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COMPOSITION AND STAGING IN THE GRAPHITE/AsF$_6$ SYSTEM AND ITS RELATIONSHIP TO GRAPHITE/AsF$_5$
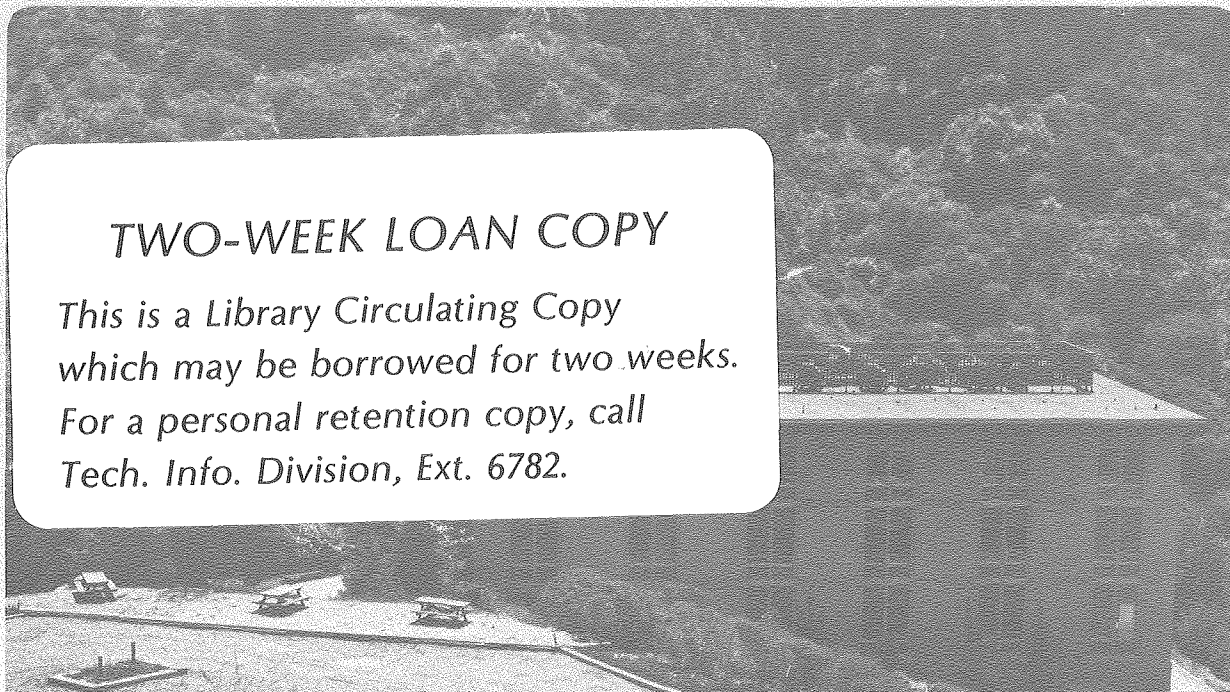
E. M. McCarron and Neil Bartlett

December 1979

DISCLAIMER

Composition and Staging in the Graphite/AsF$_6$ System and its Relationship

to Graphite/AsF$_5$

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Summary: Interconversion, of graphite/AsF$_5$ intercaltes and C$_{12n}^+$AsF$_6^-$ salts,

establishes the equilibrium: $3 \text{ AsF}_5 + 2 \text{ e}^- \rightleftharpoons 2 \text{ AsF}_6^- + \text{AsF}_3$, for AsF$_5$

intercalation, and simple staging/stoichiometry relationships exist for

both the AsF$_5$ and AsF$_6^-$ intercaltes.

INTERCALATION of AsF$_5$ into pyrolytic graphite[1] produces an excellent metal[2]

and there has been much speculation on the nature of the guest species.

