

## SOME SCIENTIFIC CENTRES.

## III.—THE LABORATORY OF HENRI MOISSAN.

THE isolation of the element fluorine in 1886, the result of a long series of investigations carried out with an enthusiasm and manipulative skill and natural resourcefulness amounting to genius, has ensured Henri Moissan a high place in the history of modern chemistry.

His appointment in 1900 to fill the chair at the Sorbonne, rendered famous by its association with the names of the illustrious Dumas and Sainte-Claire Deville, sets a seal on a career of splendid activity.

Born in Paris in the year 1852, he commenced the systematic study of chemistry in the laboratory of the late M. Paul Dehérain at the Muséum d'Histoire naturelle. His first researches were in the direction of vegetable physiology; and in 1874 he made his *début* in a paper on the respiration of plants.

In the meantime, from 1872 until 1876, he was attending the course of Henri Sainte-Claire Deville. Under the influence of this teacher his interest was aroused in "la chimie minérale," and he carried out several investigations on the nature of the various oxides of iron, amalgams and the salts of chromium.

Obtaining his degree of "Docteur ès Sciences" in 1880, he received an appointment on the staff of the École de Pharmacie as "chef des travaux pratiques de 1<sup>re</sup> année." In spite of the laborious routine duties of his position, he found time to commence the examination of some of the compounds of fluorine "in the uncertain hope of at last being able to isolate the element." The next three years find him engaged on the problem which had baffled investigators from the time of Davy onwards. With patient and indefatigable zeal he continued, bearing up under repeated failure, and accumulating that valuable experience which enabled him to triumph over difficulties, and in 1886 to announce to the world that his efforts had been crowned with success. Fluorine was at length a chemical fact.

Before going on to describe the experiments by which Moissan led up to his final result, it will be interesting to glance at the attempts of previous workers and view them in the light of later discoveries; we shall then be in a better position to appreciate the value and the scope of his research.

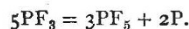
Margaff and Scheele commenced the investigation of hydrofluoric acid in the latter half of the eighteenth century. Davy devoted considerable time to the isolation of the hypothetical element, and suffered a severe illness from breathing the fumes of the acid: he advised chemists to take special precautions against its action on the skin and lungs. Gay Lussac and Thénard fared in the same way. Knox, after repeating the work of Aimé, a French chemist, who attempted to replace fluorine by chlorine in silver fluoride, had to recruit his health in Italy for three years. Louyet, the next worker on the subject, paid the price of his enthusiasm with his life.

Frémy, in 1850, was the first to obtain anhydrous hydrofluoric acid, but the failure of his laborious researches seemed only to discourage further efforts in that direction; and, with the exception of some work by Gore in 1869, nothing more was attempted. Chemists accepted the inevitable, and were content to wait. Moissan, in approaching the subject in 1880, may be supposed to have recognised the dangers as well as the difficulties of his task.

The various experiments which culminated in the isolation of the element fall under four headings.

First of all Moissan made use of the fact that the high temperature of the electric spark is often capable of splitting up binary compounds into their constituent elements. He tried its effect on certain gaseous fluorides. Those of silicon and carbon were unaffected by it. The trifluoride of phosphorus was decomposed, probably

into phosphorus and fluorine, but the latter element immediately combined with the excess of undecomposed trifluoride, and yielded the pentafluoride; thus



He then tried the pentafluoride, but found it far more stable than the corresponding chloride. It only split up under the influence of a very strong spark. Since the experiment had to be made in a glass vessel over mercury, it resulted only in the formation of the fluorides of mercury and silicon.

The trifluoride of arsenic was equally unsatisfactory. It was vaporised and sparked. There was reason to believe that decomposition occurred, but from the conditions of the experiment it was impossible to isolate the element.

Moissan now adopted a different plan of attack. Frémy had noticed that platinum fluoride, produced accidentally in one of his experiments, splits up under the influence of heat into platinum and fluorine. It was only logical to assume that, if the fluoride could be formed at a dull red heat, a sudden rise in temperature would result in the liberation of the element. The difficulty, however, was to obtain the platinum fluoride. On heating platinum in a current of the trifluoride of phosphorus, combination occurred, but not in the way desired, the chief product being a fluorophosphide of platinum.

