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COMPOSITIONAL, STRUCTURAL AND PHYSICAL STUDIES OF SOME GRAPHITE HEXAFLUOROARSENATES AND THEIR RELATIVES

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The F/As molar ratio for the vacuum-stable products obtained by treating graphite, at 20°, with (1) AsF_5, (2) AsF_5 plus F_2, and (3) O_2AsF_6, has been established to be 6. Route (1) gives mixtures of first and second-stage salts, whereas (2) and (3) readily yield first-stage material. This is attributed to the greater oxidizing potential of the reagents in (2) and (3). The volatiles from the route (1) synthesis are AsF_5 and AsF_3, and from (2) AsF_5. The interlayer spacing (I_c) of the occupied graphite galleries in the vacuum-stable hexafluoroarsenates is ca. 7.6 Å and $\underline{c} \simeq 7.6 + 3.35\ (n-1)$ Å (where n is the stage). For the products of routes (1) and (2), prior to removal of volatiles, $I_c \simeq 8.0$ Å and $\underline{c} \simeq 8.0 + 3.35(n-1)$ Å.

X-ray powder diffraction data for the first-stage salt $C_{14}AsF_6$ have established that the AsF_6^- species are nestled in contiguous three-fold sets of C-atom hexagons of the graphite. This requires a staggering of the enclosing C-atom layers, as in graphite. Each neighboring pair of C-atom sheets contains an ordered closest-packed assembly, appropriate for $C_{14}AsF_6$. Aside from the restriction imposed by AsF_6^--nestling, the layers of composition $C_{14}AsF_6$ are otherwise randomly stacked. Materials prepared by direct interaction of graphite and AsF_5, prior to removal of volatiles, have a larger interlayer spacing, $I_c \simeq 8.0$ Å than $C_{14}AsF_6$ ($I_c \simeq 7.6$ Å). X-ray data for such materials are accounted for by a random distribution of un-nestled AsF_x species, between eclipsed carbon-atom sheets.

The C_xAsF_6 salts are all good conductors (approximately the conductivity of Al metal). Addition of fluorine to the salts decreases their conductivities substantially (approximately that of graphite).