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Composition and Staging in the Graphite/AsF₆ System and its Relationship to Graphite/AsF₅

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Summary: Interconversion, of graphite/AsF₅ intercalates and C_{12n}⁺AsF₆⁻ salts, establishes the equilibrium: $3 \text{ AsF}_5 + 2 \text{ e}^- \rightleftharpoons 2 \text{ AsF}_6^- + \text{ AsF}_3$, for AsF₅ intercalation, and simple staging/stoichiometry relationships exist for both the AsF₅ and AsF₆⁻ intercalates.

INTERCALATION of AsF₅ into pyrolytic graphite¹ produces an excellent metal² and there has been much speculation on the nature of the guest species. Our interest in related AsF₆⁻ salts³ prompted our examination of the AsF₅ materials and from synchrotron-radiation As-absorption edge studies, we concluded^{4,5} that AsF₅ was entering graphite by oxidation according to the equation:

The observation⁶ that AsF₅ can be recovered from the intercalate, implied reversibility of (1), but the As-absorption edge studies⁴ did indicate essentially complete conversion to AsF₆⁻ and AsF₃. There has been much reluctance to accept this interpretation. Some of this has derived from failure to find AsF₃ in the gases from graphite-AsF₅.⁶ The failure to observe more than one ¹⁹F nmr resonance,⁷ and the large electron withdrawal from the graphite (which extensive conversion to AsF₆⁻ requires) have also presented difficulties.⁸

Our investigation of the volatiles from C_xAsF_5 shows that the earlier findings⁶ 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 $t/t_0(\text{ideal})$ 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, $c = 8.04(2) \text{ \AA}$) to a limit of C_8AsF_6 ($c = 7.86(2) \text{ \AA}$). Single crystal work establishes that the latter is hexagonal with $a = 4.92(1)$, $c = 7.86(2)$, $V = 165 \text{ \AA}^3$, which volume requires that the AsF_6^- be in close-packed 'planar' array. The 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:

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 perceptible 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 observed¹⁰ that the graphite/AsF₅ stages obey the relationship C_{8n}AsF₅ where n is the stage (see Figure 1). Since C₈AsF₅ can be represented as C₁₂⁺AsF₆⁻1/2 AsF₃ (if the equilibrium for (1) is far to the right) it is reasonable to suppose that the neutral AsF₃ molecules occupy the vacancies in the C₁₂AsF₆ anion arrangement, as proposed in Figure 2(a). The equality (within experimental error) of the c spacing for C₈AsF₅ (8.05(3) Å) with that for C₁₂⁺AsF₆⁻ (8.04(3) Å) also agrees with essentially complete conversion of AsF₅ to AsF₆⁻ and AsF₃. Recent EXAFS studies for C_xAsF₅, C_yAsF₆, AsF₅, AsF₃ and a variety of AsF₆⁻ salts¹¹ also indicate that there is unlikely to be more than 5% of free AsF₅ in C₁₀AsF₅ and are fully consistent with the guest species being AsF₆⁻ and AsF₃.

With the demonstration that AsF₃ can be removed from C_xAsF₅, attention must be paid to the preparative conditions for 'C_xAsF₅' samples, since AsF₃ departure will result in AsF₆⁻ salt formation. We suggest that the residual compounds are such salts.

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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 $C_{12}AsF_6 \cdot 1/2 AsF_3$. $\blacktriangle$ represents AsF_6^- in $C_{12}AsF_6$
 $\bullet$ represents AsF_3 in $C_{12}AsF_6 \cdot 1/2 AsF_3$.

(b) C_8AsF_6 . $\blacktriangle$ represents AsF_6^- .