Similar experiments with the pentafluoride of phosphorus indicated the hopelessness of expecting the desired result from work carried on at so high a temperature.

Moissan now had recourse to electrolysis. In the first instance he used trifluoride of arsenic contained in a platinum vessel, and found that if the material were quite pure and dry (B.P. 63°) it was decomposed into its elements. The fluorine, however, combined at once with the undecomposed trifluoride to form the penta-compound, while the arsenic sank to the bottom of the vessel, or remained suspended in the form of fine particles in the liquid.

It was found impossible to prepare the pentafluoride of arsenic by any chemical process, so that this substance, which would probably have solved the difficulty, had to be abandoned. The extremely poisonous nature of the arsenic compounds also rendered it desirable, if not indeed necessary, to find some more convenient electrolyte.

Moissan now returned to the early experiments of Davy, and took up the investigation of the effect of the electric current upon hydrofluoric acid. As both products of the electrolysis might be expected to be gaseous, a platinum U-tube had to be employed, so that the gases could be separated at the moment of their liberation. Further, to ensure the complete liquefaction of the acid, which boils at +19°·5 C., the apparatus was immersed in a bath of methyl chloride (B.P. -23° C.).

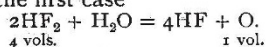
His first experiments confirmed the results which Davy had obtained, and which later on Faraday and Gore had explained, viz. that the anhydrous acid is a non-conductor. Moissan showed, in addition, that if the acid contains a small quantity of water, this latter is decomposed, until only the anhydrous acid remains in the U-tube, when the current ceases to pass. It was necessary, therefore, to add to the acid some substance which would enable it to conduct the electricity; such a substance is the acid potassium fluoride having the formula KF.HF. This can be obtained quite pure, and is very soluble in the anhydrous acid.

By this means it was found possible to decompose the hydrogen fluoride. The fluorine, however, immediately attacked the corks which had been covered with paraffin. Fluorspar stoppers were therefore substituted, and the experiment repeated. Hydrogen was evolved at the negative pole. In the other limb there collected an

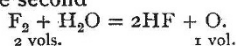
apparently colourless gas with a penetrating disagreeable odour resembling that of hypochlorous acid. It was endowed with exceedingly active chemical properties. Hydrogen combined with it with explosive violence; most of the non-metals burnt in it, while the metals were less vigorously attacked. All organic substances were immediately decomposed.

Three hypotheses suggested themselves as to the nature of the gas. First, that it was a mixture of ozone and hydrofluoric acid. No such mixture, however, was found to exhibit the properties already described. Secondly, that it was a perfluoride of hydrogen; and thirdly, that it was the wished-for fluorine itself. This last point was settled by studying the action of water on the gas.

In the first case



In the second



By measuring the volume of oxygen liberated and titrating the quantity of hydrofluoric acid formed, Moissan was able to decide in favour of the third hypothesis: the gas must be fluorine.

The value of this work was at once recognised. Moissan was rewarded with the chair of "Toxicologie" at the "École de Pharmacie." "J'avais donc," he says, in a letter to the present writer, "très jeune un laboratoire, et un préparateur; quelques élèves vinrent se grouper autour de moi, et toute mon ambition fut satisfaite."

His faculties now had free play; he was able to work on a wider basis, and became one of the most prolific contributors to the *Comptes rendus*.

The isolation of fluorine was naturally followed by a systematic examination of its properties and derivatives. This work is still being carried on; recently, however, M. Moissan collected and published in one volume<sup>1</sup> the results he has obtained. They are all interesting, and some of great theoretical importance.

He found it more convenient and less costly to carry out the electrolysis of the anhydrous acid in a U-tube made of copper immersed in a mixture of acetone and solid carbonic acid, *i.e.*, at a temperature of  $-50^\circ\text{C}$ . The electrodes as before were of platinum isolated from the apparatus by means of stoppers of flourspar. The fluorine thus obtained was purified by passing it through a spiral cooled to  $-50^\circ\text{C}$ ., and then through a horizontal tube containing fragments of sodium fluoride; thus the hydrofluoric acid was removed. Perfectly dry fluorine which has been passed through a spiral immersed in liquid air, to solidify any traces of hydrofluoric acid remaining, has no action on dry glass even at the ordinary temperature.

