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A KINETIC MODEL OF THE FIRST INTERCALATION OF GRAPHITE†

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Abstract—A model of first rapid intercalation is presented to describe the kinetics of intercalation. The model applies to interface-controlled intercalation, as for the intercalation of Br_2 and other similar intercalates. In this model, intercalation proceeds by layer-by-layer nucleation and subsequent in-plane growth; a time gap is assumed between the nucleation of two successive intercalate layers. The model has been applied to analyze the variation of the surface and thickness profiles and mass increase during intercalation. Support of the model by relevant experimental results is discussed.

1. INTRODUCTION

Graphite reacts with many chemical substances to form compounds [1]. One class of graphite compounds, known as the intercalation compounds [2], contains the reactant in the interstitial spaces between the planar hexagon layers of the graphite crystal and maintains the aromatic planar layer structure of the parent graphite. Such a reaction between graphite and the reactant is known as intercalation; the reactant is known as the intercalate.

Graphite intercalation compounds have recently received considerable attention in the areas of the electronic, lattice and structural properties [2]. However, relatively little attention has been given to the mechanism of intercalation, a process which results in the superlattice ordering of the intercalate layers with respect to the carbon layers. Bromine is the intercalate species that has been most thoroughly studied, but little work has been done to rationalize the published experimental results on the kinetics of intercalation. In this paper, we present a model of first rapid intercalation which allows for the first time a coherent explanation of many of the published results on the physiochemical effects of intercalation. However, our model does not take into consideration crack formation, which often accompanies intercalation [3] and which tends to enhance the effect of intercalate adsorption. The model rather, is directed toward an explanation of the elementary process involved in intercalation.

Of the various methods of studying the kinetics of intercalation, those of our concern here are measurements of thickness [4–8], weight gain [4, 6, 9–16], concentration profile [12, 16, 17] and surface profile [18]. The first extensive measurements on thickness expansion were obtained by Saunders *et al.*[4, 5], followed by Hooley *et al.*[6, 7]; both groups of workers advanced revealing arguments to explain their data. Gravimetric data have been obtained alone [6, 9–12, 16] or simultaneously with other data such as thickness [4], electrical conductivity [13, 14] or magnetic susceptibility [15].

Most of the attempts to explain the mass increase phenomenon during intercalation were based on Fick's laws of diffusion, which require the existence of a concentration gradient of the diffusing species. On the other hand, consequences arising from Fick's laws have not been applied to analyze the changing dimensions and the intercalate distribution during intercalation. On a closer examination of the limited published data, we find that many of the difficulties with the diffusion model possibly arise from the failure to distinguish between two types of intercalation processes which are described below, along with the reasons behind the difficulties with the diffusion model.

(i) *Concentration and surface topographical profiles*

An important test for the applicability of Fick's law

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of diffusion involves the intercalate distribution in the bulk of the solid. Results of electron microprobe analysis [12, 17] and surface topographical profilometry [18] showed that there are two types of concentration or surface topographical profiles on the *c*-face during intercalation.

The first type, as found during intercalation with Br_2, is characterized by the absence of an intercalate concentration gradient in the intercalated region [17]. This means that Fick's laws are not applicable for an intercalation process exhibiting this type of concentration profile. Furthermore, Marchand *et al.*[15, 17] found a sharp advancing bromine front on the basis of concentration profile measurements. In our surface profile measurements [18] carried out on the *c*-face during the intercalation of bromine in highly-oriented pyrolytic graphite (HOPG), the expansion effect of intercalation made the bromine front clearly visible even to naked eyes. These observations suggest that diffusion is much faster than the accompanying stress relaxation and that the intercalation process is interface-controlled.

The second type of concentration profiles, as found during intercalation with $PdCl_2$, is characterized by a gradual decrease of the intercalate concentration from the edge to the interior [12]. The profile does not exhibit a sharp front and appears to resemble one based on Fick's law of diffusion. Moreover, the *c*-face surface topographical profile obtained during intercalation with HNO_3 does not also exhibit a sharp front, being bowl-shaped rather than bucket-shaped [18]. These observations suggest that the intercalation process is different from that of the first type. Results obtained with $FeCl_3$ [16] as the intercalate species are not detailed enough to reveal the characteristic profile.

