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ON
INORGANIC AND THEORETICAL CHEMISTRY

BY

J. W. MELLOR, D.Sc.

VOLUME II

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ABBREVIATIONS

Aq. = aqueous
atm. = atmospheric or atmosphere(s)
at. vol. = atomic volume(s)
at. wt. = atomic weight(s)
T° or °K = absolute degrees of temperature
b.p. = boiling point(s)
$^\circ\theta$ = centigrade degrees of temperature
coeff. = coefficient
conc. = concentrated or concentration
dil. = dilute
eq. = equivalent(s)
f.p. = freezing point(s)
m.p. = melting point(s)
mol(s) = $\left\{\begin{array}{l}\text{gram-molecule(s)}\\ \text{gram-molecular}\end{array}\right.$
mol(s).= $\left\{\begin{array}{l}\text{molecule(s)}\\ \text{molecular}\end{array}\right.$
mol. ht. = molecular heat(s)
mol. vol. = molecular volume(s)
mol. wt. = molecular weight(s)
press. = pressure(s)
sat. = saturated
soln. = solution(s)
sp. gr. = specific gravity (gravities)
sp. ht. = specific heat(s)
sp. vol. = specific volume(s)
temp. = temperature(s)
vap. = vapour

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THE HALOGENS

§ 1. The Occurrence of Fluorine

THE four elements fluorine, chlorine, bromine, and iodine together form a remarkable family, and they are grouped under the name **halogens** or salt-formers—ἅλς, sea-salt; γεννάω, I produce. J. S. C. Schweigger used this term in 1811, and it was also employed by J. J. Berzelius[1] for the non-oxygenated negative radicles—simple or compound—which combine with the metals to form salts. J. J. Berzelius was inclined to restrict the term more particularly to the simple radicles F, Cl, Br, I, and the compound radicle CN. J. J. Berzelius' term halogen has been retained for the four elements, and cyanogen dropped from the list. The binary salts—fluorides, chlorides, bromides, and iodides—are called **halides,** *halide salts*, or *haloid salts*. This term was also employed by J. J. Berzelius for the salts formed by the union of the metals with fluorine, chlorine, bromine, iodine, and cyanogen; as before, cyanogen has again been dropped from the list.

The first member of the family of halogens, fluorine, is the most chemically active element known; the chemical activity of the other members decreases with increasing at. wt. Fluorine can scarcely be said to occur free in nature, although C. A. Kenngott (1853) and F. Wöhler (1861) suggested that the violet felspar of Wölsendorf, and H. Becquerel and H. Moissan (1890)[2] that the violet fluorspar from Quincié (Villefranche), probably contain free fluorine as an occluded gas. These varieties of fluorspar were designated *hepatischer Flussspath* and *Stinkflussspath* by K. C. von Leonhard (1821) and J. F. L. Hausmann (1847).[3] When these minerals are powdered they emit a peculiar odour recalling ozone, and this has been attributed by various observers to the presence of various substances—*e.g.* hypochlorous acid (M. Schafhäutel), ozone (C. F. Schönbein), free fluorine, or of fluorine from the dissociation of an unstable fluoride or perfluoride (O. Loew).[4] The chemical reactions of the gas, however, were found by H. Becquerel and H. Moissan to correspond with fluorine which must be present either as occluded free fluorine, or else as an unstable perfluoride. The evidence is not decisive though the former is the more probable explanation of the reactions. P. Lebeau[5] obtained similar indications of fluorine in emeralds obtained from the vicinity of Limoges.

Combined fluorine is fairly widely distributed in rocks. According to F. W. Clarke,[6] it is about half as abundant as chlorine, since he estimates that the terrestrial matter in the half-mile crust—land and sea—contains 0·2 per cent. of chlorine, and 0·1 per cent. of fluorine. F. W. Clarke places fluorine the 20th and chlorine the 12th in the list of elements arranged in the order of their estimated abundance in the half-mile crust of the earth. Small quantities of fluorine are commonly present in igneous rocks. J. H. L. Vogt estimated that fluorine is the more abundant in the acidic rocks; chlorine, in the basic rocks. The most characteristic minerals containing fluorine are *fluorspar*, *fluor*, or *fluorite*—calcium fluoride—and *cryolite*—a double fluoride of aluminium and sodium; the less important or rarer fluoriferous minerals are: *fluellite*, $AlF_3.H_2O$; *chiolite*, $5NaF.3AlF_3$; *sellaite*, MgF_2; *tysonite*, $(Ce, La, Di)F_3$; *pachnolite* and *thomsenolite*, $NaF.CaF_2.AlF_3.H_2O$; *ralstonite*, $2NaF.MgF_2.6Al(F,OH)_3.4H_2O$; *prosopite*, $CaF_2.2Al(F,OH)_3$. Fluorine is also contained in some phosphates—*e.g.* fluorapatite, phosphorite, sombrerite, coprolites, and staffelite; and in some silicates—*e.g.* topaz, tourmaline, herderite, yttrocerite, amphibole, nocerine, kodolite, melinophane, hieratite, lepidolite, and in many other silicate minerals.

