

FORMATION OF FLUORINE BY DECOMPOSITION OF CERIUM AND LEAD FLUORIDES

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Prior to the historical preparation of elemental fluorine by Moissan in 1886, this element was inadvertently obtained in 1881 by Bohuslav Brauner, professor at the Bohemian University in Prague. During his stay at the University of Manchester in England, Brauner was engaged in the analysis of metal and rare earth compounds with the aim of finding precise atomic weights of some elements and thus their correct positions in Mendeleev's new periodic system. He prepared and identified cerium tetrafluoride hydrate $CeF_4 \cdot H_2O$, potassium fluorocerate dihydrate $3KF \cdot 2CeF_4 \cdot 2H_2O$ (Brauner, B., Ber. 1881, **14**, 1944; J. Chem. Soc., 1882, **41**, 68), lead tetrafluoride PbF_4 , and potassium fluoroplumbate $3KF \cdot HF \cdot PbF_4$ (Brauner, B., J. Chem. Soc., 1894, **65**, 393). While heating the fluorides and complex fluorides of cerium and lead, Brauner noticed first evolution of water and hydrofluoric acid, and at higher temperatures, evolution of a gas which liberated iodine from potassium iodide and whose odor was reminiscent of chlorine or hypochlorous acid. "Fumes of hydrofluoric acid issued from the nose after inhaling and exhaling the gas." In spite of no more conclusive characterization, there is little doubt that the gas generated at higher temperatures from the fluorides of cerium and lead was fluorine. Later on, Brauner confirmed the presence of fluorine in the gases evolved by the thermal decomposition of the above-mentioned fluorides by igniting elemental silicon (a test developed by Moissan) (Brauner, B., Z. Anorg. Allgem. Chem., 1916, **98**, 38). Thus this most electronegative element was obtained in small quantities by a chemical process five years prior to its isolation and preparation by the electrolysis of potassium hydrogen fluoride by H. Moissan.

Brauner's experiments were not duplicated in full extent either by O. Ruff (Z. Angew. Chem., 1907, **20**, 1217), or later by W. L. Argo *et al.* (Trans. Am. Electrochem. Soc., 1919, 335; Chem. Abstr. 1919, **13**, 1188). When I repeated Argo *et al.*'s modification of the decomposition of lead tetrafluoride I did not obtain fluorine even in traces. However, a considerable quantity of nickel fluoride was found in the residue after decomposing the fluoride by heating it in a stainless steel apparatus. Evidently elemental fluorine was generated but reacted immediately with the metal of the apparatus. Similar reactions may have occurred with platinum when the lead tetrafluoride was heated at higher temperature than those used by Brauner.