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Oxidative Intercalation of Graphite by Fluoroanionic Species Evidence for Thermodynamic Species

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## EVIDENCE THAT THE BARRIER TO OXIDATIVE INTERCALATION OF GRAPHITE BY FLUOROANIONIC SPECIES IS THERMODYNAMIC

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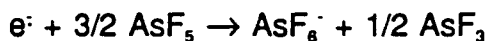
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**Abstract** Whether or not oxidative intercalation of graphite by fluoroanions can occur may be estimated from the electron affinity,  $E$ , ( $-\Delta H_{298}$  in kcal mole<sup>-1</sup>) of the oxidizing half reaction. For first-stage salts with  $MF_6^-$  guests,  $E$  must exceed exceed 120. The values of  $E$  ( $e^- + 3/2 MF_5 \rightarrow MF_6^- + 1/2 MF_3$ ) for  $AsF_5$  and  $PF_5$  (125 and 87 respectively) account for the spontaneous intercalation of graphite by  $AsF_5$  and the failure of  $PF_5$  to do so. Spontaneous intercalation by  $PF_5 + F_2$  spontaneously occurs because  $E(e^- + PF_5 + 1/2 F_2 \rightarrow PF_6^-) = 165$ . The thermodynamic nature of the barrier to intercalation is demonstrated by the reduction of  $C_xPF_6$  salts by  $PF_3$ :  $C_xPF_6 + 1/2PF_3 \rightarrow xC + 3/2 PF_5$ . Chlorine with certain fluoroacids can also bring about intercalation of fluoroanions. Polarizable neutral molecules, by improving the lattice energetics of graphite salts, may also be spontaneously intercalated: e.g.  $C_{14}AsF_6 + 1/2 AsF_5 \rightarrow C_{14}AsF_6 \cdot 1/2 AsF_5$ . When high positive charge at carbon occurs,  $F^-$  is transferred from the fluoroanion to the carbon and novel graphite fluorides (e.g.  $C_{1.3}F$ ) are formed.

## Introduction

Most of the reactants which bring about intercalation of graphite are either strong oxidants or reductants e.g. respectively nitric acid or alkali metal<sup>1,2,3</sup>. The oxidation or the reduction of the graphite that accompanies the intercalation was clearly shown by Ubbelohde and his coworkers<sup>4,5,6</sup> to be accompanied by an increase in the in-plane resistivity of the graphite, which in fully intercalated material was commonly an order of magnitude greater than in the pristine graphite from which the intercalation compounds had been obtained. The band structures for graphite of Coulson and his coworkers<sup>7</sup> nicely account for the conductivity in terms of increase in the number of electron carriers in the conduction band of the reduced graphite or an increased number of electron holes in the valence band of oxidized graphite.

The preparation of  $C_6F_6^+$  salts<sup>8</sup> and the derivation from them of polycyclic cation salts<sup>9,10</sup>, suggested that very high positive charges might be sustainable in graphite by  $AsF_6^-$  and other stable perfluoroanions and that excellent electrical conductors of high-oxidation-state carbon could thereby be obtained. This led to synthesis of graphite fluoroarsenates via interaction of graphite with  $O_2^+AsF_6^-$  and to the discovery<sup>11</sup> that the guests in the product of the interaction of graphite with  $AsF_5$  were in accord with the latter acting as an electron-oxidizer according to the equation:



The graphite/ $AsF_5$  intercalation compound had been prepared first by Selig and Agranat and their coworkers<sup>12</sup> and had aroused much interest because of Vogel's finding<sup>13</sup> that the in-plane specific conductivity of some of the graphite/ $AsF_5$  materials exceeded that of copper. Although the (graphite)  $^+AsF_6^-$  salts appeared to involve higher electron withdrawal from the graphite, higher conductivities than those of the graphite/ $AsF_5$  were not observed.<sup>14</sup> Indeed when the (graphite)  $^+AsF_6^-$  salts were prepared from the interaction of graphite with  $AsF_5/F_2$  gaseous mixtures,<sup>15</sup> the product salts were often less conductive

than their partially oxidized relative, graphite/ $\text{AsF}_5$ . It appeared that the poor electrical conductivity must be associated with bonding of fluorine to carbon, throughout the graphite structure, the fluorine migration throughout the galleries being facilitated by the intercalated species. Direct evidence<sup>14</sup> for a decrease in conductivity was obtained in the case of graphite intercalation by  $\text{IrF}_6$  when the first stage was reached. This and the finding from Mössbauer spectroscopy<sup>16</sup> that the first-stage  $\text{C}_x\text{IrF}_6$  salt contained some Ir(V) in lower than  $\text{O}_h$  site symmetry were consistent with transfer of  $\text{F}^-$  from the anion to the carbon.

