

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

By EUGENE M. MCCARRON and NEIL BARTLETT*

(The Chemistry Department, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720)

Summary Interconversion, of graphite-AsF₅ intercalates and C_{12n}⁺AsF₆⁻ salts, establishes the equilibrium: 3AsF₅ + 2e⁻ ⇌ 2AsF₆⁻ + AsF₃, 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 equation (1). 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 into 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 n.m.r. resonance,⁷ and the large electron withdrawal from the graphite (which extensive conversion into AsF₆⁻ requires) have also presented difficulties.⁸

Our investigation of the volatile products from C_xAsF₅ shows that the earlier findings⁶ were misleading. A sample of C₈AsF₅, was prepared from powdered high-purity pyrolytic graphite, which had been well dried, and pretreated with fluorine to remove any reducing species. I.r. spectroscopy showed other i.r.-active components to be absent from the

AsF₅ used in the preparation. The volatile products from a C₈AsF₅ sample at 20 °C, held under vacuum, were monitored by i.r. spectroscopy as a function of pumping time. Within the first minute the volatile product was largely AsF₅, but AsF₃ was also detected. As the composition of the intercalate approached C₁₀AsF₅₋₆, the volatile products proved to be approximately equimolar quantities of AsF₅ and AsF₃. From C₁₀AsF₅₋₆ to C₁₄AsF₆ (after several hours of pumping) the only volatile product detected was AsF₃. Removal of AsF₃ requires an increase in the AsF₆⁻ fraction of the arsenic species remaining in the graphite and all indications are that the vacuum stable product is an AsF₆⁻ salt. Although, at 20 °C, the major initial volatile product from C₈AsF₅ is AsF₅, the only one from the third stage compound C₂₄AsF₅ is AsF₃. This is consistent with a higher positive charge and electron affinity of the carbon network in the first stage C₈ compound, relative to the third stage material. Of course the reversal of (1), to produce AsF₅, requires that the carbon network should recapture electrons from the AsF₆⁻.

In a separate series of experiments, graphite was intercalated by AsF₅-F₂ mixtures to yield C_xAsF₆. At the intercalation limit,† tensimetry of the F₂ and AsF₅ consumption satisfies the equation: 8C + AsF_{5(g)} + 1/2F_{2(g)} → C₈AsF₆. The AsF₆⁻ salts are stable in a vacuum at 20 °C. 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_{12*n*}AsF₆ (*n* the stage), up to the first stage onset of C₁₂AsF₆. This means that each occupied gallery up to the first stage, has a composition C₁₂AsF₆, 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 AsF₅/F₂ the first-stage composition can be taken

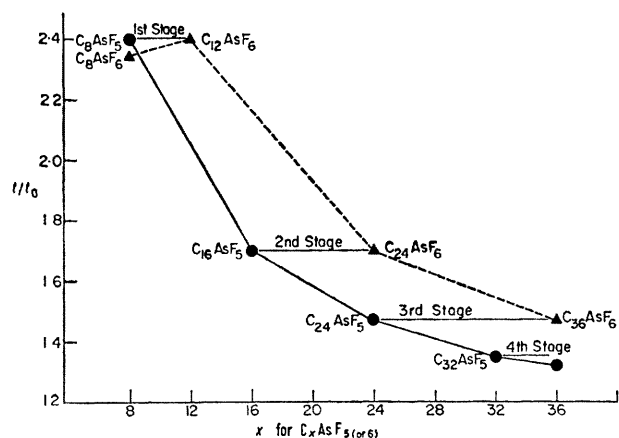


FIGURE 1. Composition/staging relationships for C_xAsF₅ and C_xAsF₆. Dashed line = C_xAsF₆, solid line = C_xAsF₅. *t*/*t*₀ = [thickness C_xAsF_{5(or 6)}]/(thickness parent graphite).

† At lower guest concentrations (e.g., C₁₂AsF₆) the material takes up fluorine to a limit C_xAsF₆·½F₂. This F₂ presumably occupies vacancies in the galleries and can be 'titrated' with more AsF₅ or AsF₃ to yield AsF₆⁻.