Several mineral waters have been reported to contain minute quantities of soluble fluorides. The spring at Gerez (Portugal) is one of the richest, for, according to C. Lepierre,[7] it contains 0·296 to 0·310 grm. of solid matter per litre, and of this, 0·022 to 0·027 grm. is an alkali fluoride; and of the 93 spring waters examined by P. Carles, 87 contained soluble fluorides. F. Parmentier has denied the existence of fluorine in many waters in which it is supposed to exist; but according to A. Gautier and P. Clausmann, all mineral waters contain fluorine, and the proportion is greatest in waters of volcanic origin. Thermal alkali bicarbonate waters are particularly rich in the element, although the proportion does not appear to depend upon the temp. As a general rule, mineral waters of the same kind show an increase of fluorine accompanying a rise in the total salts. In the case of calcium sulphate waters, whatever their origin, the amount of fluorine is about 2 mgrms. per litre. In 1849, G. Wilson reported on the occurrence of fluorine in the Clyde waters, and in the North Sea; and generally it has been found that sea water contains about three milligrammes per litre; the proportion varies slightly in different places and at different depths. A. Gautier[8] found about 0·11 mgrm. of combined fluorine per litre of gas collected from a fumerole fissure in the crater of Vesuvius; and 3·72 mgrms. per litre in the condensed water from the boric acid fumerole of a spring at Larderello (Tuscany).

At the beginning of the nineteenth century L. J. Proust and M. de la Méthérie[9] first noticed the presence of fluorine in bones, and the fact has since been confirmed by numerous others. A. Carnot found 0·20 to 0·65 per cent. of calcium fluoride in fresh bones, while old fossil bones contained much more—0·88 to 6·21 per cent. This fact was first noticed by J. Stocklasa in 1889. Modern bones were found by A. Carnot to contain a minimum proportion of fluorine; tertiary bones contained more; mesozoic bones still more; and in silurian and devonian bones, the proportion of fluorine was nearly the same as in apatite. A. Carnot attributes the progressive enrichment of bones to the action of percolating waters containing a small proportion of fluorides in soln.—*e.g.* the waters of the Atlantic contain 0·822 grm. per cubic metre. According to F. Hoppe, the enamel of the teeth contains up to 2 per cent. of calcium fluoride; and according to W. Hempel and W. Scheffler, the teeth of horses contain 0·20 to 0·39 per cent. of fluorine, and the teeth of man, 0·33 to 0·59 per cent.[10]—unsound teeth had but 0·19 per cent. of fluorine. P. Carles[11] found 0·012 per cent. of fluorine in the shells of oysters and mussels living in sea water, while fossil oyster shells contained 0·015 per cent. He also reported about one-fourth as much fluorine in fresh-water mussel shells as is present in the shells of sea-water mussels. The brain (E. N. Horsford),[12] blood (G. Wilson, and G. O. Rees), and the milk of animals (F. S. Horstmar) have some fluorine. The brain of man contains about 3 mgrms. of fluorine, and although the *rôle* of fluorine in the animal and vegetable organism has not been clearly defined, some physiologists believe that the presence of fluorine is necessary, in some subtle way, to enable the animal organism to assimilate phosphorus. G. Tammann found that least fluorine was contained in the shells of eggs, and most in the yolks. About 0·1 per cent. of fluorine occurs in the ash of vegetable matter—particularly the grasses.[13] A. G. Woodman and H. P. Talbot reported that fluorine is common in malt liquors; most malted beers contain not less than 0·2 mgrm. per litre. T. L. Phipson has reported 3·9 per cent. of fluorine, and 32·45 of phosphoric acid in fossil wood from the Isle of Wight, thus showing that the wood had been "fossilized by phosphate of lime and fluorspar."

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§ 2. The History of Fluorine

The mineral now known as **fluorspar** or **fluorite** was mentioned in 1529 by G. Agricola, in his *Bermannus, sive de re metallica dialogus* (Basiliæ, 1529), and designated *fluores*, which, in a later work[1] by the same writer, was translated into *Flüsse*. A. J. Cronstedt,[2] in 1758, used the terms *Fluss*, *Flusspat*, and *Glasspat*, synonymously. C. A. Napione (1797) called the mineral *fluorite ;* F. S. Beudant (1832), *fluorine ;* and M. Sage (1777), *spath fusible*. These terms are derived from the Latin *fluo*, I flow, in reference to the fluxing action and the ready fusibility of the mineral ; consequently, *fluor lapis*, *spatum vitreum*, and *Glasspath* mean the fluxing stone. J. G. Wallerius[3] refers to the luminescence of the mineral when warmed, and this phenomenon led to its being called *lithophosphorus* and *phosphoric spar*. The variety which gives a greenish phosphorescence is called *chlorophane*—χλωρός, green ; φαίνω, I appear—and also *pyro-emerald*.