Aside from this matter of the transfer of fluorine to the highly oxidized carbon, it did appear to Bartlett and McQuillan<sup>17</sup> that the intercalation of graphite by oxidizing fluorospecies was thermodynamically determined. Although Born-Haber cycles have long been applied to intercalation compounds of graphite (e.g. see G. R. Hennig review<sup>1</sup>) acceptance of a salt formulation for graphite compounds formed with guests capable of yielding fluorooanions (e.g.  $\text{AsF}_5$ ) was not generally accepted at that time, Bartlett and McQuillan noted that, at least for  $\text{MF}_6^-$  salts, where the nearly isodimensional nature of  $\text{MF}_6^-$  would result in similar lattice energetics for a given level of charge, the free energy of formation would depend most, with change in M, upon the electron affinity of the oxidizing half reaction. They estimated a threshold electron affinity of approximately  $125 \text{ kcal mole}^{-1}$  but they did not establish the thermodynamic nature of that threshold.

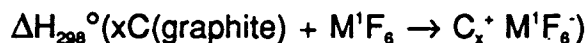
In this paper further evidence for the importance of the electron affinity of the oxidizing half reaction, in the intercalation of graphite by fluorospecies, is provided. Moreover, the simple thermodynamic model accounts for the oxidative intercalation of graphite by fluoroanions is confirmed by reversal of the intercalation in reactions of known enthalpy change. Threshold values of E for the onset of intercalation and for first-stage intercalation by  $\text{MF}_6^-$  have also been assessed.

In addition, it is seen that certain salts e.g.  $\text{C}_{28}^+\text{AsF}_6^-$  provide for the access of

fluorine throughout the galleries of the graphite and its extensive fluorination. This has resulted in the separation of a  $C_xF$  phase which has proved to be fluorinated  $sp^2$  carbon. That phase, which is an insulator, can have a fluorine content as high as  $C_{1.3}F$ .

### Discussion

The hexafluorides of the third transition series elements ( $M^I$ ) have interatomic distances which change only slightly with atomic number<sup>18</sup> and their effective packing volumes<sup>19</sup> are similar. It is therefore a good approximation for our present purposes to assume that the work done in separating the graphite-atom sheets ( $W$ ) will be the same for all in making a salt of given composition  $C_xM^IF_6$ . In addition the lattice energies ( $U$ ) for all  $M^I$  would be alike. Since for a given level of charging ( $C_x^+$ ) the work function ( $I$ ) would be the same we can therefore expect the enthalpy change for the reaction:

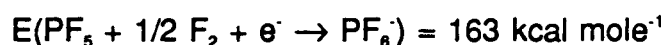


to change in step with the electron affinity,  $E$ , of  $M^IF_6$ , in accord with the cycle illustrated in Figure 1. George and Beauchamp<sup>20</sup> have measured  $E(WF_6) = 81 \text{ kcal mole}^{-1}$  and Nikitin *et al*<sup>21</sup> have evaluated  $E(PtF_6)$  to be  $184 \text{ kcal mole}^{-1}$ . Since the observed chemistry<sup>22</sup> requires a smooth increase in  $E$  with atomic number for these hexafluorides, the  $E(MF_6)$  for the other fluorides are obtained by interpolation. They provide an excellent basis for assessment of the threshold for intercalation to form  $C_x^+M^IF_6$ . Magnetic data<sup>14</sup> for the  $M=Os$  and  $Ir$  salts  $C_xM^IF_6$  have established the quinquevalence of the metals. Moreover since  $WF_6$  will not by itself bring about intercalation whereas both  $OsF_6$  and  $IrF_6$  form first stage salts, and  $ReF_6$  a higher stage salt<sup>23</sup>, it was evident that the  $E(M^IF_6)$  threshold for intercalation of graphite by  $MF_6$  had to be between 81 and 106 kcal mole (the  $E(WF_6)$  and  $E(ReF_6)$  values). Also the threshold  $E(MF_6)$  value for first-stage  $C_x^+M^IF_6$  formation had to be between  $E(ReF_6)$  and  $E(OsF_6)$  i.e. between 106 and 131 kcal mole<sup>-1</sup>.



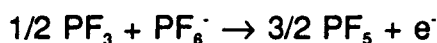
Since all  $\text{MF}_6^-$  ions have M-F distances<sup>24</sup> between 1.7 and 1.9 Å it is probably not a gross approximation to extend the assumptions of the constancy of  $\underline{W}$  and  $\underline{U}$ , used for the third transition series  $\text{M}^+\text{F}_6^-$  to all  $\text{MF}_6^-$ . This approximation appears to be valid as the following examples and the data given in Figure 2 illustrate.

Although  $\text{PF}_5$  (in contrast to  $\text{AsF}_5$ ) does not itself bring about intercalation of graphites, in admixture with fluorine first-stage salts are easily formed<sup>25,28</sup> at approximately 20°C. This is because<sup>27</sup>



which is slightly greater than  $E(\text{IrF}_6)$ . Since the electron affinity of the analogous  $\text{AsF}_5/\text{F}_2$  reaction is even greater<sup>28</sup>, the easy formation<sup>11</sup> of first-stage  $\text{C}_x^+\text{AsF}_6^-$  salts is accounted for. But the  $\text{C}_x^+\text{PF}_6^-$  salts also provide for the demonstration of the thermodynamic basis of the electron affinity threshold.

