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E. M. McCarron, Y. J. Grannec and N. Bartlett

February 1980

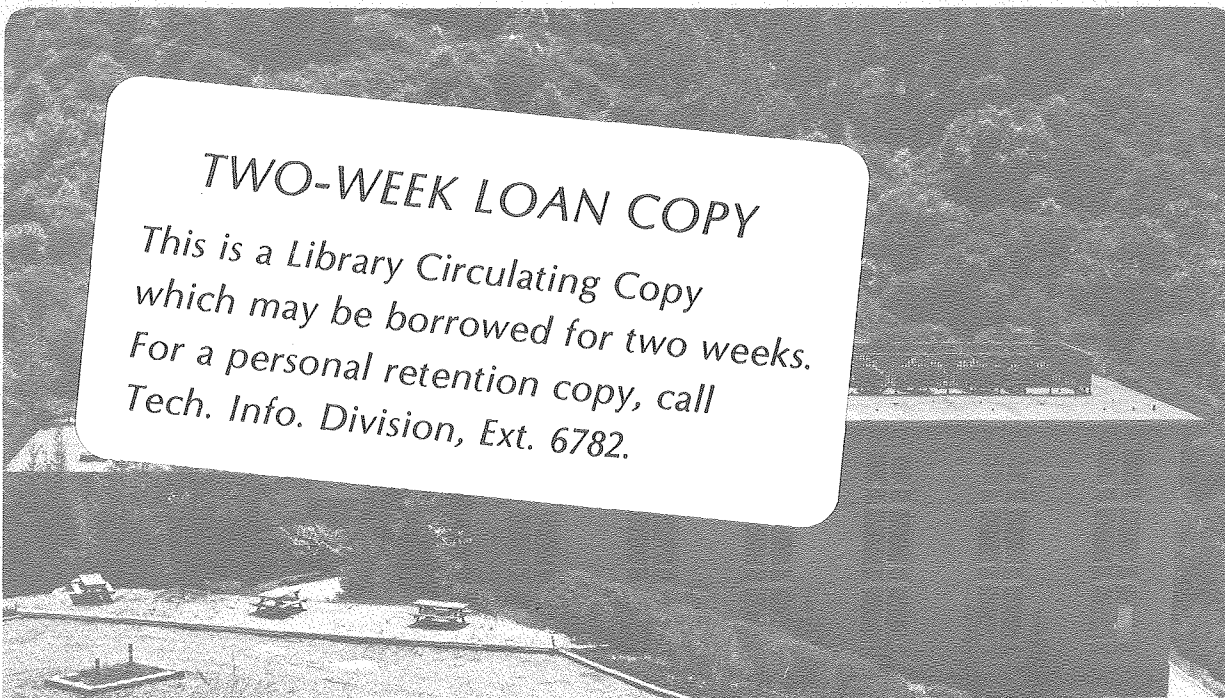
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Fluorogermanium(IV) Salts of Graphite -- A System in Equilibrium with  
Elemental Fluorine

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Summary: Pyrolytic graphite is not intercalated by  $\text{GeF}_4$  alone but is intercalated by  $\text{GeF}_4/\text{F}_2$  mixtures to yield, at the intercalation limit, at  $20^\circ$ , a first-stage material,  $\text{C}_{12}\text{GeF}_{5-6}$ , which is in equilibrium with gaseous fluorine.

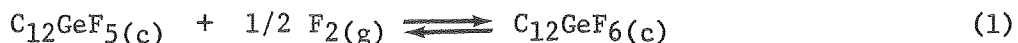
GERMANIUM tetrafluoride is a superior fluoride ion acceptor since it can stabilize the  $\text{O}_2^+$  ion and the  $\text{NF}_4^+$  ion in salts.<sup>1</sup> It is this superior fluoride-ion acceptor capability which must account for our observation that pyrolytic graphite readily intercalates  $\text{GeF}_4$  in the presence of fluorine, but does not do so, even with high pressures of  $\text{GeF}_4$ , if fluorine is absent. Similar experiments, in which  $\text{SiF}_4$  was substituted for  $\text{GeF}_4$ , failed to bring about any silicon fluoride intercalation. It has long been known<sup>2</sup> that  $\text{GeF}_4$  is a superior fluoride ion acceptor to  $\text{SiF}_4$  since, with  $\text{SF}_4$ , the former yields the salt  $(\text{SF}_3^+)_2\text{GeF}_6^{2-}$ , whereas the silicon analogue is not stable at ordinary temperatures and pressures (in spite of the lattice energy of the silicon analogue being slightly more favorable by virtue of the smaller size of  $\text{SiF}_6^{2-}$ ).