It possesses a slightly greenish-yellow colour, paler than that of chlorine. It unites with greater or less violence with all the non-metals save oxygen, nitrogen and argon; the compounds being sometimes gaseous, and sometimes solid. The tri-, penta- and oxy-fluorides of phosphorus

<sup>1</sup> "Le Fluor et ses composés." Par Henri Moissan. (G. Steinheil, Paris, 1900.)

have been studied very completely; as also the fluoride of arsenic ( $\text{AsF}_3$ ) and the tetrafluoride of carbon.

In the case of the metals the action is not so energetic the solid fluoride formed on the surface of the metal preventing further combination.

The metals of the alkalis and alkaline earths take fire in the gas; lead combines slowly. Magnesium, aluminium, nickel and silver on slightly heating burn brightly on contact with the gas. Manganese heated in a current of fluorine yields a sesquifluoride,  $\text{Mn}_2\text{F}_6$ ; this on further heating splits up into the difluoride,  $\text{MnF}_2$ , and liberates fluorine. Gold and platinum are unattacked in the cold, but combine at a dull red heat; the platinum fluoride has



FIG. 1.—Prof. Moissan in his private laboratory.

the formula  $\text{PtF}_4$ ; at a higher temperature the gold and platinum compounds are decomposed into fluorine and the respective metal.

Organic compounds rich in hydrogen are violently attacked by fluorine, and totally decomposed into hydrofluoric acid, and fluorides of carbon. Organic acids are attacked more slowly; amines and alkaloids are rapidly burnt up or decomposed into volatile products.

By indirect reactions involving the use of the fluorides of silver and zinc, Moissan and Meslans have been able to prepare and examine the properties of methyl, ethyl and isobutyl fluorides, fluoriform, acetyl fluoride, and a few other derivatives.

The latest determination gives the atomic weight of the element as 19.05.

A general survey of its chemical and physical properties confirms the surmises of Ampère and Davy: fluorine falls naturally into place at the head of the so-called "natural group" chlorine, bromine, and iodine.

In 1896, Moissan and Dewar, working in collaboration, effected the liquefaction of fluorine by passing it through a tube cooled in liquid air which was allowed to boil freely. The B.P. of liquid fluorine is about  $-187^{\circ}$ . The liquid does not solidify even at  $-210^{\circ}$ . Its density is 1.14; it exhibits no absorption spectrum, and is not magnetic. It is soluble in all proportions in liquid air and oxygen. Liquid fluorine has no chemical action on liquid oxygen, solid mercury, or ice; but even at  $-210^{\circ}$  it combines with hydrogen, and decomposes benzene with violence, and production of light and heat. It would be interesting to know the order in which the elements cease to react with fluorine as the temperature falls.

We must also refer to the hexafluoride of sulphur prepared by Moissan and Lebeau in April of 1900. It is obtained by the action of excess of fluorine on sulphur; it is one of the heaviest gases known, having a density of 5.03. Its composition, which is represented by the formula  $SF_6$ , completely establishes the hexatomic nature of the sulphur atom. It is of interest also on account of its inertness; it is unattacked by fused sodium or potassium. Resulting as it does from the union of two such active elements as sulphur and fluorine, which in combining seem thus to saturate one another completely, this compound may be regarded as additional evidence in favour of the theory of valency, though a chemical Ishmael might view it in a different light.

While engaged in studying the compounds of fluorine, Moissan's interest was aroused in the element boron; he obtained the amorphous variety in quantity, and caused it to unite with iodine, sulphur and phosphorus; he examined the action of alkali metals on boric acid, and, as we shall see later, in speaking of the electric furnace, prepared the carbide BC.

In 1891 the coveted honour of a seat in the Académie des Sciences was conferred upon him in recognition of his brilliant work. Cahours had died. To fill his place the names of Moissan, Grimaux, Ditte, Jungfleisch and Le Bel were submitted to the Comité. After a discussion lasting nearly two hours it was decided to nominate Moissan and Grimaux for election. The latter was defeated by eleven votes, and Moissan became the *confrère* of Berthelot, Friedel, Schützenberger and Troost.

The difficulty which was now hampering his work was one of temperature; he required a source of heat greater than that obtainable from the oxyhydrogen flame, and had recourse to the electric arc. In 1892 he devised the electric furnace, by means of which in its more perfect form a temperature of  $3500^{\circ}C.$  could be readily attained. The first result was the production of uranium from its oxide in fair quantities. Metals hitherto considered refractory yielded at once to the intense heat, and the electric furnace became in his hands the source of good specimens of chromium, tungsten, titanium, molybdenum, vanadium, zirconium, &c., all obtained from their oxides by reduction with charcoal.