Treatment of second and higher stage  $\text{C}_x^+\text{PF}_6^-$  salts with  $\text{PF}_3$  at approximately 20°C, reduces the salts with elimination<sup>27,29</sup> of  $\text{PF}_5$  according to the equation:



for which the enthalpy change<sup>27</sup> of 87 kcal mole<sup>-1</sup> represents the electron affinity for the reverse reaction. This is not much greater than  $E(\text{WF}_6)$ , and since  $\text{WF}_6$  by itself is not intercalated by graphite these electron affinities are inadequate to meet the requirements for graphite intercalation by  $\text{MF}_6^-$ . On the other hand, the spontaneous intercalation of graphite by  $\text{AsF}_5$  (ref. 12) is evidently a consequence of the high electron affinity of the oxidizing half reaction since<sup>27</sup>  $E(e^- + 3/2 \text{AsF}_5 \rightarrow \text{AsF}_6^- + 1/2 \text{AsF}_3) \geq 123 \text{ kcal mole}^{-1}$ .

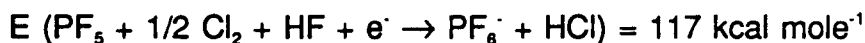
It is gratifying that the vacuum stable  $\text{C}_x\text{AsF}_6$  product obtained by removing  $\text{AsF}_5$  and  $\text{AsF}_3$  from the graphite/ $\text{AsF}_5$  material,<sup>30</sup> is a mixture of first and second stage  $\text{C}_x\text{AsF}_6$  salts. Even repeated treatment of graphite with  $\text{AsF}_5$  does not yield a pure first stage salt and treatment of first stage  $\text{C}_x^+\text{AsF}_6^-$  (made via  $\text{AsF}_5 + \text{F}_2$ ) with a half molar quantity of  $\text{AsF}_3$  leads to a mixture of second and first-stage  $\text{C}_x\text{AsF}_6$ . Here is clear evidence that

that the  $E$  for the  $\text{AsF}_5$  electron-oxidation half reaction is close to that for the first-stage  $\text{C}_x\text{AsF}_6$  thermodynamic threshold.

It now appears that this simple model for  $\text{C}_x^+\text{MF}_6^-$  salts also fits non octahedral  $\text{MF}_y^-$ , so long as the effective height of  $\text{MF}_y^-$  in the graphite galleries is close to that of  $\text{MF}_6^-$ . Recent examples<sup>31</sup> from these laboratories include the intercalation of  $\text{GeF}_5^-$  from  $\text{GeF}_4/\text{Cl}_2$  mixture, the electron affinity for the appropriate reaction being;



and  $\text{PF}_6^-$  from  $\text{PF}_5/\text{Cl}_2/\text{HF}$  mixture for which



In conformity with these electron affinities the intercalation is spontaneous but first stage salts are not produced.

In the example of  $\text{GeF}_5^-$  intercalation just described we have departed from the case of  $\text{MF}_6^-$  guest species. Since  $\text{GeF}_5^-$  has one F ligand less it must have an effective volume, based on Zachariasen's criterion<sup>32</sup>, of approximately  $17 \text{ \AA}^3$  less than  $\text{MF}_6^-$ . For closely packed guest species this would be important. First let us examine the consequences of volume on lattice enthalpy.

Figure 3 illustrates a remarkably simple correlation between lattice enthalpies and the formula unit volume for  $\text{A}^+\text{X}^-$  salts recognized by Mallouk *et al*<sup>28</sup> as being within the usual errors of rather sophisticated evaluations from known structures and partial charge distributions. The empirical relationship

$$U(\text{A}^+\text{X}^-) \text{ (in kcal mole}^{-1}\text{)} = 556.3[V(\text{in } \text{\AA}^3)]^{-1/3} + 26.3$$

should be limited in application to light-atom hard-ligand cases since the equation does not contain explicitly a closed-shell repulsion term. The advantage of the relationship is that it immediately provides for an assessment of the lattice energy of an  $\text{A}^+\text{X}^-$  salt if the close-packing volume is known.