Our interest in related AsF$_6^-$ salts[3] prompted our examination of the AsF$_5$

materials and from synchrotron-radiation As-absorption edge studies, we

concluded[4,5] that AsF$_5$ was entering graphite by oxidation according to

the equation:

$$3 \text{ AsF}_5 \ + \ 2 \text{ e}^- \ \longrightarrow \ 2 \text{ AsF}_6^- \ + \ \text{AsF}_3 \tag{1}$$
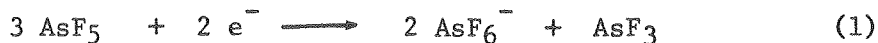
The observation[6] that AsF$_5$ can be recovered from the intercalate, implied

reversibility of (1), but the As-absorption edge studies[4] did indicate

essentially complete conversion to AsF$_6^-$ and AsF$_3$. There has been much

reluctance to accept this interpretation. Some of this has derived from

failure to find AsF$_3$ in the gases from graphite-AsF$_5$.[6] The failure to

observe more than one ^{19}F nmr resonance,[7] and the large electron withdrawal

from the graphite (which extensive conversion to AsF$_6^-$ requires) have also

presented difficulties.[8]

Our investigation of the volatiles from C_xAsF_5 shows that the earlier

findings[6] were misleading. A sample of C_8AsF_5, was prepared from powdered

high-purity pyrolytic graphite, which had been well dried, and pretreated

with fluorine to remove any reducing species. Infrared spectroscopy showed

other infrared-active components to be absent from the AsF_5 used in the

preparation. The volatiles from a C_8AsF_5 sample at 20°, held under vacuum,

were monitored by infrared spectroscopy as a function of pumping time.

Within the first minute the volatiles were largely AsF_5, but AsF_3 was

detected. As the composition of the intercalate approached $C_{10}AsF_{(5-6)}$,

the volatiles proved to be approximately equimolar quantities of AsF_5 and

AsF_3. From $C_{10}AsF_{(5-6)}$ to $C_{14}AsF_6$ (several hours of pumping) the only

volatile detected was AsF_3. Removal of AsF_3 requires an increase in the

AsF_6^- fraction of the arsenic species remaining in the graphite and all

indications are that the vacuum stable product is an AsF_6^- salt. Although,

at 20°, the major volatile from C_8AsF_5 is AsF_5, the only volatile from

the third stage compound $C_{24}AsF_5$ is AsF_3. This is consistent with a higher

positive charge and electron affinity of the carbon network of the first

stage compound, in comparison with the third stage material. Of course

the reversal of (1), to produce AsF_5, requires that the carbon network

should recapture electrons from the AsF_6^-.

In a separate series of experiments, graphite was intercalated by

AsF_5/F_2 mixtures to yield C_xAsF_6. At the intercalation limit,[9] tensimetry

of the F_2 and AsF_5 consumption satisfies the equation: $8 C + AsF_5{(g)} +$

$1/2 F_2{(g)} \rightarrow C_8AsF_6$. The AsF_6^- salts are stable in a vacuum at 20°. By

monitoring highly oriented (c axis) pyrolytic-graphite slabs (of thickness

t) both by micrometry and X-ray diffraction, it has been established that

the composition for each stage is $C_{12n}AsF_6$ (n the stage), up to the first stage onset of $C_{12}AsF_6$. This means that each occupied gallery up to first stage, has a composition $C_{12}AsF_6$, as indicated in Figure 1. The micrometer t/t_0 (t_0 being the thickness of the original graphite) compares closely with the t/t_0(ideal) derived from the X-ray diffraction gallery-height measurements. With sufficient AsF_5/F_2 the first-stage composition can be taken from $C_{12}AsF_6$ (with a gallery height, $\underline{c} = 8.04(2)$ Å) to a limit of C_8AsF_6 ($\underline{c} = 7.86(2)$ Å). Single crystal work establishes that the latter is hexagonal with $a = 4.92(1)$, $c = 7.86(2)$, $V = 165$ Å^3, which volume requires that the AsF_6^- be in close-packed 'planar' array. The $\underline{c}$-axis contraction from $C_{12}AsF_6$ to C_8AsF_6 can be attributed to the increased Coulomb attraction of guest and host, with the change from C_{12}^+ to $C_8^+AsF_6^-$.