Whether the intercalation process is interface-controlled or not seems to depend on the intercalation temperature relative to the order–disorder transformation temperature (T_c) for intralayer intercalate position ordering, although this dependence needs to be confirmed. The composition and surface profile measurements discussed above were performed at room temperature, which was the same as the sample temperature for the intercalation of Br_2 and HNO_3, but was much less than the sample temperature for the intercalation of $PdCl_2$. Because the transformation temperature (T_c) varies with the intercalate species, some intercalation compounds (e.g. graphite–Br_2) exhibit intralayer intercalate position ordering at room temperature [3], whereas others (e.g. graphite–$PdCl_2$, graphite nitrate) do not [12, 19]. The results of composition and surface topographical profile measurements thus suggest that the interface-controlled intercalation process applies to those compounds which are intercalated at a temperature below T_c, whereas a different type of intercalation process applies to those compounds which are intercalated at a temperature above T_c. A change in the reaction rate can be expected when a phase transformation occurs if the order-parameter is coupled to the kinetic process [20]. The isothermal desorption rate of Br_2 from graphite–Br_2 has been reported to increase significantly at a temperature close to the intralayer disordering temperature T_c (~ 100°C) [21].

(ii) *Edge thickness along* c-*axis*

An implicit assumption in the in-plane diffusion model of intercalation, which has been previously suggested, is that all the interlayer spaces appropriate for a given stage are open to intercalation simultaneously from the start of intercalation, resulting in an increase in the *c*-axis thickness at the edge to its limiting value almost immediately. However, results of the thickness measurements of Saunders *et al.*[4, 5] and particularly of Hooley *et al.*[6] showed that the edge of the sample parallel to the *c*-axis did not expand fully as soon as intercalation began. Objections against the simultaneous occupation of all interlayer spaces have also been raised on the basis of energetics [16].

(iii) *Weight increase*

Gravimetric data taken during intercalation had been obtained and interpreted by a number of investigators. Croft *et al.*[10] and Hooley *et al.*[9] used two diffusion coefficients to fit their data, which were were obtained with natural graphite flakes. Croft *et al.* explained this by assuming the dependence of the diffusion coefficients on the intercalate concentration, whereas Hooley *et al.*, in addition, attributed this to irregularities at the edge of the flakes. As a result, they suggested that intercalation was a two-stage process. If Fick's laws of diffusion were applicable to the intercalation process, the curve of weight uptake vs $(\text{time})^{1/2}$ should be concave toward the $(\text{time})^{1/2}$ axis [22]. Hooley *et al.*[6] reported that this curve was concave for some samples and convex for others, and related such differences to differences in thickness and in the degree of crystallite alignment in the pyrolytic graphite samples used. Similar curves obtained by Marchand *et al.*[15] and Metz *et al.*[16] were linear in time in the early part of inercalation.

In addition to the commonly used diffusion model, two other models have been suggested. One model, suggested by Marchand *et al.*[15] and of some importance to the present work, considers the simultaneous growth of all intercalate layers and consequently cannot explain the results of both thickness and surface profile measurements. However, the concept of growth of intercalate layers proves useful in the present work. The other model is based on the concept of "layer islands" [16] and has the same shortcomings as the former model. Both these models have time dependences which are essentially the same for short times and can be derived from the model proposed here as particular cases.

Of particular significance to this paper is the strain model of Hooley[23]. Although this model is very qualitative, it pointed out the importance of considering the elastic effect of the insertion of intercalate in graphite in explaining the mechanism of intercalation. As discussed in Section 3, the elastic effect is the underlying basis of the model proposed in this paper.

In this paper, Section 2 describes the model of interface-controlled intercalation. In Section 3.1, the predictions of the model are compared with available experimental results and further comments on certain features of the model are given. In Section 3.2, attention is drawn to the possibility of applying the proposed model to the intercalation of materials other than graphite.

2. MODEL OF INTERFACE-CONTROLLED INTERCALATION

The proposed model is based on a mechanism of nucleation and subsequent growth, considered for simplicity in a perfect graphite structure.