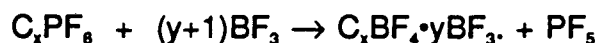
It is apparent that if the cation is large, e.g.  $[(n\text{-butyl})_4\text{N}]^+$ , changing the anion from  $\text{PF}_6^-$  to  $\text{BF}_4^-$  changes the lattice enthalpy less than in the case of  $\text{K}^+$  salts. Indeed

for  $\text{KPF}_6$  and  $\text{KBF}_4$  salts the difference in lattice enthalpy is approximately 10 kcal to the advantage of  $\text{KBF}_4$ . But the fluoride ion affinities<sup>28</sup> ( $-\Delta H^\circ_{298}, \text{MF}_y + \text{F}^- \rightarrow \text{F}_{y+1}^-$ ; in kcal mole<sup>-1</sup>) are:  $\text{BF}_3$ , 92;  $\text{PF}_5$ , 101). Therefore



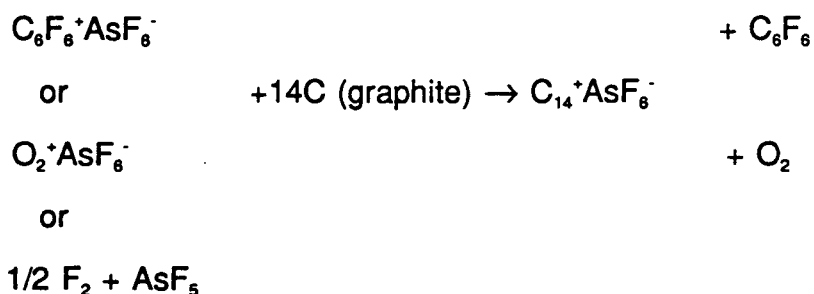
Although the entropy change is slightly unfavorable it is not sufficient to render  $\Delta G^\circ_{298}$  positive.<sup>33</sup> On the other hand in the case of the  $[(n\text{-butyl})_4\text{N}]^+$  salts the lattice energy favors the  $\text{BF}_4^-$  much less than in the  $\text{K}^+$  case. The entropy change is nearly as in the  $\text{K}^+$  salt situation. The consequences are dramatic to the chemistry.  $\text{KPF}_6$  is quantitatively converted<sup>34</sup> to  $\text{KBF}_4$  by  $\text{BF}_3$  at 20°C, whereas the mixed butyl ammonium salts are in equilibrium with  $\text{BF}_3$  and  $\text{PF}_5$  at ordinary pressures.

Since graphite has a much smaller effective radius than  $[(n\text{-butyl})_4\text{N}]^+$ , at least normal to the sheet ( $r_{\text{eff}} \approx 1.7 \text{ \AA}$ ), the impact of volume of the anion upon the lattice energy is important. Thus the graphite hexafluorophosphate salt, like  $\text{KPF}_6$ , and unlike  $[(n\text{-butyl})_4\text{N}]^+ \text{PF}_6^-$ , is quantitatively converted<sup>34</sup> by  $\text{BF}_3$  to the fluoroborate

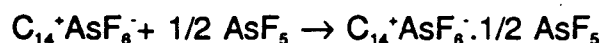


But as the equation demonstrates, more  $\text{BF}_3$  is taken up than  $\text{PF}_5$  liberated. This is an oddity of the graphite salt situation. Here, in contrast to the  $\text{K}^+$  and butyl ammonium salts, the anions are exposed to one another in the galleries between the carbon sheets. Evidently the additional  $\text{BF}_3$  uptake provides for increased screening of anion from anion. Indeed  $y$  can be as great as 3 with ordinary pressures (approximately 1 atmos.) of  $\text{BF}_3$  and a second stage  $\text{C}_x\text{PF}_6$  salt can yield a first stage salt  $\text{C}_x\text{BF}_4 \cdot 3\text{BF}_3$ .

A more dramatic instance of the effect of 'dielectric spacers' in graphite salts is provided<sup>30</sup> by the first stage fluoroarsenate of composition  $\text{C}_{14}\text{AsF}_6$ . This material is prepared by the following routes



and is identical to the first-stage component of the vacuum-stable product of the interaction of graphite and  $\text{AsF}_5$  gas. The  $\text{AsF}_6^-$  are nestled in ordered domains within the graphite galleries as shown in Figure 4. This is an accidental consequence of the F - F nearest neighbor distance in  $\text{AsF}_6^-$  being similar to the distance between the centers of contiguous hexagons in the graphite sheet structure. As may be seen from Figure 4 closer packing of the nestled  $\text{AsF}_6^-$  is not possible and this arrangement is in harmony with the observed composition of this phase,  $\text{C}_{14}\text{AsF}_6$ . When the solid is exposed to a sustained pressure of  $\text{AsF}_5$  (approximately 1 atmosphere at approximately  $20^\circ \text{C}$ ) the X-ray diffraction pattern changes dramatically and the composition changes in accord with the equation:



The X-ray data show that this uptake of  $\text{AsF}_5$  by the  $\text{C}_{14}\text{AsF}_6$  expands the carbon-sheet separation from 7.6 Å in the nestled salt to 8.1 Å in the  $\text{C}_{14}\text{AsF}_6 \cdot 1/2 \text{AsF}_5$ . Evidently the dielectric screening effect [or bonding of the  $\text{AsF}_5$  to yield a  $\mu$ -fluoro-bridged species such as  $(\text{F}_5\text{As}-\text{F}-\text{AsF}_5)$ ] provides sufficient favorable energy to more than compensate for the diminished attraction energy, which must accompany the expansion, and the unfavorable entropy change, associated with the uptake of gaseous  $\text{AsF}_5$ . The observed diffraction pattern of the  $\text{C}_{14}^+\text{AsF}_6^-$  is satisfactorily accounted for<sup>30</sup> with the structure illustrated in Figure 4. This requires that adjacent carbon-atom sheets are in staggered relationship to each other, As atoms, of course, always residing mid-way between eclipsed carbon atoms of these adjacent staggered sheets. With the uptake of  $\text{AsF}_5$  (to composition  $\text{C}_{14}\text{AsF}_6 \cdot 1/2 \text{AsF}_5$ ) the carbon atom-sheets move into registry with one another

(as well as farther apart). The observed diffracted X-ray intensities require that the As atoms be placed midway between the enclosing carbon sheets. In the ab plane all of the guest atoms are fully disordered in this phase. In  $C_{14}AsF_6 \cdot 1/2 AsF_5$  the guests are therefore like a two dimensional liquid. Removing the  $AsF_5$  restores the nested, relatively ordered,  $C_{14}AsF_6$  phase.

Much the same sort of structural change as observed for  $C_{14}AsF_6$  to  $C_{14}AsF_6 \cdot 1/2 AsF_5$  occurs when  $AsF_3$  is added to the nested salt but on removal of volatiles,  $AsF_5$  is observed as a consequence of the reduction of the carbon already alluded to:



and the resulting solid is a mixture of first and second stage  $C_xAsF_6$  nested- $AsF_6$  salts.

Perhaps the most unexpected aspect of graphite fluorosalt chemistry was the finding that salts such as  $C_xAsF_6$  rapidly consume additional gaseous fluorine<sup>15,30</sup> at approximately 20°C, this uptake being accompanied by a marked loss of electrical conductivity. Okino found<sup>30</sup> that this material of composition  $C_{14}AsF_6 \cdot \sim 2F$  was less conductive than the graphite from which it was made. Since the carbon sheets in  $C_{14}AsF_6$ , which itself shows a specific conductivity comparable with that of aluminum metal, bear a charge  $C_{14}^+$ , they are unlikely to be attacked by elemental fluorine which is an electrophile. The attack to generate C-F bonds most probably involves transfer of  $F^-$  to a positive carbon atom. The fluorination of  $C_{14}AsF_6$  and other  $C_xAsF_6$  salts may therefore occur via a species  $AsF_7^-$ . This like most seven-coordinate species<sup>36</sup> (e.g.  $IF_7$  and  $ReF_7$ ) would undergo intramolecular and intermolecular fluorine-ligand exchange. The latter via transient fluorine-bridged species to  $AsF_6^-$ , i.e.  $[F_6As-F-AsF_6]^{2-}$ , could provide for the observed facile distribution of fluorine throughout the graphite galleries. Such mechanisms could also in part provide a plausible basis for understanding the formation of a fluorinated graphite of composition  $C_{1.3}F$  which is formed<sup>37</sup> as a black first stage solid concurrently with first-stage fluorinated graphite salt  $C_{14}AsF_6 \cdot xF$ , when second or

third stage  $C_xAsF_6$  salts are fluorinated at  $\sim 20^\circ\text{C}$  in the presence of anhydrous hydrogen fluoride (AHF). However the separation of the  $C_xF$  phase in the presence of AHF, must also involve fluoride ion transport as  $(\text{HF})_n\text{F}^-$  species.

The  $C_{1,3}F$  is a more highly fluorinated relative of the  $sp^2$  carbon fluorides first described<sup>36</sup> by Rudorff and Rudorff. It possesses remarkable kinetic stability and its resistance to oxidation by perchloric acid at  $160^\circ\text{C}$  provides for its separation from  $C_{1,4}AsF_6 \cdot xF$ , which the acid destructively oxidizes at that temperature. Since the X-ray diffraction data<sup>37</sup> for  $C_{1,3}F$  show the hexagonal carbon-atom array to be only slightly expanded relative to graphite itself, with a graphite-cell  $a_0 = 2.46 \text{ \AA}$ , most of the fluorine ligands in this material must have neighbors at  $2.46 \text{ \AA}$ . This is remarkably short. In harmony with the use of so many of the  $\pi$  system electrons in binding F ligands (each C to which F is bound must be an insulating point in the network)  $C_{1,3}F$  is an insulator. Its specific conductivity,  $\sigma \approx 10^{-7} \text{ ohm}^{-1}\text{cm}^{-1}$ , is attributable to  $F^-$  transport in the gallery.