In a gallery occupancy of $C_{12}AsF_6$, each anion need have only three anion neighbors, whereas in C_8AsF_6 each is constrained to have six (see Figure 2). We attribute the $C_{12n}AsF_6$ staging-composition relationship to the reduced repulsive interactions offered by the $C_{12}AsF_6$ gallery occupancy. Evidently, opening of virgin galleries is preferred over filling beyond $C_{12}AsF_6$, as long as virgin galleries are available.

Treatment of $C_{12}AsF_6$ with AsF_3 leads to consumption of the latter according to the equation:

$$2\ C_{12}AsF_6\ +\ AsF_3\ \longrightarrow\ 3\ C_8AsF_5$$
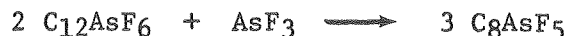
In a vacuum it loses AsF_5 and AsF_3 as for C_8AsF_5 made directly from graphite and AsF_5. Similar conversions can be made at other compositions. There is no perceptable change in t/t_0 when AsF_3 is added to or removed from a monolithic sample and X-ray diffraction findings indicate no change

in stage. It had previously been observed[10] that the graphite/AsF_5 stages obey the relationship $C_{8n}AsF_5$ where n is the stage (see Figure 1). Since C_8AsF_5 can be represented as $C_{12}^+AsF_6^-{\cdot}1/2\ AsF_3$ (if the equilibrium for (1) is far to the right) it is reasonable to suppose that the neutral AsF_3 molecules occupy the vacancies in the $C_{12}AsF_6$ anion arrangement, as proposed in Figure 2(a). The equality (within experimental error) of the $\underline{c}$ spacing for C_8AsF_5 (8.05(3) Å) with that for $C_{12}^+AsF_6^-$ (8.04(3) Å) also agrees with essentially complete conversion of AsF_5 to AsF_6^- and AsF_3. Recent EXAFS studies for C_xAsF_5, C_yAsF_6, AsF_5, AsF_3 and a variety of AsF_6^- salts[11] also indicate that there is unlikely to be more than 5% of free AsF_5 in $C_{10}AsF_5$ and are fully consistent with the guest species being AsF_6^- and AsF_3.

With the demonstration that AsF_3 can be removed from C_xAsF_5, attention must be paid to the preparative conditions for 'C_xAsF_5' samples, since AsF_3 departure will result in AsF_6^- salt formation. We suggest that the residual compounds are such salts.

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5. N. Bartlett, B. W. McQuillan and A. S. Robertson, _Mat. Res. Bull._, 1978, _13_, 1259.

6. H. Selig, M. J. Vasile, F. A. Stevie and W. H. Sunder, _J. Fluorine Chem._, 1977, _10_, 299.

7. L. Ebert and H. Selig, _Mat. Sci. Eng._, 1977, _31_, 177.

8. M. J. Moran, J. E. Fischer and W. R. Salaneck, personal communication.

9. At lower guest concentrations (e.g. $C_{12}AsF_6$ the material takes up more fluorine, which presumably occupies vacancies in the galleries. This fluorine can be 'titrated' with more AsF_5 to yield AsF_6^-.