According to the mechanism suggested by Hooley[6] for the intercalation of bromine in graphite, we assume that intercalation starts at the interlayer spaces at the two ends and proceeds toward the inner region in such a way that there are n graphite layers between two successive, nucleated intercalate layers for an eventual nth stage intercalation compound [24]. We further assume that that nucleation of an intercalate layer occurs at the edge of the layer, and that once nucleated, the intercalate layer grows toward the inside at a velocity v, which is in general a function of time. The structure of the resulting intercalate layer corresponds to that of an nth stage compound. As the first intercalate layer grows, nucleation occurs at the interlayer space separated by n graphite layers from the first intercalate layer. In this way, the nucleation and growth of an intercalate layer eventually take place at every interlayer space appropriate for the nth stage compound. Let the time gap between the nucleation of two successive intercalate layers by ΔT, which we assume to be constant at a given pressure and temperature.

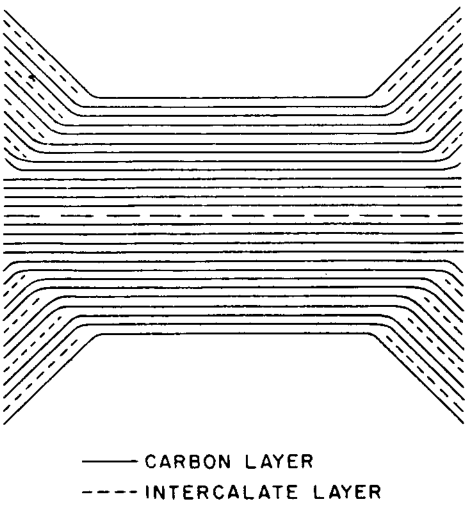

Fig. 1. Schematic diagram of a sample at an instant of time during intercalation to a stage 2 compound.

A schematic diagram of a sample at an instant of time during intercalation to a stage 2 compound is shown in Fig. 1. When the intercalate enters an interlayer space, it forces the spacing between the bounding graphite layers to expand. Thus, the thickness profile as well as the weight of the sample change as intercalation proceeds. On the basis of the above model, these changes can be expressed analytically as functions of the time of intercalation. For simplicity, we have restricted our consideration to cylindrical samples with the thickness along the c-direction, though the analysis can be extended to samples of other shapes. Let the radius of the cylinder be R_0; let there be Nn graphite layers in the cylinder, where n is the stage of the compound that eventually forms. This means that the number of intercalate layers in the cylinder after the completion of intercalation is N. The thickness of the cylinder before intercalation is Nnd, where d is the interlayer spacing in pure graphite.

The proposed model indicates the existence of several time lengths that are of importance. Let the time taken for the nucleation of all intercalate layers be t_N, which is given by

$$t_N = \left(\frac{N}{2} - 1\right)\Delta T \approx \frac{N}{2}\Delta T. \tag{1}$$

The above approximation is used in the rest of this paper without mentioning.

Let $r(t) = R_0 g(vt/R_0)$ denote the radius of the advancing (inner) front of an intercalate layer at time t after its formation. If the layer grows at a steady velocity v, g is simply given by

$$g\left(\frac{vt}{R_0}\right) \equiv 1 - \frac{vt}{R_0}. \tag{2}$$

In what follows, each intercalate layer is assumed to grow with the same velocity v in the manner described by eqn (2). The radius of the intercalate front contour for the jth intercalate layer at time t is given by

$$r_j = R_0 - v(t - j\Delta T). \tag{3}$$

Clearly, the time of completion of growth of the outermost layers is $t_G = R_0/v$. The time when intercalation is finished corresponds to the time at which the $N/2$th intercalate layer (the middle intercalate layer) completes its growth. This occurs at a time $t_I = t_N + t_G$ after the start of intercalation.

Depending on the ratio of the thickness to the radius of the cylindrical sample at a given pressure and temperature, one of two cases occurs during intercalation.

Case 1: $t_N \le t_G$.

This means that the nucleation of all intercalate layers is completed before the growth of the outermost layers is completed.

Case 2: $t_N \ge t_G$.

This means that the nucleation of intercalate layers continues after the growth of the outermost layers is completed.

The proposed model has been used to express analytically the changes with time of the surface topographical profile and of the weight of the sample during intercalation, as described in Sections 2.1 and 2.2.

2.1 *Surface and thickness profile*

To follow the variation in the surface profile during intercalation for Case 1, consider separately three time intervals: (a) $0 \le t \le t_N$, (b) $t_N \le t \le t_G$ and (c) $t_G \le t \le t_I$.

