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THE EFFECT OF FLAKE THICKNESS ON THE INTERCALATION OF GRAPHITE*

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Abstract—The peripheral expansion of single flakes of natural graphite 0·5 to 3 mm in diameter has been measured during intercalation by solutions of 12 metal chlorides in nitromethane (NM) and by ICl and by H_2SO_4. As concentration is decreased and thickness is increased the percentage expansion decreases. At 0·1 M the expansion varies by a factor of 200 from $SbCl_3$ to WCl_6 and the amount is not related to the intercalation behavior of the vapor of that metal chloride in graphite. For flakes greater than 10–30 μm thick, the expansion in $FeCl_3$ solution stops at a certain amount which increases with $FeCl_3$ concentration and with flake diameter. It can be started again by first shrinking the flake in NM and then re-exposing it to $FeCl_3$ solution. Such alternating treatment finally causes a maximum total expansion of 150 per cent. The rate of initial expansion is constant until it abruptly falls to zero in a time which increases with flake thickness and which is greater for flakes of smaller diameter. Gravimetric data show that about 1 mole of NM is intercalated for each mole of $FeCl_3$ and that by a cyclic process of exposure to solution and then driving off the NM by heat, a maximum composition of about C_7FeCl_3 can be obtained.

1. INTRODUCTION

Staudenmaier[1] reported that the composition of graphite oxide was a function of flake size and he used repeated treatment of larger flakes to reach a uniform product. This was confirmed by Clauss[2] who found that for flakes < 0·03 mm across, 10 days in the H_2SO_4–HNO_3 solution gave the maximum composition. For flakes of 0·2–2 mm however, this composition could not be reached unless the product was washed, dried and again oxidized. In 1965 Hooley[3] noted that the threshold pressure of Br_2 required to intercalate a 2500°C pyrolytic graphite increased with the thickness of the sample in the *c* direction. He also noted[4] that the fraction of $FeCl_3$ removed from C_6FeCl_3 by acetone was a negative exponential function of thickness. Thickness is also a factor in the Mossbauer spectrum of C_6FeCl_2 [5], the oxidation of graphite[6] and the resistance and Hall coefficient of graphite[7]. That it is a factor in the intercalation of graphite by a solution of $FeCl_3$ in nitromethane (NM) was shown after trying to duplicate the results of Ginderow and Setton [8]. They exposed a Ceylon graphite of 40 μm average size to a 1 M solution and found, after washing with NM, a $C_{26}FeCl_3$ assuming all weight increase was $FeCl_3$. X-ray diffraction showed that the product was not homogeneous and still contained regions of graphite. My initial interest in the reaction was that NM appears to take the place of the Cl_2 required for the intercalation of all metal chloride vapors. It led to the discovery that flake thickness has a marked effect on this reaction and also on intercalation by ICl and by H_2SO_4. Also that a variety of metal chloride solutions in NM will intercalate graphite and that all show a thickness effect.

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2. MATERIALS

Nitromethane – Fisher certified.

$FeCl_3$ – Fisher purified by sublimation. The solutions were prepared in a dry box but were cloudy and so were centrifuged and decanted.

$AlCl_3$, $SbCl_3$ – Fisher certified.

WCl_6, $TaCl_5$, $ZrCl_4$ – Alpha Inorganics.

$SbCl_5$ – B & A reagent grade.

$GaCl_3$, $InCl_3$, $TlCl_3$, $AuCl_3$, $MoCl_5$ were all prepared by chlorination of the pure metal (or TlCl) in a flow system from which the product could be transferred under anhydrous conditions to a dry box.

TlCl – from BDH reagent $TlNO_3$ by precipitation.

Graphite – Madagascar or New York flake purified by alternate treatment with hot 8M HCl and hot 40% HF solutions.

3. PROCEDURE AND RESULTS

3.1. *$FeCl_3$ in nitromethane (NM)*

The initial gravimetric experiments are more easily understood if the effect of flake thickness, which they predicted, is first described.