10. E. R. Falerdeau, L. R. Hanlon and T. J. Thompson, _Inorg. Chem._, 1978, _17_, 301.

11. A. S. Robertson, Ph.D. Thesis, The University of California, Berkeley, LBL report 9840, 1979.

Figure Captions

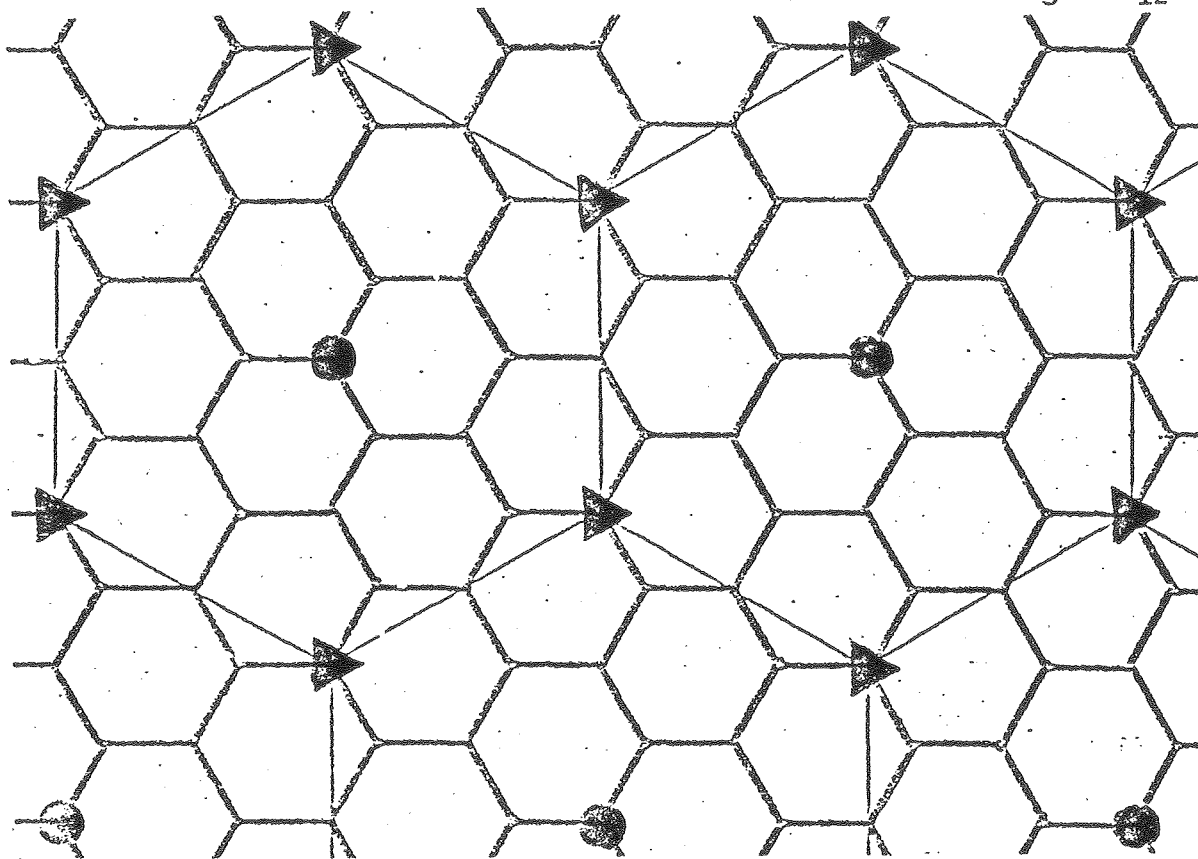Figure 1. Composition/staging relationships for C_xAsF_5 and C_xAsF_6.