‡ We have noted similar effects of charging on the gallery height ('*c*') in other systems (N. Bartlett, E. M. McCarron, B. W. McQuillan, and T. E. Thompson, *Synthetic Metals*, 1980, 1, 221). Thus C₁₂²⁺PtF₆²⁻ and C₈⁺IrF₆⁻ have '*c*' values of 7.56 and 8.06 Å, respectively. Since the formula unit volumes of NO⁺IrF₆⁻ and NO⁺PtF₆⁻ are 129.32 and 129.25 Å³, respectively (N. Bartlett, *Angew. Chem.*, 1968, 7, 433). IrF₆⁻ and PtF₆⁻ must have almost the same volume. The volume of PtF₆²⁻ must be greater than that of PtF₆⁻, therefore we can be sure that the smaller value of '*c*', for C₁₂⁺PtF₆²⁻ relative to C₈⁺IrF₆⁻, must be a consequence of the greater Coulomb attraction, between guest and host, in the platinum salt.

from C₁₂AsF₆ [with a gallery height, *c* = 8.04(2) Å] to a limit of C₈AsF₆ [*c* = 7.86(2) Å].‡ Single crystal work establishes that the latter is hexagonal with *a* = 4.92(2), *c* = 7.86(2), *V* = 165 Å³, the volume of which requires that the AsF₆⁻ be in close-packed 'planar' array. The *c*-axis contraction from C₁₂AsF₆ to C₈AsF₆ can be attributed to the increased Coulomb attraction of guest and host, with the change from C₁₂⁺ to C₈⁺AsF₆⁻.

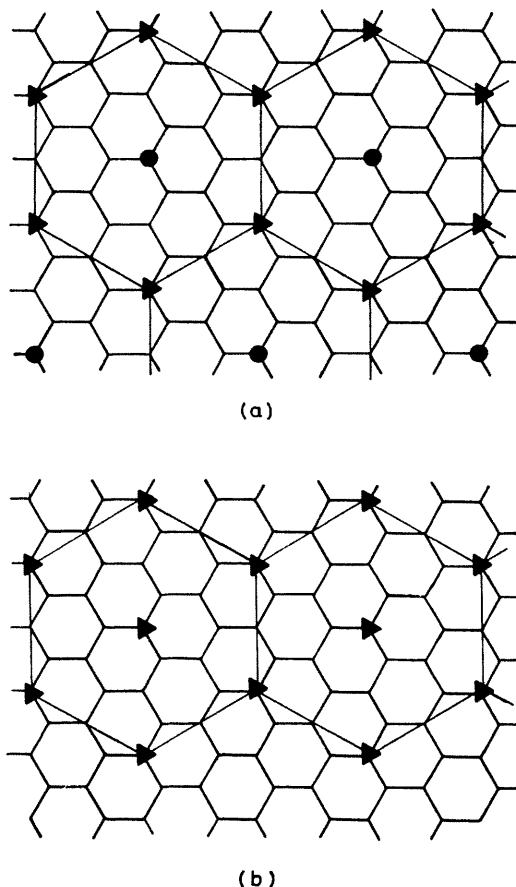


FIGURE 2. Structural models for (a) C₁₂AsF₆ or C₁₂AsF₆·½AsF₃; ▲ AsF₆⁻ in C₁₂AsF₆; ● AsF₃ in C₁₂AsF₆·½AsF₃ and (b) C₈AsF₆; ▲ AsF₆⁻.

In a gallery occupancy of C₁₂AsF₆, each anion need have only three anion neighbours, whereas in C₈AsF₆ each is constrained to have six (see Figure 2). We attribute the C_{12*n*}AsF₆ staging-composition relationship to the reduced repulsive interactions offered by the C₁₂AsF₆ gallery occupancy. Evidently, opening of virgin galleries is preferred over filling beyond C₁₂AsF₆, as long as virgin galleries are available.

Treatment of $C_{12}AsF_6$ with AsF_3 leads to consumption of the latter according to equation (2):



In a vacuum it loses AsF_5 and AsF_3 as in 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 observed⁹ 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 $C_{12}^+AsF_6^- \cdot 1/2AsF_3$ [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 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 into 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^- salts¹⁰ 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.

We thank the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, EXXON Corporation, and the University of California, Berkeley, Committee on Research for support, and Dr. A. Moore of Union Carbide for a supply of pyrolytic graphite.

(Received, 7th January 1980; Com. 009.)

¹ Lin Chun-Hsu, H. Selig, M. Rabinovitz, I. Agranat, and S. Sarig, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 601.

² E. R. Falardeau, G. M. T. Foley, C. Zeller, and F. L. Vogel, *J. Chem. Soc., Chem. Commun.*, 1977, 389.

³ T. J. Richardson and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 1974, 427; and N. Bartlett, R. N. Biagioni, E. M. McCarron, B. W. McQuillan, and F. Tanzella, 'Molecular Metals,' ed. W. E. Hatfield, Plenum, New York, 1979, p. 293.

⁴ N. Bartlett, R. N. Biagioni, B. W. McQuillan, A. S. Robertson, and A. C. Thompson, *J. Chem. Soc. Chem. Commun.*, 1978, 200.

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 E. R. Falardeau, L. R. Hanlon, and T. J. Thompson, *Inorg. Chem.*, 1978, **17**, 301.

¹⁰ A. S. Robertson, B. W. McQuillan, M. P. Klein, and N. Bartlett, to be published.