3.1.1. *Expansion of individual flakes.* A device was constructed to measure the edge thickness of one flake of graphite during intercalation. It is shown in Fig. 1 and consists of a Teflon cylinder A with a shallow groove into which the edge of a flake can be placed. It is a loose fit made firm with a few strands of glass wool. The loaded cylinder is dropped in to the tube B which in turn is placed in the vertical tube C. The device is then aligned under a microscope with a working distance of 10 cm. A magnification of 37·5 was used at which 1 div. on the thumbscrew controlling the cross hair corresponded to 1·9 μm in the field. A Teflon tap D allows one to adjust the level of the added solution to any desired height. A hole in the bottom of B and slots in the side of A are essential. With this device the effect of several variables on the expansion was studied for flakes from 20 to 300 μm thick and of 0·6, 1·3 and 3 mm dia. Diameter is defined as average minimum cross section and the ranges were, respectively, 35–40 mesh, 1·2 to 1·4 mm and 2 to 3 mm. For all three diameters only planar flakes were used. This was ensured by measuring the thickness with the microscope and with a dial gauge. The latter gives the maximum thickness and if this did not agree within 2 μm with the microscope thickness at the edge then the flake was presumably not planar and so was not used.

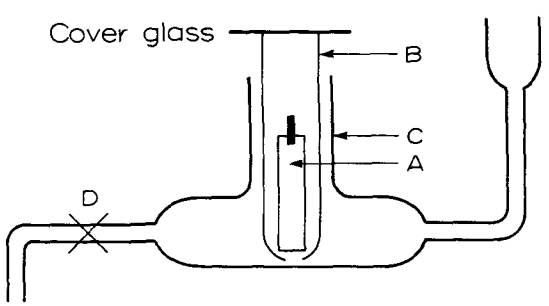

Fig. 1. Device to measure flake thickness in a solution.

3.1.2. *Initial expansion in $FeCl_3$ in NM.* Figures 2, 3 and 4 are all for 0·61 M solution. This contains 5·0 g $FeCl_3$ in 50 ml of NM. Figure 2 is a typical plot of percentage expansion against time for three thicknesses. It shows that the rate of expansion falls off somewhat with time and more or less abruptly becomes zero and remains so for as long as any flakes were ever followed which was several days. In Fig. 3 the maximum percentage expansion and in Fig. 4 the time to reach that maximum are plotted against initial thickness on a log scale for each of the three diameters used. It is apparent that for a given diameter an increase in thickness lowers the percentage expansion and increases the time to reach that maximum expansion. Furthermore, for a given thickness, in the 20–200 μm range at least, it appears that the maximum percentage expansion increases with diameter. In addition, the time to reach that maximum is an inverse function of diameter. Hence a flake

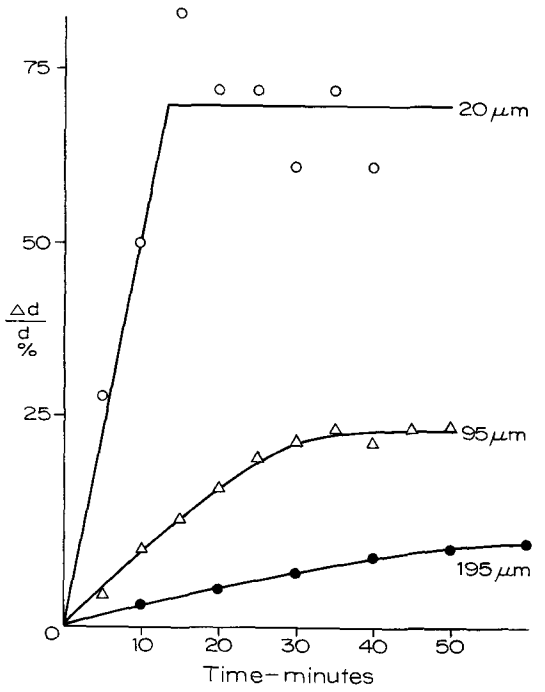

Fig. 2. Rate of expansion for 1·3 mm dia. flakes in 0·61 M $FeCl_3$ in NM.

At the thin end, the flakes are available but the data are uncertain with the equipment used.