H. Kopp reports[4] that H. Schwanhardt in 1670 etched glass by the action of fluorspar and sulphuric acid, and that in 1725, M. Pauli made a liquid for etching glass by mixing nitric acid and powdered fluorspar. In 1764, A. S. Marggraff[5] distilled the mixture of sulphuric acid and fluorspar in a glass retort, and found a white powder to be suspended in the water of the receiver. He therefore concluded that the sulphuric acid separates a volatile earth from the fluorspar. C. W. Scheele[6] repeated A. S. Marggraff's experiment, and, in his *Examen chemicum fluoris mineralis ejusque acidi* (1771), concluded that the sulphuric acid liberates a peculiar acid which is united with lime in fluorspar. The acid was called *Flusssäure*—fluor acid—and fluorspar was designated *flusssäurer Kalk*. After the expulsion of the fluor acid from the lime by sulphuric acid, selenite—calcium sulphate—remained in the retort. He found that hydrochloric, nitric, or phosphoric acid could also be used in place of sulphuric acid with analogous results. M. Boullanger[7] took the view that Scheele's fluor acid was nothing but muriatic acid combined with some earthy substance, and A. G. Monnet that it was a volatile compound of sulphuric acid and fluor. C. W. Scheele,[8] however, refuted both hypotheses in 1780; and concluded:

> I hope that I have now demonstrated that the acid of fluor is and remains entirely a mineral acid *sui generis*.

C. W. Scheele generally used glass retorts for the preparation of the acid, and he was much perplexed by the deposit of silica obtained in the receiver. C. W. Scheele thought that the new acid had the property of forming silica when in contact with water, and it was therefore regarded as containing combined silica. The source of the silica was subsequently traced by J. C. F. Meyer and J. C. Wiegleb [9] to the glass of the retorts, and was not formed when the distillation was effected in metal vessels, and the acid vapours dissolved in water contained in leaden vessels. The gas obtained when the fluorspar is treated with sulphuric acid in metal vessels is hydrofluoric acid, and if in glass vessels, some hydrofluosilicic acid is mixed with the hydrofluoric acid.

In Lavoisier's system,[10] Scheele's acid of fluor became *l'acide fluorique*—a combination of oxygen with an unknown radicle, *fluorium*; and in 1789, A. L. Lavoisier wrote:

> It remains to-day to determine the nature of the fluoric radicle, but since the acid has not yet been decomposed, we cannot form any conception of the radicle.

In 1809, J. L. Gay Lussac and L. J. Thénard [11] attempted to prepare pure hydrofluoric acid, and although they did not succeed in making the anhydrous acid, they did elucidate the relation of silica and the silicates to this acid. H. Davy's work on the elementary nature of chlorine was published about this time; and he received two letters—dated Nov. 1st, 1810, and Aug. 25th, 1812 [12]—from A. Ampère suggesting "many ingenious and original arguments" in favour of the analogy between hydrochloric and hydrofluoric acids. In the first letter, A. Ampère said:

> It remains to be seen whether electricity would not decompose liquid hydrofluoric acid if water were removed as far as possible, hydrogen going to one side and oxyfluoric acid to the other, just as when water and hydromuriatic acid are decomposed by the same agent. The only difficulty to be feared is the combination of the oxyfluoric acid set free with the conductor with which it would be brought into contact in the nascent state. Perhaps there is no metal with which it would not combine, but supposing that oxyfluoric acid should, like oxymuriatic acid, be incapable of combining with carbon, this latter body might be a sufficiently good conductor for it to be used with success as such in this experiment.

In the second letter, A. Ampère suggested that the supposed element be called *le fluor*—*fluorine*—in agreement with the then recently adopted name *chlorine*—French, *le chlore*. A. Ampère's suggestion has been adopted universally. No one doubted the existence of the unknown element fluorine although it successfully resisted every attempt to bring it into the world of known facts. Belief in its existence rested on the many analogies of its compounds with the other three members of the halogen family. For over seventy years it was neither seen nor handled. During this time, many unsuccessful experiments were made to isolate the element. H. Davy [13] thus describes his attempts:

> I undertook the experiment of electrizing pure liquid fluoric acid with considerable interest, as it seemed to offer the most probable method of ascertaining its real nature, but considerable difficulties occurred in executing the process. The liquid fluoric acid immediately destroys glass and all animal and vegetable substances, it acts on all bodies containing metallic oxides, and I know of no substances which are not rapidly dissolved or decomposed by it, except metals, charcoal, phosphorus, sulphur, and certain combinations of chlorine. I attempted to make tubes of sulphur, of muriates of lead, and of copper containing metallic wires, by which it might be electrized, but without success. I succeeded,

however, in boring a piece of horn silver in such a manner that I was able to cement a platina wire into it, by means of a spirit lamp, and by inverting this in a tray of platina filled with liquid fluoric acid I contrived to submit the fluid to the agency of electricity in such a manner that in successive experiments it was possible to collect any elastic fluid that might be produced.