Consider first the interval $0 \le t \le t_N$. Let $h(r, t)$ be the increase in thickness at a distance r from the center and at a time t from the start of intercalation. Note that, for a cylindrical sample, the intercalate front is circular, so that h is radially symmetrical.

Let us assume that the increase in the separation of two consecutive graphite layers at r is proportional to the concentration at r of the intercalate layer in between them. In interface-controlled intercalation, there is no intercalate concentration gradient in the intercalated region. Thus, half of the total increase in thickness is given by

$$h(r, t) = d'j, \tag{4}$$

where $2j$ is the number of intercalate layers that have progressed up to point r at time t and d' is the change in the spacing between two adjacent graphite layers due to the insertion of an intercalate layer in between (3.7 Å for Br_2 intercalation). Putting eqn (4) in eqn (3) yields the equation for the thickness profile for $t \le t_N$:

$$r = R_0 - v\left(t - \frac{h\Delta T}{d'}\right). \tag{5}$$

It follows from eqn (5) that, at $r = R_0$ (i.e. the edge) the total expansion $2h = h_E$ is given by

$$h_E = 2d' \frac{t}{\Delta T}. \tag{6}$$

Equation (6) gives the increase in thickness at the edge with time. The intercalate front corresponds to $h = 0$ in eqn (5) and its position $r = r_I$ is given by:

$$r_I = R_0 - vt. \tag{7}$$

Rearrangement of eqn (5) gives

$$h(r, t) = \begin{cases} \dfrac{d'}{v\Delta T}[r - (R_0 - vt)], & r \ge r_I \\ 0 & , r \le r_I. \end{cases} \tag{8}$$

Before intercalation begins ($t \le 0$), the profile is flat, as shown in Case 1 of Fig. 2 by curve 0. As time progresses, the profile corresponding to eqn (8) on one of the c-faces becomes bucket-shpaed, as indicated by the line *abcd* (curve 1). The slanted linear portions (*ab*, *cd*) have a slope equal to $d'/v\Delta T$ and the intercalate front (b, c) moves with a constant velocity equal to v. As intercalation proceeds further, the straight lines *ab* or *cd* translate parallel to themselves toward the center.

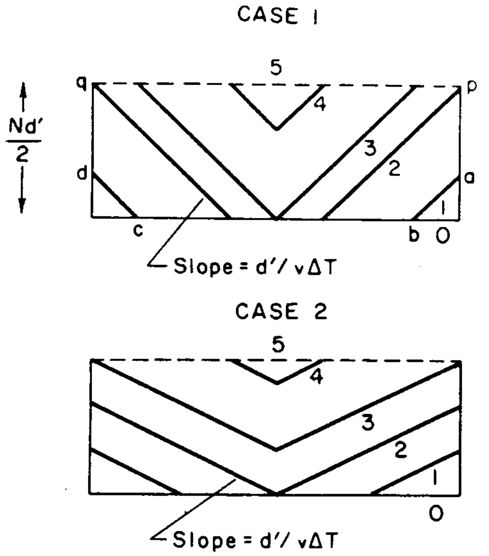

Fig. 2. Schematic diagram of the sequence of surface profiles as interface-controlled intercalation proceeds with time.
Case 1 ($t_N \le t_G$). Curve 0: $t = 0$; 1: $t < t_N$; 2: $t = t_N$; 3: $t = t_G$; 4: $t > t_G$; 5: $t = t_I$
Case 2 ($t_N \ge t_G$). Curve 0: $t = 0$; 1: $t < t_G$; 2: $t = t_G$; 3: $t = t_N$; 4: $t > t_N$; 5: $t = t_I$.

At the same time, the edge thickness continues increasing until the increment reaches its maximum value $h_\infty = Nd'$ at time $t = t_N$. After time $t = t_N$, the lines *ab* and *cd* continue to translate parallel to themselves until time $t = t_G$, when these lines meet at the center of the sample and result in a V-shaped profile, as shown by curve 3. At this time, the formation of the first intercalate layers is completed. After this, the V-shaped part of the profile becomes smaller as more intercalate layers are completely formed, as shown by curve 4. When intercalation is completed ($t = t_I$), the V-shaped part of the profile vanishes, leaving a flat surface, as shown by the line *pq* (curve 5). This line is parallel to line *bc* and is at a height of $(N/2)d'$ from line *bc*.