Another way of looking at the data is shown in Fig. 5 where the actual maximum increase in thickness Δd is plotted against the initial thickness for the 3 diameters. For one of these diameters 3 concentrations were used. In spite of the scatter and the experimental difficulties below about 20 μm one can make the following observations. The curves all start, of course, at the origin and may well have the same initial slope of about 150 per cent although the data in the region below 20 μm is not conclusive. The initial slope, however, is not maintained and falls off to zero above a certain thickness. Above that thickness the Δd is independent of the initial thickness and increases both with the concentration of $FeCl_3$ and with the diameter of the flake. It is as if the intercalation proceeds only a certain distance from the two end basal planes toward the center and then stops. The distance travelled increases

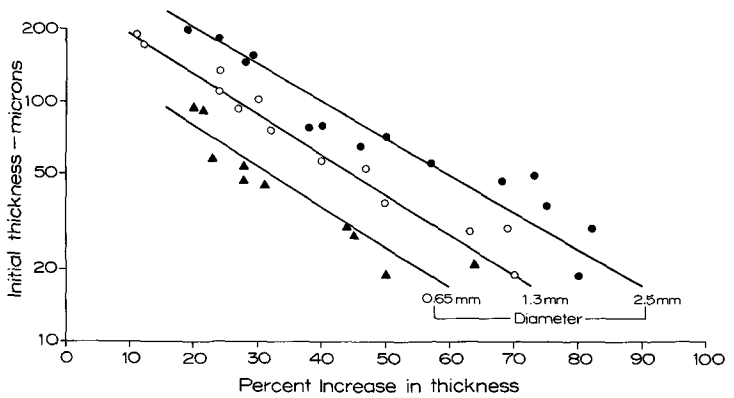

Fig. 3. Percentage expansion in 0·61 M $FeCl_3$ in NM as a function of initial thickness.

of small diameter not only suffers a smaller percentage expansion but requires a longer time to reach that state than a flake of large diameter. The extrapolation of the data is uncertain. At the thick end, flakes > 200 μm are not common, especially of small diameter.

with the concentration of $FeCl_3$ and with the diameter of the flake and is independent of the initial thickness.

3.1.3. *Expansion during cyclic treatment with $FeCl_3$ solution and nitromethane.* If a large flake, say 3 mm × 50 μm thick reaches its

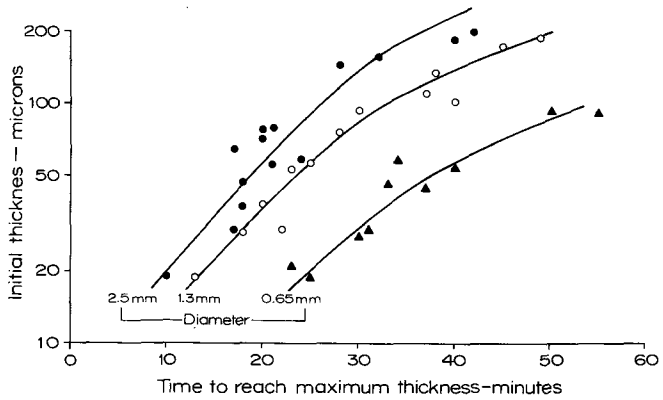

Fig. 4. Time to reach maximum expansion in 0·61 M $FeCl_3$ in NM as a function of initial thickness.

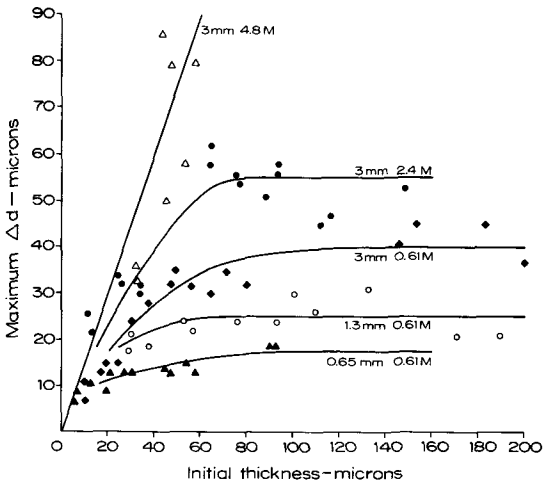

Fig. 5. Maximum expansion as a function of initial thickness.

maximum expansion in 2·4 M solution and is then exposed to air, it will split and therefore increase in apparent thickness. Presumably the loss of NM to the air causes exfoliation. If, however, the solution is replaced by pure NM without exposing the flake to air, the thickness decreases and soon reaches a constant value.