## Conclusions

Evidently the  $sp^2$  carbon-network is remarkably stable to electron oxidation to high charge levels (at least  $C_{1,4}^+$ ). Good conductors are thereby generated. For high positive charge development however it is essential to have anions of very low fluorobasicity otherwise  $F^-$  transfers to the carbon. The  $sp^2$  bonding of graphite persists even when 70% of the  $\pi$  bonding electrons are consumed in bonding F ligands, as in the insulator  $C_{1,3}F$ .

## Acknowledgments

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## The Role of Lattice Energetics...

Figures

- Figure 1. A thermodynamic cycle for oxidative intercalation of graphite.
- Figure 2. Intercalation of graphite by perfluoroanions as a function of the electron affinity of the oxidizing half reaction.
- Figure 3. Correlation of lattice energies for  $A^+B^-$  salts with formula unit volume. Open circles represent lattice enthalpies calculated as described in ref. 28. The circles are lattice energies from A. F. Kapustinskii (Zh. Fiz. Khim. 1934, 5, 59).
- Figure 4. The idealized nestled structural model for a single layer of  $AsF_6^-$  guests in  $C_{14}AsF_6$ . The unit cell is outlined.

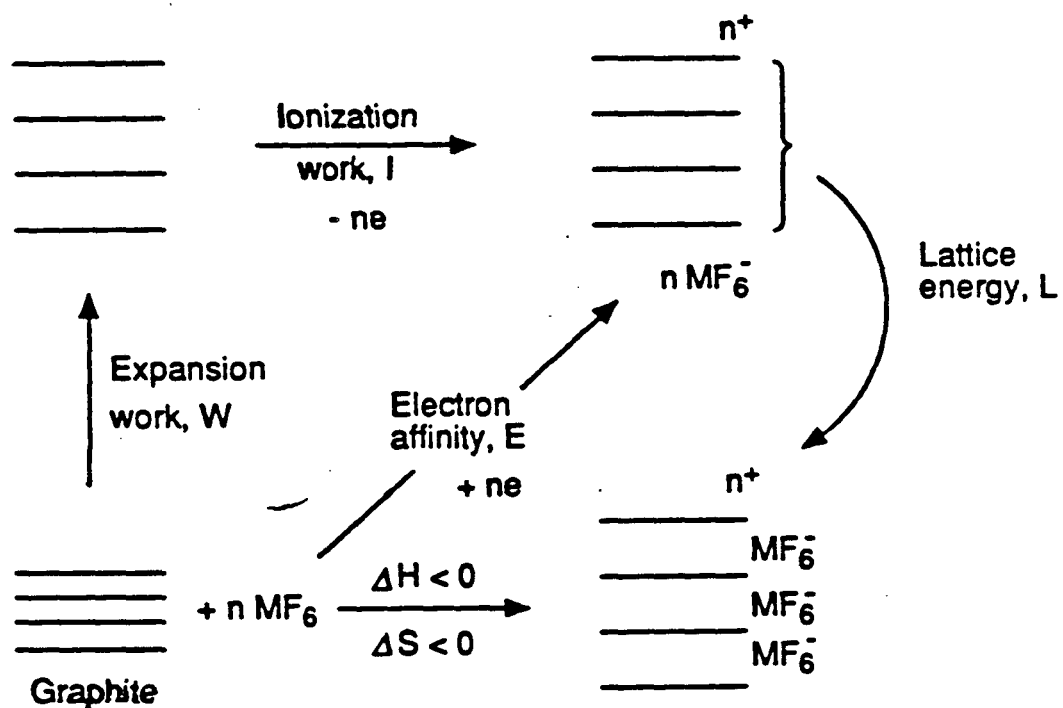


Figure 1. A thermodynamic cycle for oxidative intercalation of graphite.