Having failed to isolate the element by the electrolysis of hydrofluoric acid and the fluorides, H. Davy tried if the element could be driven from its combination by double decomposition. He attempted to drive the "fluoric principle" from the dry fluates of mercury, silver, potassium, and sodium by means of chlorine. He said:

> The dry salts were introduced in small quantities into glass retorts, which were exhausted and then filled with pure chlorine; the part of the retort in contact with the salt was heated gradually till it became red. There was soon a strong action, the fluate of mercury was rapidly converted into corrosive sublimate, and the fluate of silver more slowly became horn silver. In both experiments there was a violent action upon the whole of the interior of the retort. On examining the results, it was found that in both instances there had been a considerable absorption of chlorine, and a production of silicated fluoric acid gas and oxygen gas. I tried similar experiments with similar results upon dry fluate of potassa and soda. By the action of a red-heat they were slowly converted into muriates with the absorption of chlorine, and the production of oxygen, and silicated fluoric acid gas, the retort being corroded even to its neck.

H. Davy assumed that his failure to obtain the unknown element was due to the potency of its reactions. H. Davy tried vessels of sulphur, carbon, gold, horn silver, and platinum, but none appeared to be capable of resisting its action, and "its strong affinities and high decomposing agencies" led to its being regarded as a kind of alcahest or universal solvent. G. Aimé (1833) employed a vessel of caoutchouc, with no better result. The brothers C. J. and T. Knox (1836) [14] sagaciously tried to elude this difficulty by treating silver or mercury fluoride with chlorine in an apparatus made of fluorspar itself. E. Frémy believed that the failure in this as well as in P. Louyet's analogous attempt with fluorspar or cryolite vessels, in 1846, was due to the fact that the two fluorides do not decompose when moisture is rigorously excluded; and, if moisture be present, they form hydrofluoric acid. E. Frémy also did not succeed in decomposing calcium fluoride by means of oxygen, when heated to a high temp. in a platinum tube. E. Frémy electrolyzed fused fluorides—calcium, potassium, and other metal fluorides—in a platinum crucible with a platinum rod as anode. The platinum wire electrode was much corroded, and a gas was evolved which E. Frémy believed to be fluorine because it decomposed water forming hydrofluoric acid, and displaced iodine from iodides. He was able to decompose calcium fluoride at a high temp. by means of chlorine, and particularly when the fluoride is mixed with carbon. E. Frémy, however, made no further progress in isolating the elusive element, although he did show how anhydrous hydrofluoric acid could be prepared.

G. Gore [15] made some experiments on the electrolysis of silver fluoride and on the action of chlorine or bromine on silver fluoride at 15·5° for 38 days, and at 110° for 6 days, in vessels of various kinds—with vessels of carbon, a volatile carbon fluoride was formed. H. Kammerer [16] failed to prepare the gas by the action of iodine on silver fluoride in sealed glass tubes; according to L. Pfaundler, the product of the action is a mixture of silicon fluoride and oxygen. O. Loew heated cerium tetrafluoride, $CeF_4.H_2O$, or the double salt, $3KF.2CeF_4.2H_2O$, and obtained a gas, which he considered to be fluorine, when the tetrafluoride decomposed forming the trifluoride, CeF_3. B. Brauner also obtained a gas resembling chlorine by heating lead tetrafluoride, or double ammonium lead tetrafluoride, or potassium hydrogen lead fluoride, K_3HPbF_4. In the latter case a mixture of potassium fluoride, KF, and lead difluoride, PbF_2, remained. O. Ruff claims to have made a little fluorine by heating the compound $HKPbF_6$. As H. Moissan has said, it is possible that fluorine might be obtained by a chemical process in which a higher fluoride decomposes into a lower fluoride with the liberation of fluorine—say, $2CeF_4=2CeF_3+F_2$. O. Ruff has failed to confirm B. Brauner's observations with the fluorides in question. With lead tetrafluoride in a platinum vessel, lead difluoride and platinum tetrafluoride are formed; liquid or gaseous silicon tetrafluoride is practically without action on the salt although a small quantity of a gas which acts on potassium iodide is formed without altering the composition of the gas. Antimony pentafluoride acts similarly. With sulphur and iodine the corresponding higher fluorides are formed. Other suggestions have also been made to prepare fluorine by chemical processes—O. T. Christensen[17] proposed heating the higher double fluorides of manganese ; A. C. Oudemans, potassium fluochromate ; and H. Moissan, platinum fluophosphates. About 1883, H. B. Dixon and H. B. Baker made an attempt to displace fluorine by oxygen from uranium pentafluoride, UF_5. A. Baudrimont tried the action of boron trifluoride on lead oxide without success. Abortive attempts have been made by L. Varenne, J. P. Prat, P. Cillis, and T. L. Phipson[18] to prepare the gas by wet processes analogous to those employed for chlorine by the oxidation of soln. containing hydrofluoric acid. We now know that this is altogether a wrong line of attack. Some of the dry processes indicated above may have furnished some fluorine; for example, in H. B. Dixon and H. B. Baker's experiment, silver foil in the vicinity of the uranium fluoride was spotted with white silver fluoride; gold foil, with yellow auric fluoride; and platinum foil, with chocolate platinic fluoride.