Similar arguments give the evolution of the surface profile for Case 2 ($t_N \ge t_G$), as illustrated in Fig. 2.

Measuring the radius of the bromine front in the surface profile as a function of time gives directly $g(vt/R_0)$, and hence the velocity, whereas ΔT can be obtained directly from measurement of the edge expansion vs time [eqn (6)] or indirectly from the slope $d'/v\Delta T$ of the slanted linear portion of the surface profile.

2.2 *Mass increase*

The proposed model of intercalation has also been used to obtain the expression for the increase in mass (M_t) as a function of the time of intercalation (t).

The mass increase is proportional to the total area of the intercalate layers. Let M_∞ be maximum mass increase. The fractional mass increase M_t/M_∞ at time t is given by the following equations.

Case 1:

$$\frac{M_t}{M_\infty} = \begin{cases} f(t), & 0 \le t \le t_N \quad (9.1) \\ f(t) - f(t - t_N), & t_N \le t \le t_G \quad (9.2) \\ \dfrac{t - t_G}{t_N} + f(t_G) - f(t - t_N), & t_G \le t \le t_I \quad (9.3) \end{cases}$$

Case 2:

$$\frac{M_t}{M_\infty} = \begin{cases} f(t), & 0 \le t \le t_G \quad (10.1) \\ \dfrac{t - t_G}{t_N} + f(t_G), & t_G \le t \le t_N \quad (10.2) \\ \dfrac{t - t_G}{t_N} + f(t_G) - f(t - t_N), & t_N \le t \le t_I \quad (10.3) \end{cases}$$

where

$$f(t) = \frac{t^2}{t_N t_G}\left(1 - \frac{t}{3t_G}\right). \tag{11}$$

and

$$t_I = t_N + t_G.$$

Thus, according to the proposed model, M_t/M_∞ is initially a parabolic function of time [eqn. (11)]. However, if t_N/t_G in Case 1 or t_G/t_N in Case 2 is very small compared to unity, the mass increase is effectively linear with time [eqn (9.2) or (10.2)].

3. DISCUSSION

3.1 *Comparision of model with experimental results*

The proposed model of intercalation was strongly motivated by the results of our surface profile measurements, which are conveniently discussed in a separate publication [18]. This discussion is restricted to thickness expansion and gravimetric results.

Thickness expansion. The time needed for the mass to attain its maximum value is $t_I = t_N + t_G$ for the interface-controlled process. It is a trivial consequence of the model that this time is always greater than the time (t_N) needed for the edge to attain its maximum thickness. This explains the observation made by Saunders *et al.*[4] that the edge thickness increased to almost its limiting value at ~1/3 of the bromine mass uptake. A similar behavior is observed in many other cases of intercalation.

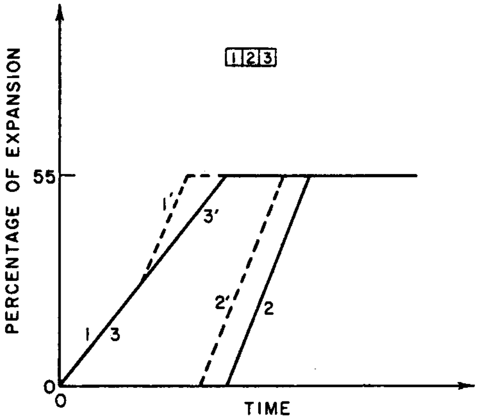

Fig. 3. Edge expansion of a cylindrical sample with three marked sections according to the proposed model. The dashed curves indicate the consequence of disc production.

