

planet's centre was $24''\cdot 4$. Prof. Schaeberle now somewhat reluctantly publishes these facts in connection with his measures of the known satellite, as he has not on any subsequent occasion been able to detect any object in the neighbourhood of Neptune in apparent orbital motion about the planet. The unusual clearness and steadiness of the night of September 24, 1892, however, is not considered to have been equalled in the later observations.

PROFESSOR MENDELÉEFF ON ARGON.

AT the meeting of the Russian Chemical Society, on March 14, Prof. Mendeléeff made some interesting remarks on the relations of argon to the periodic system. His views are summed up as follows in a proof-issue of the *Proceedings* of the Society :—

" As regards argon we must consider, first, whether it is a chemical individual, or a mixture, and then, whether it is a simple or a compound body. The supposition that it be a mixture, lies beyond all probabilities ; it is contradicted by the researches of Olszewski into the liquefaction and solidification of argon. The supposition that it may be a compound has also little in its favour. The remarkable inactivity of argon testifies in favour of its being a simple body, although there are, of course, some compounds, also endowed with the same property to some extent. The spectrum of argon, too, is characteristic of a simple body.

" Taking it as a simple body, we must then consider its possible atomic weight, the weight of its molecule being near to 40 (although, probably, a little over 40, because of a slight mixture of nitrogen with the argon). The atomic weight of argon evidently depends upon the number of atoms which its molecule contains. We must, therefore, consider the series of possible molecular formulae : A , A_2 , A_3 , . . . A_n .

" Upon the first supposition, A , the atomic weight of argon would be about 40, and, like cadmium and mercury, it would be a monatomic gas.

" In favour of this supposition we have the specific heat ratio at constant volumes and pressures, K , found by Rayleigh and Ramsay to be near to 1.65, i.e. to the value which is considered as characteristic for monovalent gases. It must, however, be borne in mind that K varies for compound molecules, even when these last contain the same numbers of atoms ; thus, for most bivalent gases (nitrogen, oxygen, &c.) K is near to 1.4, while for chlorine it is 1.3. This last figure makes one think that K depends not only upon the number of atoms in the molecule, but also upon chemical energy, that is, upon the stock of internal motion which determines the chemical activity of a body, and the quantity of which must be relatively great with chlorine. If, with the chemically-active chlorine, K is notably less than 1.4, we may admit that for the inactive argon it is much more than 1.4, even though the molecule of argon may contain two or more atoms.

" If we admit that the molecule of argon contains but one atom, there is no room for it in the periodic system ; because, even if we suppose that its density is much below 20 (although this is very unlikely to be the case, and the contrary could rather be surmised), and that the atomic weight of argon should fall between the atomic weights of chlorine and potassium, the new body ought to be placed in the eighth group of the third series ; but the existence of an eighth group in this series could hardly be admitted. In fact, an eighth group is characteristic of the large periods ; and it establishes a link between the metallic elements of the seventh groups of the even series, with the metallic elements akin to them, of the first groups of the uneven series. It appears, therefore, very unlikely that the atomic weight of argon might be about 40.

" Upon the second supposition (A_2), its atomic weight would be about 20, and in such a case argon would find its place in the eighth group of the second series, i.e. after fluorine. But the same objections as above could then be raised. Fluorine and sodium are, moreover, strikingly unlike to each other. However, it must be said in favour of this hypothesis that it would have the advantages of analogy, by giving a new eighth group to an even series. If we take also into consideration that the typical series are possessed of several peculiarities, we may be justified, to some extent, in supposing that the atomic weight of argon is 20, this hypothesis being already much more probable than the former ($A = 40$).

" If we suppose, further, that the molecule of argon contains three atoms, its atomic weight would be about 14, and in such case we might consider argon as condensed nitrogen, N_3 . There is much to be said in favour of this last hypothesis. First of all, the concurrent existence of nitrogen and argon in nature ; then, the fact that many of the bright lines of the two spectra are very near to each other. Then, again, the inactivity of argon would be easily explained, if it originates from nitrogen, N_2 , with giving up heat. And finally, the fact of its having been obtained, though in a relatively small quantity, from artificially obtained nitrogen. The supposition of Rayleigh and Ramsay, according to which argon has been disengaged in this last case from water, is very probable, but at any rate it is not yet proved. The hypothesis of argon being condensed nitrogen might be tested by means of introducing boron, or titanium, into an atmosphere of argon, strongly heated, and through which electric sparks would be passed.

" If we suppose, next, that the molecule of argon contains four or five atoms, its atomic weight will be 10, or 8, and in such case there is no room for argon in the periodic system.

" And finally, if we admit that its molecule contains six atoms, and that its atomic weight is 6.5, we must place it in the first series. In such case, it would probably take its place in the fifth group. Accordingly, the suppositions that argon is condensed nitrogen, N_3 , or that, containing six atoms in the molecule, its place is in the first series of the system, appear to be the more probable ones, if it is a pure simple chemical body.