In 1834, M. Faraday[19] thought that he had obtained fluorine "in a separate state" by electrolyzing fused fluorides, but later, he added :

> I have not obtained fluorine; my expectations, amounting to conviction, passed away one by one when subject to rigorous examination.

This was virtually the position of the fluorine question about 1883, when H. Moissan,[20] a pupil of E. Frémy, commenced systematic work on the subject, and the reports of the various stages of his work have been collected in his important monograph *Le fluor et ses composés* (Paris, 1900). He first tried (1) The decomposition of gaseous fluorides by sparking—*e.g.* the fluorides of silicon, SiF_4 ; phosphorus, PF_5 ; boron, BF_3; and arsenic, AsF_3. The silicon and boron fluorides are stable. Phosphorus trifluoride forms the pentafluoride. The fluorine derived from phosphorus pentafluoride reacts with the material of which the vessel is made ; similarly with arsenic fluoride. (2) The action of platinum at a red heat on the fluorides of phosphorus and silicon. Phosphorus pentafluoride furnishes some fluorine which unites with the platinum of the apparatus used ; phosphorus trifluoride formed the pentafluoride and fluo-phosphides of platinum ; silicon tetrafluoride gave no signs of free fluorine ; H. Moissan came to the conclusion that no reaction carried out at a high temp. was likely to be fruitful. (3) The electrolysis of arsenic trifluoride to which some potassium hydrogen fluoride was added to make the liquid conducting ; any fluoride given off at the anode was absorbed by the electrolyte forming arsenic pentafluoride.

H. Moissan then tried the electrolysis of highly purified anhydrous hydrofluoric acid, but he found, consonant with G. Gore's and M. Faraday's observations,[21] that anhydrous hydrofluoric acid is a non-conductor of electricity. If a small quantity of water be present, this alone is decomposed, and a large quantity of ozone is formed. As the water is broken up, the acid becomes less and less conducting, and, when the whole has disappeared, the anhydrous acid no longer allows a current to pass. He obtained an acid so free from water that "a current of 35 ampères furnished by fifty Bunsen cells was totally stopped." The current passed readily when fragments of dry potassium hydrogen fluoride KF.HF, were dissolved in the acid, and a gaseous product was liberated at each electrode. Success ! The element fluorine was isolated by Henri Moissan on June 26th, 1886, during the electrolysis of a soln. of potassium fluoride in anhydrous hydrofluoric acid, in an apparatus made wholly of platinum. In this way, H. Moissan solved what H. E. Roscoe called one of the most difficult problems in modern chemistry.

While the new element possessed special properties which gave it an individuality of its own, and a few surprises occurred during the study of some of its combinations ; yet the harmonious analogy between the members of the halogen family—fluorine, chlorine, bromine, and iodine—was fully vindicated. With fluorine in the world of reality, chemists were unanimous in placing the newly discovered element at the head of the halogen family, and in that very position which had been so long assigned to it by presentiment or faith.

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§ 3. The Preparation of Fluorine

When an electric current is passed through a conc. aq. soln. of hydrogen chloride, chlorine is liberated at the anode, and hydrogen at the cathode. When aq. hydrofluoric acid is treated in the same way, water alone is decomposed, for oxygen is liberated at the anode, and hydrogen at the cathode. The anhydrous acid does not conduct electricity, and it cannot therefore be electrolyzed. H. Moissan found that if potassium fluoride be dissolved in the liquid hydrogen fluoride, the soln. readily conducts electricity, and when electrolyzed, hydrogen is evolved at the cathode, and fluorine at the anode. In the first approximation, it is supposed that the primary products of the electrolysis are potassium at the anode, fluorine at the cathode : $2KHF_2=2HF+2K+F_2$. The potassium reacts with the hydrogen fluoride reforming fluoride and liberating hydrogen: $2K+2HF=2KF+H_2$. The reaction is probably more complex than this, and the platinum of the electrodes plays a part in the secondary reactions. Possibly the fluorine first forms platinum fluoride, PtF_4, which produces a double compound with the potassium fluoride.

This compound is considered to be the electrolyte which on decomposition forms the two gases and a double potassium platinum fluoride which is deposited as a black mud. This hypothesis has been devised to explain why the initial stage of the electrolysis is irregular and jerky, and only after the lapse of an hour, when the substances in soln. are in sufficient quantities to make the passage of the current regular, is the evolution of fluorine regular. O. Ruff[1] has shown that ammonium fluoride can be used in place of the potassium salt.

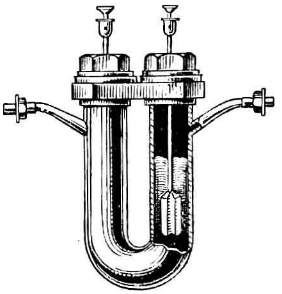

FIG. 1.—Tube for the Electrolysis of Hydrofluoric Acid.