If the NM is then replaced by $FeCl_3$ solution without exposing the flake to air the thickness increases and soon reaches a constant value greater than the previous maximum. This can be continued until finally the thicknesses in solution and in pure NM return always to the same two values as shown in Fig. 6 for the 88 μm flake. The time scale has been distorted to make all cycles equal in length. For the 88 μm flake, seven cycles were required to reach the steady state in which the maximum expansion was 142 per cent and the minimum 110 per cent. This final maximum is about the same as the 150 per cent observed in Fig. 5 and is presumably the value for complete intercalation. For the 148 μm flake in Fig. 6 the maximum expansion was 100 per cent after 6 cycles and was still increasing after each cycle. If it is to reach the same value as did the other flake, more than 7 cycles will be required. Hence a thick flake requires more cycles to reach the steady state than a thin flake.

3.1.4. *Gravimetric composition of* $C_x(NM)_y FeCl_3$. When 0·5 g of 25–35 mesh graphite is treated with 5M$FeCl_3$ in NM and filtered, the excess solution can of course be washed away with NM but as can be seen in Fig. 6 most of the adduct will also be removed. This explains why in 3 runs the final weight was only 8 per cent greater than that of the graphite used. If this increase were all $FeCl_3$ the formula would be $C_{170}FeCl_3$. Subsequent treatment with 1M HCl reduced the weight

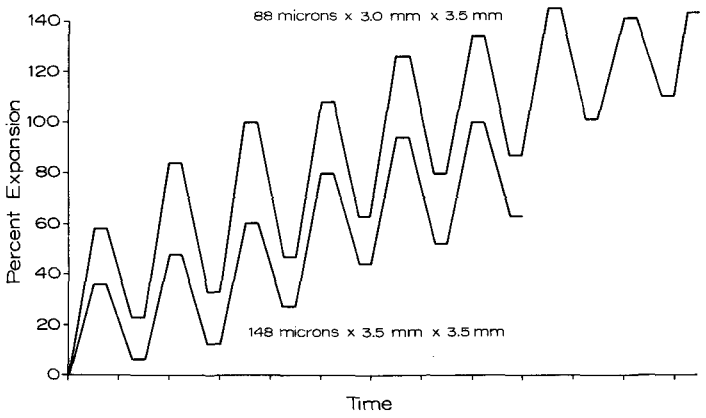

Fig. 6. Cyclic treatment in 2·4 M $FeCl_3$ in NM and in NM.

to that of the original graphite. The adduct is apparently far more labile than when intercalated from the vapor phase. In that case[4] acid removed only 20 per cent from the 25–35 mesh product.

Instead therefore of washing the product it was sucked with dry air on a fritted glass filter and then transferred to a vacuum of 10^{-4} cm for 6 hr to further remove NM before weighing. Although this weight was not changed by further vacuum treatment, the sample was still moist. The weight increase varied in a random way with the time in the 5 M solution. Thus, in 9 runs in 20 ml of solution for times from 5 min to 20 hr the weight increase varied from 50 to 80 per cent. However, these samples were heated to constant weight to remove all the NM during which exfoliation occurred. A minimum of 105°C was required. From the above gravimetric data and assuming that all the weight loss in the oven was intercalated NM, the value of x was 24 ± 2 and of y $0{\cdot}73 \pm 0{\cdot}08$ in $C_x(NM)_y$ $FeCl_3$. The unknown factor here is the contribution of the $FeCl_3$ solution remaining on the surface of the compound and, because of this, no further studies were made of its composition. However, the final oven treated product, which is C_xFeCl_3 plus residual $FeCl_3$, was of interest. It was washed to constant weight with 1M HCl which should remove all the residual $FeCl_3$ from the surface plus a fraction of the intercalated $FeCl_3$. This fraction will depend on the thickness of the exfoliated flakes[4] but this could not be determined. The final weight was found to be much greater than when the original wet product was washed with NM or acid. Its value increased with time in the solution and levelled off sooner for finer graphites. The final, maximum value increased with $FeCl_3$ concentration and was an inverse function of flake size as shown in Fig. 7. That the above process leaves an appreciable residue on the surface of the graphite was disproven by runs on a carbon black Sterling MT 3000 from Cabot Corporation. The final washed product was of the same weight as the original sample showing neither intercalation nor surface residue.