" From a letter received by D. I. Mendeléeff from Prof. Ramsay, it appears that the investigation of argon is being continued, and that the body finds its place in the periodic system ; but the ultimate results of the researches of the two authors, who have brought before chemistry such an important new problem, and given it such an exemplary investigation, are not yet known."

TERRESTRIAL HELIUM (?).

WE referred last week to Prof. Ramsay's discovery of another new gas obtained from cleveite. The following papers, by Prof. Ramsay and Mr. Crookes, on this subject were communicated to the Chemical Society at its anniversary meeting.

Prof. Ramsay's paper was as follows :—

In seeking a clue to compounds of argon, I was led to repeat experiments of Hillebrand on cleveite, which, as is known, when boiled with weak sulphuric acid, gives off a gas hitherto supposed to be nitrogen. This gas proved to be almost free from nitrogen ; its spectrum in a Pfücker's tube showed all the prominent argon lines, and, in addition, a brilliant line close to, but not coinciding with, the D lines of sodium. There are, moreover, a number of other lines, of which one in the green-blue is especially prominent. Atmospheric argon shows, besides, three lines in the violet which are not to be seen, or, if present, are excessively feeble, in the spectrum of the gas from cleveite. This suggests that atmospheric argon contains, besides argon, some other gas which has as yet not been separated, and which may possibly account for the anomalous position of argon in its numerical relations with other elements.

Not having a spectroscope with which accurate measurements can be made, I sent a tube of the gas to Mr. Crookes, who has identified the yellow line with that of the solar element to which the name " Helium " has been given. He has kindly undertaken to make an exhaustive study of its spectrum.

I have obtained a considerable quantity of this mixture, and hope soon to be able to report concerning its properties. A determination of its density promises to be of great interest.

The spectrum of the gas was next discussed by Mr. Crookes, who said

By the kindness of Prof. Ramsay I have been enabled to examine spectroscopically two Pfücker tubes filled with some of the gas obtained from the rare mineral cleveite.¹ The nitrogen had been removed by "sparking." On looking at the spectrum, by far the most prominent line was seen to be a brilliant yellow one apparently occupying the position of the sodium lines.

¹ Cleveite is a variety of uraninite, chiefly a uranate of uranyl, lead, and the rare earths. It contains about 13 per cent. of the rare earths, and about 2.5 per cent. of a gas said to be nitrogen.

Examination with high powers showed, however, that the line remained rigorously single when the sodium lines would be widely separated. On throwing sodium light into the spectroscope simultaneously with that from the new gas, the spectrum of the latter was seen to consist almost entirely of a bright yellow line, a little to the more refrangible side of the sodium lines, and separated from them by a space a little wider than twice that separating the two sodium components from one another. It appeared as bright and as sharp as D_1 and D_2 . Careful measurements gave its wave-length 587'45; the wave-lengths of the sodium lines being D_1 589'51, and D_2 588'91. The differences are therefore—

	Wave-lengths.	Differences.
D_1	589'51	0'60
D_2	588'91	1'46
New line	587'45	

The spectrum of the gas is, therefore, that of the hypothetical element Helium, or D_3 , the wave-length of which is given by Angström as 587'49, and by Cornu as 587'46.

Besides the Helium line, traces of the more prominent lines of argon were seen.

Comparing the visible spectrum of the new gas with the band and line spectrum of nitrogen, they are almost identical at the red and blue end, but there is a broad space in the green where they differ entirely. The Helium tube shows lines in the following positions:—

	Wave-length.	
(a) D_3 , yellow...	587'45	Very strong. Sharp.
(b) Yellowish green ...	568'05	Faint. Sharp.
(c) Yellowish green ...	566'41	Very faint. Sharp.
(d) Green ...	516'12	Faint. Sharp.
(e) Greenish blue ...	500'81	Faint. Sharp.
(f) Blue ...	480'63	Faint. Sharp.

I have taken photographs of the spectrum given by the Helium tube. At first glance the ultra-violet part of the spectrum looks like the band spectrum of nitrogen, but closer examination shows considerable differences. Some of the lines and bands in the nitrogen spectrum are absent in that from the Helium tube, whilst there are many fine lines in the latter which are absent in nitrogen. Accurate measurements of these lines are being taken.

ISOLATION OF FREE HYDRAZINE, N_2H_4 .