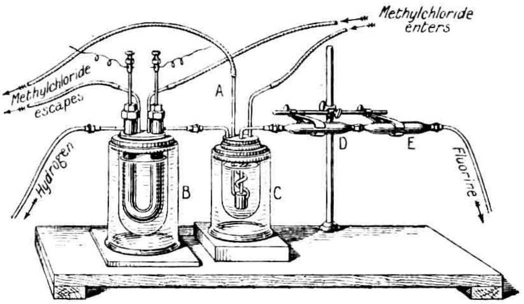

FIG. 2.—Moissan's Process for Fluorine.

H. Moissan first conducted the electrolysis in a **U**-tube made from an alloy of platinum and iridium which is less attacked by fluorine than platinum alone. Later experiments showed that a tube of copper could be employed. The copper is attacked by the fluorine, forming a surface crust of copper fluoride which protects the tube from further action. Electrodes of platinum iridium alloy were used at first, but later electrodes of pure platinum were used, even though they were rather more attacked than the alloy with 10 per cent. of iridium. The electrodes were club-shaped at one end so that they need not be renewed so often. The positive electrode was often completely corroded during an experiment, but the **U**-tube scarcely suffered at all. A copper tube is illustrated in Fig. 1. The open ends of the tube are closed with fluorspar stoppers ground to fit the tubes and bored with holes which grip the electrodes. The joints are made air-tight with lead washers and shellac. The **U**-tube, during the electrolysis, is surrounded with a glass cylinder, *B*, into which liquid methyl chloride is passed from a steel cylinder *viâ* the tube *A*, Fig. 2. Liquid methyl chloride boils at $-23°$, and it escapes through an exit tube. The fluorine is passed through a spiral platinum tube also placed in a bath of evaporating liquid methyl chloride, *C*. This cools the spiral tube down to about $-50°$, and condenses any gaseous hydrogen fluoride, which might escape with the fluorine from the **U**-tube. The electrolysis was carried out at a low temp. in order to prevent the gaseous product being dil. with the vapour of hydrogen fluoride, and also to diminish the destructive action of the fluorine on the apparatus. In his later work, H. Moissan cooled the **U**-tube used for the electrolysis by using a bath of acetone with solid carbon dioxide in suspension. This cooled the apparatus down to about $-80°$. The temp. of the electrolysis vessel should not be so low that the potassium hydrogen fluoride crystallizes out. Hence, O. Ruff and P. Ipsen[2] preferred to cool the electrolysis vessel with a freezing mixture of calcium chloride, and condensed the hydrogen fluoride vapours in a copper condenser *C*, Fig. 2, cooled with liquid air. The fluorine which leaves the condenser *C*, travels through two small platinum tubes, *D* and *E*, containing lumps of sodium fluoride, which remove the least traces of hydrogen fluoride by forming NaF.HF. A glass cylinder is placed outside each of the two cylinders containing methyl chloride. The outer cylinders contain a few lumps of calcium chloride, so as to dry the air in the vicinity of the cold jacket, and prevent the

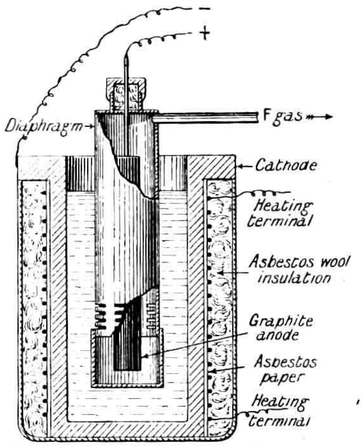

FIG. 3.—Fluorine by the Electrolysis of Fused Alkali Hydrofluoride.

deposition of frost on the cylinders. With a current from 26 to 28 Bunsen cells in series, and an apparatus containing from 90 to 100 grms. of anhydrous hydrofluoric acid containing in soln. 20 to 25 grms. of potassium hydrogen fluoride, H. Moissan obtained between two and three litres of fluorine per hour.

C. Poulenc and M. Meslans[3] have devised a copper apparatus for the preparation of fluorine on a large scale; and likewise a portable laboratory apparatus, also of copper. They substitute a perforated copper diaphragm in place of the **U**-tube for keeping the two electrode products separate. The platinum anode is hollow, and is cooled internally. G. Gallo did not get good results with this apparatus. W. L. Argo and co-workers prepared fluorine by the electrolysis of molten potassium hydrofluoride in an electrically heated copper vessel which served as cathode, the anode being made of graphite. A copper diaphragm with slots was used as illustrated in Fig. 3. The bubbles of hydrogen evolved during the electrolysis were deflected from the interior of the diaphragm by means of a false bottom. The graphite anode was connected with a copper terminal and insulated by a packing of powdered fluorspar —current, 10 amps., 15 volts; temp., 240°–250°; efficiency, 70 per cent. These co-workers also recommend sodium hydrofluoride because it is non-deliquescent; decomposes below the fusion temp.; contains more available fluorine for a given weight; and is less expensive.

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§ 4. The Properties of Fluorine

Is fluorine an element? Since fluorine had never been previously isolated, it remained for H. Moissan to prove that the gas he found to be liberated at the positive pole is really fluorine. Many of its physical and chemical properties, as will be shown later, agree with those suggested by the analogy of the fluorides with the chlorides, bromide, and iodides. It was found impossible to account for its properties by assuming it to be some other gas mixed with nitric acid, chlorine, or ozone; or that it is a hydrogen fluoride richer in fluorine than the normal hydrogen fluoride.