The final composition in Fig. 7 is not only far less than the 200 per cent weight increase obtained in the gas phase[9] but is a function of flake size. Perhaps the repeated treatment used by Staudenmaier[1] for graphite oxide will increase the $FeCl_3$ content and the data in Table 1 show that this is true. Each treatment consists of 24 hr in 2·4 M solution at 25°C followed by centrifuging in a CRC Filtermatic centrifuge, drying overnight at 110°C, washing with 100 ml 1M HCl and

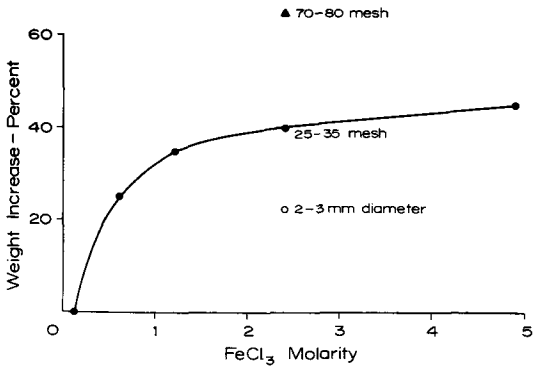

Fig. 7. Weight increase for oven dried and acid washed product.

Table 1. Weight increase for repeated treatment of 25–35 mesh in 2·4M $FeCl_3$ in NM

Sample	1	2	3	4	5
Treatment 1	43%	33%	39%	45%	37%
Treatment 2	55	36	53	55	51
Treatment 3	162	123	146	151	148
Treatment 4	187	188	185	197	187
Treatment 5	350	324	318	306	305
Acid wash 1	290	277	235	227	231
Acid wash 2	280	267	196	197	192
Acid wash 3	268	230	192	186	189
Acid wash 4	246	220	191	185	186
Acid wash 5	236	208	187	184	182
Acid wash 6	—	—	187	182	181

acetone and finally drying and weighing. The bulk volume increased during each cycle in the oven because of the expulsion of intercalated NM. The area therefore increased and also the weight of residual absorbed solution. Hence more than one washing with acid was required to remove this material after decomposition in the oven. In fact 7 washings were required to produce a constant weight. The final value of 183 per cent corresponds to $C_{7·4}$ $FeCl_3$ which is not far from the $C_{6·3}$ $FeCl_3$ obtained in the gas phase reaction [9]. Similar runs were made in duplicate at two different concentrations. For 5M solution the final weight was up 210 per cent corresponding to $C_{6·5}$ $FeCl_3$ and for 0·61M it was up 85 per cent or to $C_{16}FeCl_3$.

3.2. *Expansion in NM solutions of other metal chlorides*

The expansion of 3 mm dia. flakes in NM solutions of 12 metal chlorides was studied as a function of flake thickness and of concentration. The expansion of 20 μm thick flakes is seen in Fig. 8 to be proportional to concentration at least for expansions below 100 per cent. Above this, $FeCl_3$ levels off at 150 per cent around 5M as can be calculated from Fig. 5 and the expansions in $SbCl_5$ and in $SbCl_3$ solutions are also depressed at the upper end. For the line labelled $GaCl_3$ to $TaCl_5$ only the points for $TaCl_5$ are shown. The others are equally close.

The relative expansions caused by the 12 metal chlorides in Fig. 8 show no relationship to the behavior of the same chlorides as vapors in Cl_2. Thus $AlCl_3$ vapor has a threshold relative pressure for intercalation of 10^{-4} and forms C_9AlCl_3 whereas WCl_6 has a threshold of 0·5 and forms $C_{60}WCl_6$. As solutions, however, the relative behavior is reversed.

The expansion of flakes 200 μm thick × 3 mm dia. was also measured in these solutions. The maximum expansions were all between 3 and 10 per cent. Presumably cycles of solution and of NM would, as with $FeCl_3$, increase this.

3.3. *Expansions in other solutions*

3.3.1. *Iodine chloride (5 ml) in NM(10 ml).* A 3 mm dia. flake 55 μm thick expanded 142 per cent in 75 min whereas one that was 200 μm thick expanded 61 per cent in 85 min.

3.3.2. *Iodine in NM.* There have been many unsuccessful attempts to intercalate iodine in graphite. The current attempts used a saturated solution – about 0·13 M – and a 22 and a 23 μm thick flake of 3 mm dia. and were also unsuccessful.

