronger in the spectrum. The entire amount of neon had become, by these operations, so divided up that it was not possible to carry out a further purification without preparing a greater quantity of crude neon. On this Dr. Travers and I are at present engaged.

In the meantime Mr. Baly has made exact measurements of the lines of the neon spectrum, at the same time eliminating all the lines which belong to argon and to helium by superposed plates. The values were compared with iron lines photographed upon the same plate, and the measurements were carried out by means of different pairs of these known lines. . . .

Up to the present we have had little time to study thoroughly the other companion of argon in the atmosphere. Dr. Travers and I have, however, worked upon it. . . .

Krypton, the Hidden Gas

As regards krypton, which is distinguished by three brilliant lines, one in red, one in yellow and one in green, we are in much the same position. We have collected a considerable quantity of the impure gas, which shows the spectrum finely, although that of argon is also present. We hope that we shall soon be able to pursue this portion of our work further. We can merely note here that the specific gravity of the gas which shows this spectrum in such a marked way is not far different from that of argon.

The heaviest of these gases we have weighed, although in impure condition. Its density is 32.5. I need not call your attention to the fact that there is space for an element of the helium group between bromin and rubidium. Such an element should have an atomic weight of 81 to 83, which corresponds to a density of 40.5 to 41.5, under the very probable supposition that, like the other gases of this group, it is monatomic. The spectrum of this gas, which we have named "xenon"—the stranger—has many lines; none of these are of marked intensity, and in this respect the spectrum resembles somewhat that of argon. It is also analogous to argon in another particular, that the spectrum undergoes a remarkable change when a Leyden jar is put into the circuit. As with argon, many new blue and green lines appear, while other lines, mostly in the red, either disappear or lose much of their intensity.

Science News-Letter, August 2, 1930