To show the absence of hydrogen, H. Moissan allowed the gas to pass directly from the positive pole through a tube containing red-hot iron; any hydrogen so formed was collected in an atm. of carbon dioxide. The latter was removed by absorption in potassium hydroxide. In several experiments a small bubble of gas was obtained which was air, not hydrogen. The increase in weight of the tube containing the iron corresponded exactly with the fluorine eq. of the hydrogen collected at the negative pole. The vapours of hydrogen fluoride were retained by a tube filled with dry potassium fluoride. For example: In one experiment a platinum tube containing iron increased in weight 0·138 grm. while 80·01 c.c. of hydrogen were collected at the negative electrode. This represents 0·00712 grm. of hydrogen, and $0{\cdot}00712 \times 19 = 0{\cdot}134$ grm. of fluorine. This number is virtually the same as the weight of fluorine actually weighed.

Fluorine at ordinary temp. is a greenish-yellow gas when viewed in layers a metre thick; the colour is paler and more yellow than that of chlorine. The liquid gas is canary-yellow; the solid is pale yellow or white. Moissan's gas has an intensely irritating smell said to recall the odour of hypochlorous acid or of nitrogen peroxide. Even a small trace of gas in the atm. acts quickly on the eyes and the mucous membranes; and, in contact with the skin, it causes severe burns, and rapidly destroys the tissues. If but a slight amount is present, its smell is not unpleasant. The **relative density** [1] of the gas (air unity) determined by H. Moissan in 1889, by means of a platinum flask, was 1·26; that calculated for a diatomic gas of at. wt. 19·5 is 1·314, and B. Brauner attributed the difference to the presence of some atomic fluorine. H. Moissan's later results (1904) rendered B. Brauner's hypothesis unnecessary since a density of 1·31 was obtained. The gas employed previously is supposed to have been contaminated with a little hydrogen fluoride. Most of the physical properties of fluorine at a low temp. have been determined by H. Moissan himself and in conjunction with J. Dewar.[2] The sp. gr. of liquid fluorine is 1·14 at —200°, and 1·108 at its b.p. —187°. The sp. vol. of the liquid is 0·9025; and the mol. vol. 34·30. The **capillary constant** of the liquid is about one-sixth of that of liquid oxygen, and seven-tenths of that of water. The **coefficient of expansion** [3] of the gas is 0·000304. The volume of the liquid changes one-fourteenth in cooling from —187° to —210°. When the gas is cooled by rapidly boiling liquid air, it condenses to a clear yellow liquid which has the **boiling point** —187° at 760 mm. press.; and the liquid forms a pale yellow solid when cooled by liquid hydrogen. The solid has the **melting point** —233°. The solid loses its yellow tint and becomes white when cooled down to —252°. Chlorine, bromine, sulphur, etc., likewise lose their colour at low temp.

J. H. Gladstone's [4] estimate for the **atomic refraction** of fluorine for the D-line is 0·53; for the A-line 0·63; and for the H-line 0·35 with the μ-formula, and 0·92 and 0·84 respectively with the μ^2-formula. F. Swarts estimated 0·94 H_α, 1·015 D, and 0·963 H_γ with the μ^2-formula for fluorine in sat. organic compounds; and for unsaturated compounds with the ethylene linkage, H_α, 0·588; D, 0·665; H_γ, 0·638. The **atomic dispersion** is 0·022 with sat. and 0·05 with the unsaturated compounds. J. H. Gladstone also made several estimates of the index of refraction of fluorine, and his 1870 estimate gave 1·4 (chlorine 9·9); in 1885 he placed it at 1·6; and in 1891, he considered it to be "extremely small, in fact, less than 1·0." The difficulty is due to the fact that when the magnitude of a small constant is estimated by subtraction from two large numbers the probability of error is large. A direct determination by C. Cuthbertson and E. B. R. Prideaux gave for the **index of refraction** of fluorine for sodium light, μ=1·000195, which makes the refractivity $(\mu-1)\times10^6$ to be 195. The **emission spectrum** of fluorine has been investigated by H. Moissan and G. Salet.[5] The last named, in 1873, compared the spectra of silicon chloride and fluoride, and inferred that five lines in the spectrum of silicon fluoride must be attributed to the fluorine. H. Moissan's measurements, in 1889, measured 13 lines in the red part of the spectrum. The lines of wave-length 677, 640·5, 634, and 623 are strong; the lines 714, 704, 691, 687·5, 685·5, 683·5 are faint; and 749, 740, and 734 are very faint. Liquid fluorine has no absorption spectrum when in layers 1 cm. thick.

According to P. Pascal,[6] fluorine is diamagnetic; the specific **magnetic susceptibility** is $-3·447\times10^{-7}$; and the atomic susceptibility calculated from the additive law of mixtures for organic compounds is -63×10^{-1}. Ionic fluorine is univalent and negative. The **decomposition voltage** required to separate this element from its compounds is 1·75 volts.[7] The ionic velocity (transport number) [8] of fluorine ions at 18° is 46·6, and 52·5 at 25° with a temp. coeff. of 0·0238.