3.3.3. *H_2SO_4, HNO_3 mixture.* A mixture of 63 g H_2SO_4, 22 g H_2O and 5 g 16 M HNO_3

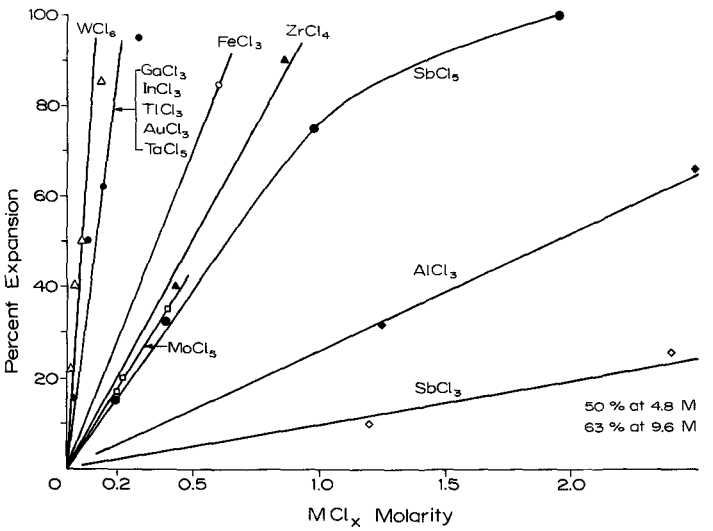

Fig. 8. Percentage expansion of flakes 20 μm thick × 3 mm dia.

is said to give the third stage compound and was used on 3 flakes of 3 mm dia. The maximum expansions were for

22 μm thick, 69% in 25 min
68 μm thick, 28% in 25 min
200 μm thick, 8% in 40 min.

4. DISCUSSION

Peripheral expansion of a graphite flake is a very convenient measure of intercalation although it does suffer from a scattering of the data which may be inherent in the flakes. Thus, variations in perfection could lead to either higher or lower expansions than for a perfect crystal. Then we look at only one segment of the edge and so do not even get an average expansion for the flake. If that segment has been partly delaminated the expansion may be greater. Also the cross section of the flake is a very irregular polygon whose minimum dimension is used as a diameter. Finally, we do not know whether the center of the flake expands as well as the periphery. In spite of all this, the following generalities appear for at least the 20–200 μm range of thickness and 0·6–3 mm dia.

First, assume that the intercalation starts at the periphery of the two spaces bounded by the two end basal planes of the flake. Although this has not been observed for natural flakes because they are too thin, it has been observed for thick pyrolytic graphite[3] and it would be difficult to explain the results in this paper on a basis of intercalation throughout the layer system from time zero. Now it appears that this peripheral expansion proceeds through only a certain number of the spaces between an end one and the central one and then stops. The maximum value of this number is, of course, half the number of spaces in the flake and for this, one observes the maximum percentage expansion. In the $FeCl_3$–NM system this is about 150 per cent whether determined from initial expansions as in Fig. 5 or from cyclic treatment as in Fig. 6. Note that in Fig. 5 each point is for one flake whose percentage expansion is the slope of a straight line from the origin to that point. Hence for all points along the line for 3 mm dia. flakes in 4·8 M solution the intercalation proceeds in a continuous fashion to the center of the flake. This includes lower concentrations if the flake is sufficiently thin – around 15 for 2·4 M and perhaps 10 μm for 0·6 M. However, for

all points to the right of that line the percentage expansion is less than 150 per cent and the two intercalation fronts do not meet, there being a core of graphite between them. Furthermore, the depth of penetration levels off as the original thickness increases and the final value, independent of thickness to at least 200 μm is an interesting function of concentration and diameter. Specifically, it increases with concentration, as one might expect, and increases with flake diameter. This is the first time a diameter effect has been observed in intercalation. Note that it is based on measurements on about 40 flakes – 10–15 at each of the 3 diameters.