Figure 2. Structural models for (a) $C_{12}AsF_6$ or $C_{12}AsF_6 \cdot 1/2 \ AsF_3$ and (b) C_8AsF_6.
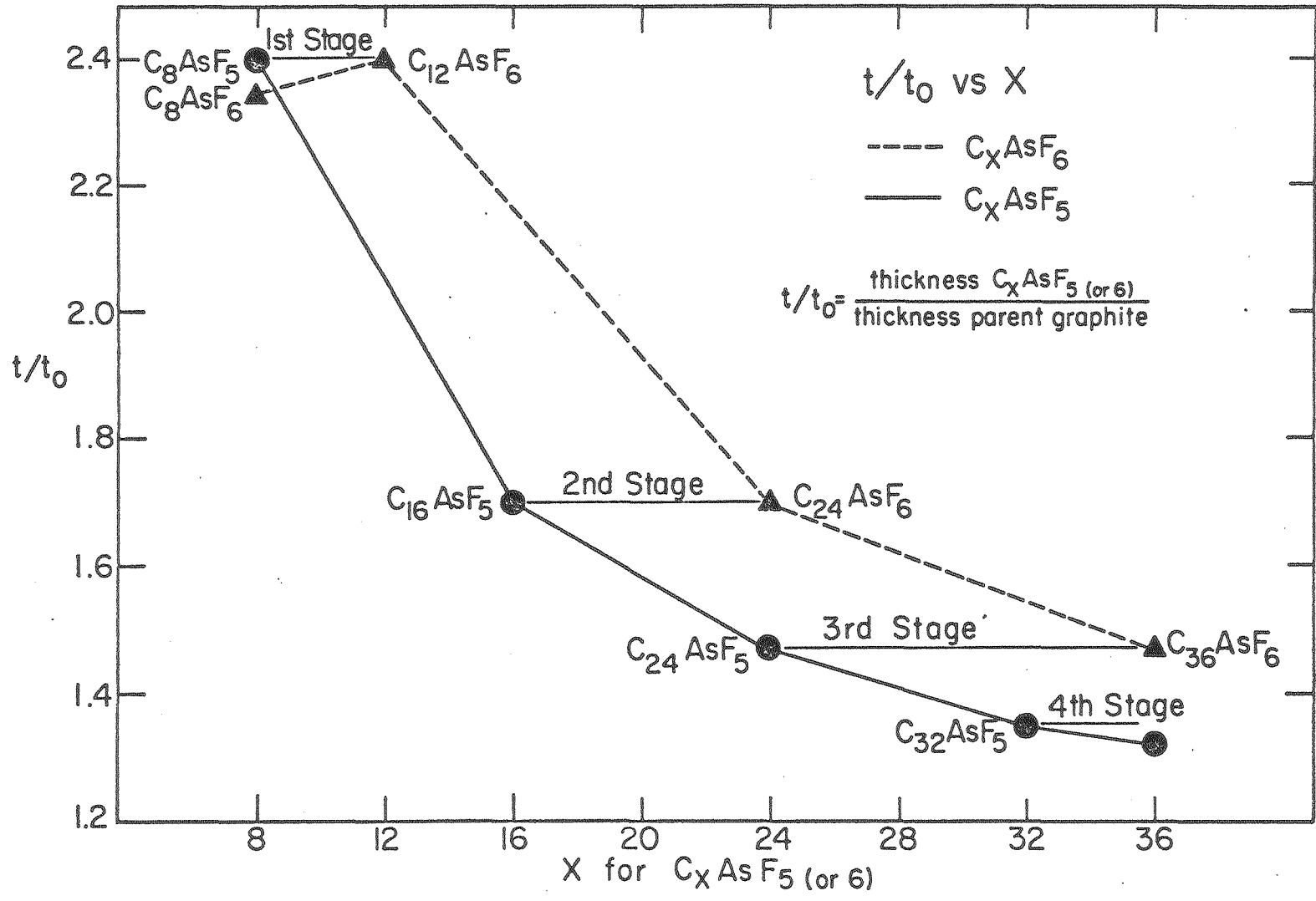
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Figure 2. Structural models for (a) $C_{12}AsF_6$ or $C_{12}AsF_6 \cdot 1/2\ AsF_3$ and (b) C_8AsF_5.

(a) $C_{12}AsF_6$ or $C_{12}AsF_6 \cdot 1/2\ AsF_3$. ▲ represents AsF_6^- in $C_{12}AsF_6$
● represents AsF_3 in $C_{12}AsF_6 \cdot 1/2\ AsF_3$.

(b) C_8AsF_6. ▲ represents AsF_6^-.