Fluorine possesses special characters which place it at the head of the halogen family. It forms certain combinations and enters into some reactions in a way which would not be expected if the properties of the element were predicted solely by analogy with the other members of the halogen family. From this point of view, said H. Moissan, *l'étude des composés fluorés réserve encore bien des surprises*. Fluorine is the most chemically active element known. It combines additively with most of the elements, and it usually behaves like a univalent element although it is very prone to form double or complex compounds in which it probably exerts a higher valency. It also acts as an oxidizing agent. In the electrolysis of manganese and chromium salts a higher yield of chromic acid or manganic acid is obtained in the presence of hydrofluoric acid than in the presence of sulphuric acid.[9] Fluorine unites explosively with **hydrogen** in the dark with the production of a flame with a red border, and H. Moissan showed this by inverting a jar of hydrogen over the fluorine delivery tube of his apparatus. The product of the action is hydrogen fluoride which rapidly attacks the glass vessel when moisture is present, but not if the two gases are dry. Fluorine retains its great avidity for hydrogen even at temp. as low as —252·5° when the fluorine is solid, and the hydrogen is liquid. H. Moissan and J. Dewar[10] broke a tube of solid fluorine in liquid hydrogen. A violent explosion occurred which shattered to powder the glass apparatus in which the experiment was performed. It is rather unusual for the chemical activity of an element to persist at such a low temp. The affinity of fluorine for hydrogen is so great that it vigorously attacks organic substances, particularly those rich in hydrogen. The reaction is usually accompanied by the evolution of heat and light, and the total destruction of the compound. The products of the reaction are hydrogen fluoride, carbon, and carbon fluorides. The avidity of fluorine for hydrogen persists at very low temp., for turpentine and anthracene may explode in contact with fluorine at —210°. Even **water** is vigorously attacked by fluorine. If a small quantity of water is introduced into a tube containing fluorine, it is decomposed, forming hydrogen fluoride and ozone; the latter imparts an indigo-blue tinge to the gases in the jar. By measuring the volume of oxygen liberated when fluorine reacts with water, and measuring the exact quantity of hydrofluoric acid formed, H. Moissan showed that equal volumes of hydrogen and fluorine form hydrogen fluoride. If the reaction between fluorine and water be symbolized, $H_2O+F_2=2HF+O$, it follows that for every volume of hydrogen collected at the negative pole, half a volume of oxygen should be obtained. In one experiment H. Moissan collected 26·10 c.c. of oxygen, 52·80 c.c. of hydrogen. In another experiment he obtained 6·4 c.c. of oxygen per 12·5 c.c. of hydrogen and eq. of 24·9 c.c. of hydrogen fluoride. Liquid fluorine does not react with water. At —200°, liquid fluorine can be volatilized from the surface of ice without reaction.

Neither **oxygen** nor **ozone** appears to react with fluorine, and no oxygen compound of fluorine has yet been prepared. According to H. Moissan,[11] an unstable intermediate compound of ozone and fluorine is possibly formed when water acts on fluorine to form ozonized oxygen because the ozone smell does not appear until some time after the fluorine has been passed into the water. O. Ruff and J. Zedner have tried the effect of heating oxygen and fluorine in the electric arc, but obtained no signs of the formation of a compound of fluorine with oxygen or ozone, for when the gaseous product is passed over calcium chloride (which fixes the fluorine) a mixture is obtained quite free from fluorine. G. Gallo obtained signs of a very unstable compound of ozone and fluorine which is explosive at —23°. Liquid oxygen dissolves fluorine, and if the temp. rises gradually, the first fraction which volatilizes is almost pure oxygen; the last fraction contains most of the fluorine. If liquid air, which has stood by itself for some time, be treated with fluorine, a precipitate is formed which is very liable to explode. H. Moissan thinks it is probably *fluorine hydrate*.[12]

Solid **sulphur, selenium,** and **tellurium** inflame in fluorine gas at ordinary temp.; sulphur burns to the hexafluoride, SF_6. The reactivity of sulphur or selenium with fluorine persists at —187°, but tellurium is without action at this temp. **Hydrogen sulphide** and **sulphur dioxide** also burn in the gas—the former produces hydrogen fluoride and sulphur fluoride. Each bubble of sulphur dioxide led into a jar of fluorine produces an explosion and thionyl fluoride, SOF_2, is formed; but if the fluorine be led into the sulphur dioxide, there is no action until the sulphur dioxide has reached a certain partial pressure when all explodes. If the fluorine be led into an atm. of sulphur dioxide at the temp. of the reaction, sulphuryl fluoride, SO_2F_2, is formed quietly without violence. **Sulphuric acid** is scarcely affected by fluorine.

Fluorine does not unite with **chlorine** at ordinary temp. O. Ruff and J. Zedner also obtained no result by heating fluorine and chlorine at the temp. of the electric