XVI.—*Note on Fluoride of Methyl.*

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IN a paper published in the *Comptes rendus* (1888, **107**, 1155), a new method is described by Moissan and Meslans for the preparation of fluoride of methyl. But as they do not seem to be aware that Dr. Lawson and myself prepared this substance by the action of heat on the fluoride of tetramethylammonium, I now take the opportunity of bringing before this Society the results of some further experiments made with this gas, although they are not yet completed. Determinations have been made of the vapour-pressures of methyl fluoride at various temperatures; the sp. gr. and critical point have also been ascertained; and the combined action of chlorine and sunlight on this gas has been studied.

The method given by Moissan for the production of methyl fluoride, namely, the action of methyl iodide on silver fluoride, is by no means so easily carried out as the one employed by Lawson and myself, for the products of the reaction have to be passed through a lead spiral cooled to -50° , and then over silver fluoride heated to 90° , in order to free the gas from traces of iodine and methyl iodide. By the action of heat on fluoride of tetramethylammonium, a mixture of pure trimethylamine and methyl fluoride is produced, and the former can be completely absorbed by passing the vapour through a U-tube filled with pumice stone moistened with strong sulphuric acid, leaving the methyl fluoride perfectly pure.

A determination of the sp. gr. of the gas gave 17.38 as compared with hydrogen, the theoretical sp. gr. being 17.05. The following measurements of some of the physical constants of methyl fluoride were made in conjunction with Professor Ramsay. A modified Andrews apparatus, of which a drawing and description is to be found in the *Philosophical Transactions* (1887, A, p. 59), was employed. Its volume tube was filled with methyl fluoride by repeatedly exhausting and admitting the gas. The gas was then compressed and liquefied. The following table shows the vapour pressures of methyl fluoride. The pressures, it should be remarked, are absolute, the actually read pressures in the air gauges being converted by means of Amagat's measurements of the compressibility of air. The lower temperatures were secured by jacketing with water; the higher temperatures, which are more accurate, by means of alcohol vapour boiling under reduced pressures. (See *Trans.*, 1885, **47**, 640.)

Temp.	Press.	Temp.	Press.	Temp.	Press.
	mm.		mm.		mm.
-5° C.	11365	15° C.	23003	35° C.	36204
0	14696	20	25621	40	40496
5	17740	25	28840	45	46010
10	20091	30	32756	—	—

A second series was obtained with gas presumably not so pure, inasmuch as the numbers are somewhat higher. Still the methyl fluoride must have been even then very nearly pure, as the following results at 40° show:—

	mm.		mm.
(a.) All liquid	42962	(d.) Trace of liquid .	41951
(b.) Half gas	41584	(e.) Smaller trace ..	41052
(c.) Liquid gone	39868	(f.) Minute trace ...	40622

It will be observed that the last observation is nearly coincident with that of the former series at 40°. In each series, the small bubble of air was absorbed by the liquid without much rise of pressure.

The critical temperature and pressure were determined by direct observation. It need hardly be remarked that a laborious series of researches is necessary to determine the point accurately; for it can only be ascertained by constructing sets of isothermals, and deducing from them the true temperature, pressure, and volume. Still the numbers may be regarded as far more accurate than many similar determinations. The substance assumed the critical state at 44·9°, and at a pressure of 47123 mm.; here again, the pressure is probably a little too high owing to the presence of a trace of air; and the temperature too low. The error in pressure probably does not exceed 1500 mm., and the temperature 0·2°.

Action of Chlorine on Methyl Fluoride.

When chlorine and methyl fluoride are mixed in equal volumes and exposed to sunlight, substitution of the hydrogen in the methyl fluoride takes place at once, and in a few hours the mixture becomes quite colourless. Several experiments were made, and always with the same result, a chlorofluoride of methylene and hydrogen chloride was produced, and no diminution occurred in the volume of the gas; equal volumes of the two gases were formed. In one experiment, the amount of hydrogen chloride produced was titrated with decinormal ammonia solution. 128·5 c.c. of methyl fluoride were mixed with 128·5 c.c. of pure chlorine, and exposed in the sunlight for three

hours; the amount of hydrogen chloride obtained was 0.207 gram, while the amount required by theory is 0.209 gram, supposing the reaction to take place as follows:—

The methylene chlorofluoride seems to be more soluble in water than fluoride of methyl, but is easily expelled again when the aqueous solution is warmed. This property can be made use of in purifying the gas from traces of air.

The sp. gr. of the gas was found to be 34.18, while the theoretical sp. gr. is 34.25. The gas is hardly inflammable, and considerable difficulty was experienced in exploding it with oxygen alone, the combustion only taking place when a powerful electric spark was passed through the mixture; when mixed, however, with hydrogen and oxygen, it explodes easily with an ordinary electric spark.

Several analyses were made, with the following results:—

	I.	I.	III.
Taken of gas	4.1 c.c.	8.5 c.c.	8.5 c.c.
Carbon dioxide produced ..	4.0 „	7.5 „	8.0 „

Thus showing that the gas produced its own volume of carbon dioxide after combustion.

An estimation of the chlorine was also made; 0.03526 gram gas gave 0.072 gram AgCl = 50.6 per cent. Cl .

	Found.	Calculated for CH_2ClF .
Cl	50.5	51.8

An attempt was made to estimate the fluorine, but the results were 3 per cent. too low.

Methylene chlorofluoride seems to be much more easily decomposed by water than methyl fluoride, for if an aqueous solution of this gas be allowed to stand for two or three days, both hydrochloric and hydrofluoric acids can be detected in the water.

Methylene chlorofluoride does not seem to react easily with chlorine, and the two gases when mixed in equal volumes and exposed to sunlight for many days, remain partly uncombined. I hope, however, to be able to continue the investigation.

I may mention that experiments made to obtain tetrafluoride of carbon, by passing a mixture of fluoride of silicon and carbon dioxide through a platinum tube heated to bright redness, were not successful. Silica was certainly formed in the platinum tube, and traces of a liquid were obtained which might possibly have been tetrafluoride of carbon, but unfortunately only in such small quantities that no analysis could be made.

During these experiments, when the mixture of carbon dioxide and silicon tetrafluoride was passed through a red-hot platinum tube, the following piece of apparatus was found to be extremely useful, and might doubtless be also used in many other experiments where the same result is desired. The object was to enable a continuous stream of the same gas to be slowly passed again and again through the red-hot platinum tube.

A was connected with the platinum tube, beyond which was a balloon (with two stopcocks) containing the mixed gases. B was connected directly with the balloon. The tube C was made of the ordinary glass tubing, such as is used for the Sprengel pump. When the receiver D was filled with mercury and raised just high enough to allow the mercury to flow down the tube C, gas was carried down with the falling mercury into the wider tube E; here the mercury escaped into the basin F, while the gas was forced through B back again into the balloon, and was then ready to be used again.