The rate of expansion is of interest and, as noted above, is fairly constant until, at maximum expansion, it falls abruptly to zero. The time for this is greater for thicker flakes and for those of smaller diameter. Hence, in the region where the initial bite is independent of thickness, that initial bite is not only less for a flake of smaller diameter but takes longer to occur. It may well be that in that region the carbon layer planes in the 10 or more microns next to each end basal plane become dished, the two end planes being most dished of all. Perhaps the layer spacing in these two outer regions is that of graphite along the center axis and 250 per cent of that of graphite at the periphery. The core between the two regions would still be entirely of the graphite spacing. It is interesting to calculate the curvature of the end basal planes for such a structure. Thus, for a 0·65 mm dia. flake in 0·61 M solution the maximum expansion is 17 μm (Fig. 5) or a curvature of 8·5 μm in 0·32 mm or 2·6 per cent at each end. For the 1·3 mm dia. flakes it would be 1·9 per cent and for the 2–3 mm flakes, 2·0–1·3 per cent. This should be measured and also other properties to find out why the intercalation stops and can be started again for another bite in to the core simply by exposing the flake to NM and then to $FeCl_3$ solution again. The NM presumably removes some $FeCl_3$ to cause the measured shrinkage, and if this occurs unevenly around the flake it may cause some splitting so that on re-exposure to $FeCl_3$ further intercalation occurs. There is evidence, however, in Fig. 6 that the two end regions do not become separate entities in this process. Thus, for the 88 μm flake, the initial expansion of 51 μm (58 per cent) represents a bite of 21 μm being expanded 140 per cent. This would leave a graphite core of $88-21=67$ μm thickness which, according to Fig. 5 should expand 53 μm if it is a separate entity. However, the net increase from the first to the second cycle is only from 139 μm to 162 μm or 23 μm. The presence of the end regions has therefore decreased the increment of expansion.

The intercalation of pyrolytic graphite by Br_2[3] may be of significance. It was observed that expansion was initiated in the two regions bounded by the two end basal planes. It was also observed that discs about 200 μm thick broke off from the cylinder as intercalation proceeded. The theory was that peripheral expansion produced a tension along the core of the cylinder which finally reached the tensile strength of the material and hence a disc split off. In the case of natural flakes this does not occur. Instead, because the flake is more flexible than the pyrolytic graphite used, the tension produced in the core is less and so no disc splits off. But the process of intercalation does stop and the reason is unknown.

When the 88 μm flake in Fig. 6 reaches the steady state it is behaving rather like the flakes of C_6FeCl_3 exposed to the solvent acetone[4]. In that case the fraction of spaces emptied of $FeCl_3$ by acetone was a negative exponential function of flake thickness and amounted to 10 per cent for a flake initially 88 μm thick × 1 mm diameter. In the present case the oscillation in the steady state is about 25 μm for a flake originally 88 μm thick × 3 mm dia. This would be the expansion if 18 μm of graphite

expanded 140 per cent. The subsequent contraction of 25 μm in NM is therefore emptying 20 per cent of the layer spaces in the original 88 μm of graphite. This is for a 3 mm dia. flake and, according to Fig. 5 it would be less for a 1 mm dia. flake. Hence the 10 per cent observed for acetone and 1 mm flakes is remarkably close to the value for NM.

Some of the gravimetric data is predictable from the expansion data. Thus, the 25–35 mesh flakes initially used had an average thickness of 20 μm and hence the compound produced should and did lose most of its $FeCl_3$ by washing with NM. Before washing, however, it probably contained about 1 mole of NM for each mole of $FeCl_3$. Although the amount of NM is uncertain it is definitely between the layers of carbon because at 110°C its loss caused considerable exfoliation and left the $FeCl_3$ in such a state that much less was leached out by acid than from the NM containing compound. Furthermore, the product would now intercalate additional $FeCl_3$ and NM and, indeed, by a cyclic process of exposure to solution and driving off NM a C_7FeCl_3 was obtained in 2·4 M solution. Mossbauer and X-ray diffraction studies should be made of this product to see how it compares with the C_6FeCl_3 made from $FeCl_3$ vapor. Presumably they are both stage one compounds with every space filled. If so, the carbon layer plane separation has gone from 3·35 to 9·40 Å [10]—an expansion of 180 per cent. This is not much more than the 150 per cent observed for the NM containing compound.

The expansions in other metal chloride solutions in NM is of particular interest. As far as studied, they show the same behavior as did $FeCl_3$. Thus, percentage expansion is proportional to concentration but levels off at higher values. Also, the percentage expansion is greater for thinner flakes. Note that although all the 12 metal chlorides in Fig. 8 have been reported to intercalate graphite as vapors in the presence of Cl_2, only $FeCl_3$ has previously been reported to intercalate from a solution in NM.

The case of $SbCl_3$ is special because its vapor will not intercalate unless Cl_2 is present and then it becomes $SbCl_5$. Hence the intercalation of $SbCl_3$ is being reported here for the first time.

Finally, that intercalation decreases as flake thickness increases is true not only for NM solutions of metal chlorides but also for ICl and for H_2SO_4. Conversely, intercalation by certain compounds may have been missed because the wrong flake shape was used. It now appears that the best shape is a very thin one of large diameter.

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