- Intercalation to 1<sup>st</sup> stage
- ◐ Partial intercalation
- No reaction

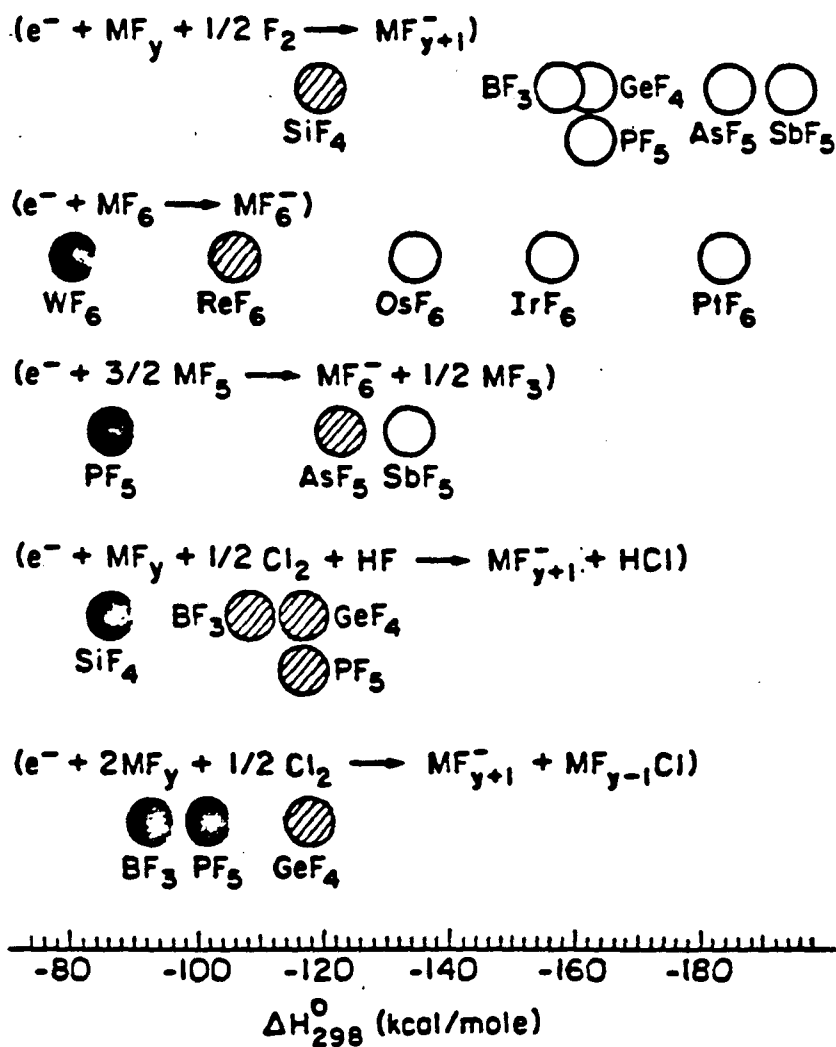


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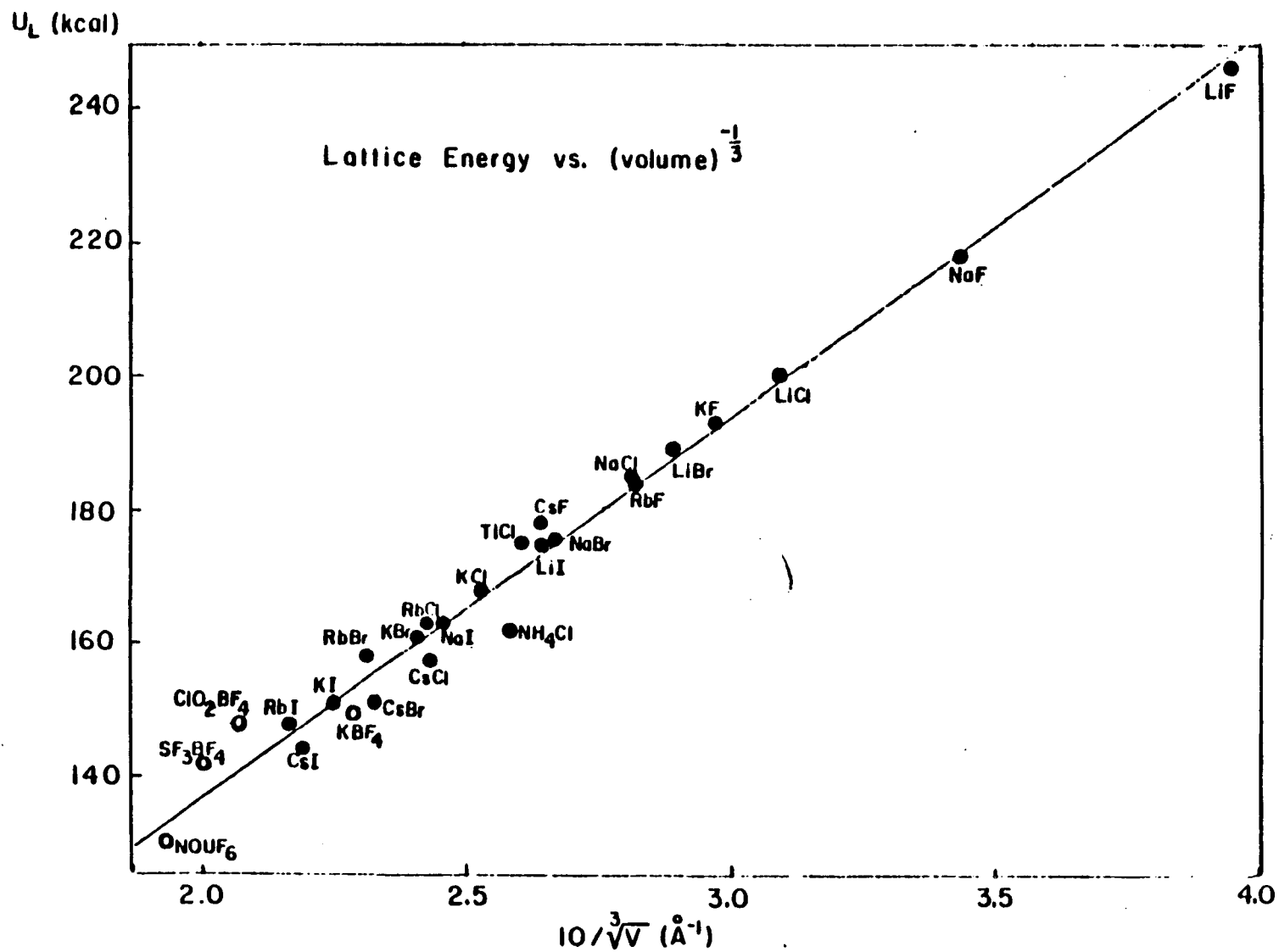