Treatment of either powder or pieces of highly oriented pyrolytic graphite (HOPG), with  $\text{GeF}_4/\text{F}_2$  mixtures, results in a  $\text{GeF}_4$  uptake which is dependent upon the quantity of  $\text{F}_2$  available. The quantity of  $\text{F}_2$  determines the stage. A given  $\text{C}_{12n}\text{GeF}_5$  stage takes up  $\text{GeF}_4$  to reach a limiting

composition  $C_{12n}GeF_5 \cdot 1/2 GeF_4$ . In a dynamic vacuum this material loses  $GeF_4$ , but not fluorine. When the  $F_2/GeF_4$  ratio is 1:1, and in abundant supply, the limiting composition of the graphite intercalate is  $C_{12}GeF_6$ . Also, if a first-stage material, which is richer in germanium than  $C_{12}GeF_5$ , is fluorinated,  $GeF_4$  is eliminated and fluorine consumed to again yield  $C_{12}GeF_6$ :



The first-stage material  $C_{12}GeF_6$ , at  $20^\circ$ , loses  $F_2$  in a dynamic vacuum, but not  $GeF_4$ , to yield  $C_{12}GeF_5$ . The change is reversed by applying a 2 atmospheres pressure of fluorine at  $20^\circ$ , the consumption (by tensimetry) being appropriate for the conversion expressed in equation (1):



These observations imply that the free-energy change for equation (1), at  $\sim 20^\circ$ , is close to zero.

It is probable that the formulations for the graphite compounds are  $C_{12}^{2+}GeF_6^{2-}$  and  $C_{12}^+GeF_5^-$ . X-ray diffraction data, from intercalated HOPG pieces, show that the gallery height, "c", (i.e. the graphite-network to next graphite-network spacing) is  $7.80 \text{ \AA}$  for  $C_{12}GeF_6$  and  $8.10 \text{ \AA}$  for  $C_{12}GeF_5$ , which is consistent with marked increase in the Coulombic attraction between guest and host for  $C_{12}^{2+}GeF_6^{2-}$  compared with  $C_{12}^+GeF_5^-$ . The  $C_{12}^{2+}GeF_6^{2-}$  formulation is related to that proposed for the limiting composition<sup>3</sup> of the  $PtF_6$  intercalate,  $C_{12}PtF_6$ . The platinum salt, being diamagnetic, must be  $C_{12}^{2+}PtF_6^{2-}$ , which contrasts with the iridium hexafluoride limiting-composition salt, which is  $C_8^+IrF_6^-$ .<sup>3</sup> The ordered structure for  $C_{12}GeF_6$  is probably as indicated in the Figure.

The remarkable equilibrium (1), must be a consequence of a close balancing of the fluoride ion affinities of  $\text{GeF}_4$ , the lattice energies of  $\text{C}_{12}^{2+}\text{GeF}_6^{2-}$  and  $\text{C}_{12}^+\text{GeF}_5^-$  and the work functions of the graphite. There is no such equilibrium for  $\text{C}_{12}\text{PtF}_6$ , undoubtedly because of much higher stability of  $\text{PtF}_6^{2-}$ , compared with  $\text{GeF}_6^{2-}$ . Even  $\text{PF}_5$ , which is a poorer  $\text{F}^-$  acceptor than  $\text{AsF}_5$ , intercalates in graphite, in the presence of fluorine,<sup>4</sup> to yield at the limit  $\text{C}_8\text{PF}_6$ , but this, like its arsenic and transition metal analogues, is vacuum stable at  $\sim 20^\circ$ .

Clearly  $\text{C}_{12}\text{GeF}_6$  is a solid which must have an oxidizing and fluorinating capability close to that of elemental fluorine itself.

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† on leave from Laboratoire de Chimie du Solide du C.N.R.S., de l'Université de Bordeaux I.

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Figure Structural Model  
for  $C_{12}MF_6$