M. LOBRY DE BRUYN contributes a memoir of special interest to the current issue of the *Recueil des Travaux Chimiques des Pays-Bas*. It is not long since the distinguished Amsterdam chemist succeeded in preparing for the first time free anhydrous hydroxylamine, and now he announces that he has likewise been successful in isolating free hydrazine by a similar method. Eight years ago the important discovery of hydrazine was made by Prof. Curtius, and since that time the amount of knowledge which has been accumulated concerning the base and its compounds by Prof. Curtius and his assistants is so large that a separate volume might well be devoted to it. Nevertheless, the free anhydrous base itself has not hitherto been satisfactorily prepared; indeed it would now appear, in the light of M. de Bruyn's remarkable work, that it has not hitherto been in any way isolated. The hydrate of the base has been obtained in the pure state and fully described by Prof. Curtius, but in his later communications he has expressed the view that the free base is so unstable that most probably it is incapable of separate existence. The hydrate only is produced when the salts are decomposed by a caustic alkali, and even digestion in a sealed tube at 170° with anhydrous baryta, has failed to detach the water molecule from its combination with hydrazine. It appeared, however, to M. de Bruyn that the nature of the salts and other compounds of hydrazine rendered it scarcely probable that the base was less stable than hydroxylamine, and he considered it not unreasonable to hope that it might therefore be isolated in an analogous manner to the latter base, namely, by reacting upon the chloride with sodium methylate in methyl alcohol solution. The experiments made in this direction are only preliminary, but their result is so interesting that an account of them is at once published.

The salt employed was the chloride $N_2H_4 \cdot HCl$, prepared as described by Prof. Curtius. Ten grams of this salt in powder were added to 200 c.c. of pure methyl alcohol, and a solution of the calculated quantity of sodium methylate CH_3ONa in methyl alcohol were subsequently added. Common salt was immediately precipitated without any perceptible rise of temperature. The mixture was consequently boiled for half an hour in a flask fitted with an upright condenser. After cooling the sodium chloride was removed by filtration, and the solution submitted to distillation. At first mainly methyl alcohol passed over, but after a time the distillate began to contain augmenting quantities of hydrazine; the pressure was then reduced, and four further quantities separately collected. The temperature of ebullition rose to 55°, although the pressure was materially reduced. The last 20 c.c. contained the greater portion of the base. This last fraction was then again distilled at the ordinary pressure, until a residue was left which contained 73 per cent. of hydrazine. The hydrate of hydrazine only contains 64 per cent. of the base, hence it was evident that some free hydrazine had been obtained, and that hydrazine is a comparatively stable substance boiling at a temperature higher than that of methyl alcohol.

In a second experiment 42 grams of chloride of hydrazine were treated in a similar manner with methyl alcohol and sodium methylate. This larger quantity evinced some rise of temperature after the admixture, and the heat caused by the reaction of the hydrazine chloride, which at first had not all dissolved, was just sufficient to keep the liquid boiling for several minutes, when once it had been brought to the boiling point by extraneous heating. After the conclusion of the reaction the contents were cooled, avoiding the access of moisture and carbon dioxide, the sodium chloride filtered off as before, and distillation proceeded with, at first in an ordinary distillation apparatus and afterwards with the aid of a Le Bel-Henninger apparatus. A residual 40 c.c. was again fractionated under reduced pressure and six portions collected. The sixth fraction contained no less than 82'6 per cent. of N_2H_4 . A smaller quantity passing over after removing the sixth fraction contained over 84 per cent. The fifth and sixth portions solidified when cooled by a freezing mixture of ice and salt. The crystals melted about 4°. Although the crystals when exposed to the air exhaled dense white fumes, owing to the attraction of moisture, a number of them were quickly pressed between cooled blotting paper, weighed, and volumetrically analysed. The analytical numbers corresponded to 92 per cent. of N_2H_4 , a result which, considering the extremely hygroscopic nature of the crystals, would appear to indicate that they consisted of practically pure N_2H_4 . The dried crystals melted at -1° to -2°.

A drop of the liquid obtained by fusion of the crystals did not explode when heated with a naked flame; a yellow flame was produced, however, accompanied by a hissing noise. The liquid base is heavier than water and considerable heat is evolved upon mixing it with a small quantity of the latter liquid. Dry oxygen slowly oxidises it. When paper is moistened with a drop of hydrazine and exposed to the air, it becomes hot spontaneously and fumes strongly. Crystals of sulphur dissolve promptly in the liquid base with considerable rise of temperature and formation of a reddish-brown liquid whose odour reminds one of ammonium sulphide; upon the addition of water to this liquid, sulphur is precipitated. The halogens react very violently with hydrazine, producing their acids, and liberating nitrogen. Iodine disappears instantly, and a quantitative experiment showed that the reaction proceeded in accordance with the equation $N_2H_4 + 2I_2 = N_2 + 4HI$. Potassium permanganate or bichromate act with great violence upon the liquid base, but the reaction is unaccompanied by either incandescence or explosion. The liquid appears to possess the further property of readily dissolving many salts, such as the potassium salts of the halogen acids, and nitre.

It would thus appear that, instead of being a gas, as at first supposed by Prof. Curtius, free hydrazine is at the ordinary temperature a liquid, which, however, solidifies at a temperature in the neighbourhood of that of the freezing-point of water, to colourless crystals. The base is, moreover, endowed with a very much higher degree of stability than was supposed. M. de Bruyn is now engaged in preparing it upon a very much larger scale, in order more completely to study its properties.

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