Figure 3

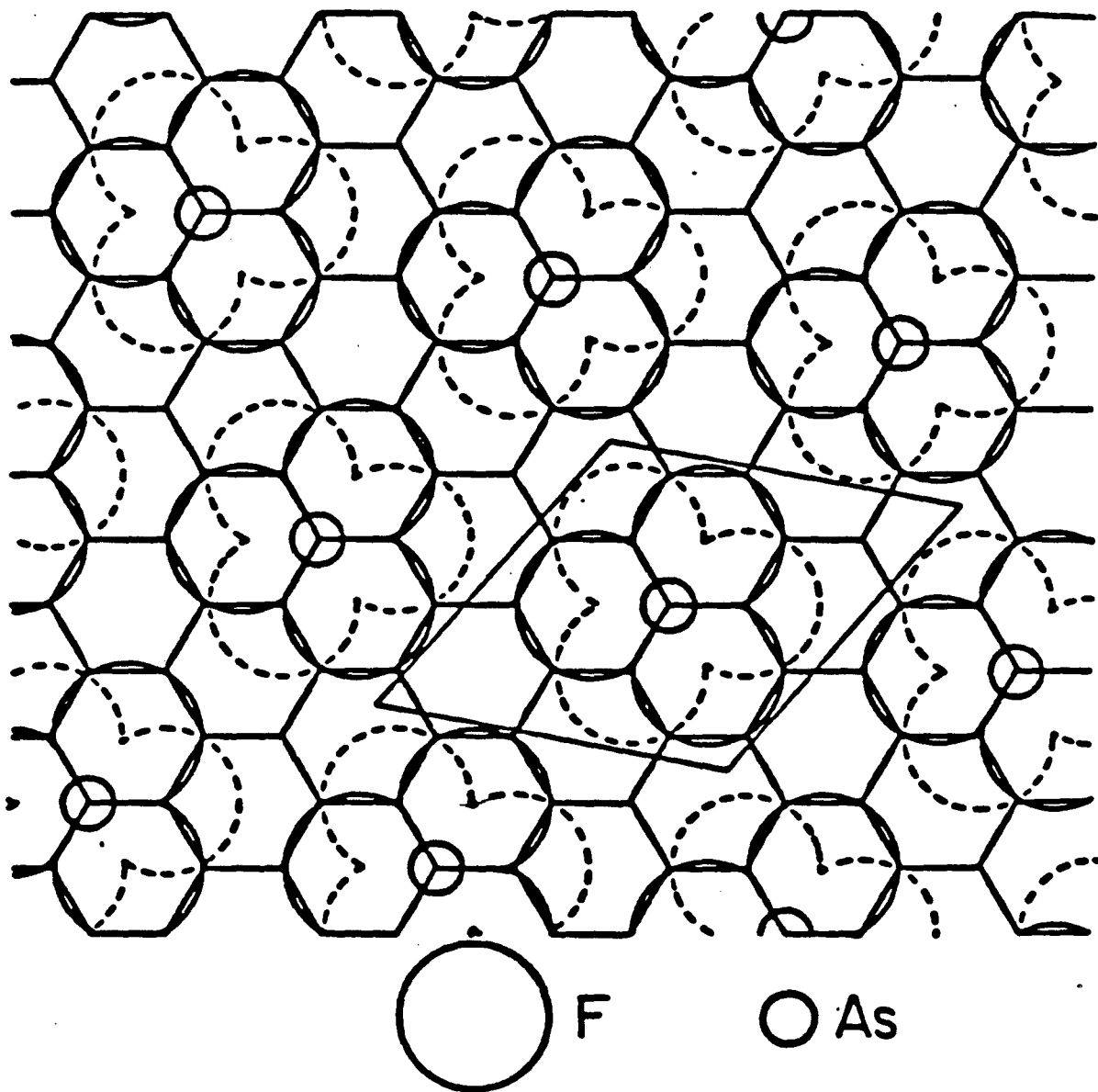


Figure 4. The idealized nested structural model for a single layer of  $\text{AsF}_6^-$  guests in  $\text{C}_{14}\text{AsF}_6$ . The unit cell is outlined.

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