In the following year, 1893, came the production of artificial diamonds, and Moissan's name became the prey of newspaper men and popular lecturers; chemistry began to appeal to the man in the street.

Moissan now took up the compounds of carbon with the metals, and obtained a whole series, comprising the carbides of sodium, potassium, calcium, strontium, barium, yttrium, lanthanum, thorium, aluminium, titanium, zirconium, chromium, uranium and manganese, and of the metalloids, boron and silicon. Quite recently he has added the carbides of neo- and praseodymium to the list. Proceeding in the same way with silicon and boron, he prepared the silicides of iron, chromium, tungsten, titanium, molybdenum, &c., and the borides of iron, nickel, cobalt, titanium, molybdenum, calcium, strontium and barium.

In 1898 he succeeded in his efforts to make calcium

assume the crystalline form by dissolving it in sodium at a dull red heat, and dissolving away the sodium by absolute alcohol; from this crystalline variety he was able to pass to the hydride, nitride and phosphide of the element. By the electrolysis of fused calcium iodide he was the first to obtain the metal calcium in a state of purity.

When this series of experiments is completed, we shall be in a position to generalise from his results. Not the least interesting feature of the work is the bearing it will have on the Periodic classification; in this connection it should be of supreme importance.

But for the present we must be content with this necessarily brief *résumé* of the scientific work of Henri Moissan. As an experimenter he is unrivalled. "J'avais commencé à manipuler," he says, "de l'âge de 14 à 15 ans; et mes premières leçons de chimie, données par mon père, sont encore gravées dans ma mémoire." He is no theorist in the ordinary sense of the word. His work has been confined to the sphere of the purely practical; and for him a theory exists only that it may be submitted to the test of rigorous experiment, and for the sake of what it leads to. We can conceive of him working out a theory for the origin of diamonds; we find it difficult to conceive of him formulating a theory for the origin of man.

Unlike his distinguished compatriots, M. Berthelot and the late C. Friedel, who worked in both fields, organic and inorganic, Henri Moissan has remained true to the enthusiasm inspired by his first great teacher, Deville. "Je me suis appliqué à cultiver cette chimie minérale que l'on croyait épuisée, et je pense que mes travaux, ainsi que les belles recherches des savants anglais, ont pu démontrer que cette science réserve encore bien des découvertes à ceux qui voudront l'aimer et l'étudier avec tenacité." "To love it and pursue it with zeal" is the secret of Moissan's success, as it was of that of Davy and Faraday and Lavoisier.

In the midst of the gayest capital of Europe, but untouched by all the vicissitudes of its political life, he lives and works. "Ma vie a eu toute la simplicité de ma carrière de professeur, et mon existence s'est partagée, heureuse jusqu'ici, entre mon laboratoire et ma maison."

We can only wish him a continuance of this happiness, and in his new sphere an equal measure of success. The Science Faculty of the University of Paris is to be congratulated on the acquisition of so eloquent and so distinguished a teacher.

#### NOTES.

THE Geological Society of London will this year award its medals and funds as follows:—The Wollaston medal to M. Friedrich Schmidt of St. Petersburg, the Murchison medal to Mr. F. W. Harmer, and the Lyell medals to Mr. R. Lydekker and Prof. Anton Fritsch, of Prague; the Wollaston fund to Mr. L. J. Spencer, the Murchison fund to Mr. T. H. Holland, the Lyell fund to Dr. Wheelton Hind, and the Barlow-Jameson fund to Mr. W. M. Hutchings.

PROF. J. H. MARSHALL, who for three years past has been associated with Mr. Bosanquet in archaeological researches at Athens, has been appointed Director-General of the Archaeological Survey of India, for a period of five years in the first instance.

THE objects found during the recent excavations at Stonehenge will be on view in the library of the Anthropological Institute, Hanover Square, until January 21.

A MEDALLION bust of Sir George Airy is to be placed in the north-east wall of St. Alphage Parish Church, Greenwich, by his daughters. The bust has been copied from the one in the Royal Observatory, Greenwich.