The model indicates that the edge expansion is linear with time, as given by eqn (6). This prediction is largely supported by experimental curves of expansion vs time obtained during the intercalation of bromine [5] and various metal halides, particularly $FeCl_3$ [7], except probably at the very end of the expansion. Expansion vs time curves have recently been measured by Bardhan *et al.*[8] for the intercalation of HOPG. Deviation from linearity was observed for Br_2 and ICl intercalation before full expansion. Further support is obtained from the results of the marked cylinder experiment performed during bromine intercalation by Hooley *et al.*[6]. However, the results of this experiment are complicated by disc production, by which the sample cylinder splits into discs perpendicular to the c-axis. The main features of the experiment are illustrated in Fig. 3, where the expansion of a cylinder with three marked sections is considered according to the proposed model. Note that the slope of Section 2 is $2d'/\Delta T$, whereas those of the other sections are half of this value, because intercalation proceeds from only

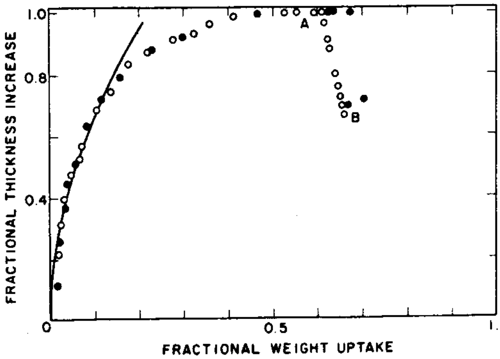

Fig. 4. Comparison between the theory and the experimental data of fractional expansion vs fractional mass increase during Br_2 intercalation. For explanation of the symbols A and B, refer to the text. (Experimental data after Saunders *et al.*[4] with permission of authors.)

one side for Sections 1 and 3. Corresponding curves for the case of disc production are indicated by the dashed curves in Fig. 3. The curves are not linear. Moreover, Section 2 starts expanding before Section 3 finishes expanding.

Saunders *et al.*[4] ascribed the observed variation of thickness with weight to the formation of a metastable compound. They further mentioned the spontaneous decrease in thickness (of the edge) when the metastable compound A, with fully expanded edge but only 50% of the saturated composition, transformed to the stable compound B with the same Br_2 content (Fig. 4) due to the withdrawal from the bromine vapor and immersion in Br_2–CCl_4 solution of an appropriate concentration. It should be noted that the model is in full agreement with the explanation given in terms of incomplete layers [27], although we think that the notion of non-equilibrium is preferable to that of metastability. The data of Saunders *et al.* indicated that the thickness (edge) of the equilibrium compound B was ~2/3 that of the non-equilibrium compound A from which it transformed, and that the bromine uptake of the equilibrium compound was 2/3 of the maximum. This amount of thickness change is expected if the sample changed from the second stage structure to the third stage structure, which is consistent with the bromine uptake of the equilibrium compound. This further substantiates the point that a compound possesses the layer sequence of the destined stage from the beginning of intercalation.

Interpretation of ΔT. As mentioned before, ΔT can be obtained directly and more accurately from expansion data or indirectly from surface profile data. Its value is very sensitive to the pressure, the degree of crystallite alignment and, to some extent, the thickness of the sample. Values of ΔT corresponding to different values of these parameters are to be published in Ref. [8].

Although ΔT is a convenient phenomenological parameter, it may be given a more fundamental meaning in terms of the stress state at the interface of the intercalated and unintercalated regions. In the interface-controlled process, if the interface is viewed as an array of dislocations whose Burgers vectors are perpendicular to the basal plane, it can be shown [28] that the force between two parallel dislocations in adjacent planes increases with decreasing separation. While the separation along the c-axis is fixed, that along the direction perpendicular to the c-axis is variable. Consequently there must be a characteristic in-plane separation between dislocations corresponding to a balance of the strain energy with the available reaction energy. A large separation between two adjacent intercalate layer fronts implies a small surface slope. As the whole interface is moving inward with some velocity, ΔT may be viewed as the time necessary to move the separation distance, or equivalently, the length of the time between the start of growth of two consecutive intercalate layers. This interpretation is a more concrete form of similar ideas expressed in the strain model [23]. In this context, the steady velocity is simply the velocity of dislocation movement (climb). Investigation of the dependence of the velocity on the intercalate vapor pressure, the temperature and other relevant thermodynamic variables is expected to yield quantitative information on the various energy parameters involved in the intercalation process.

Based on the data in Ref. [5], it appears that the variation of ΔT with pressure at a given temperature might be written as

$$\Delta T = A \exp \frac{B}{p - p_{th}},$$

where A and B are functions of temperature for a given sample and p_{th} is the threshold pressure [8]. At $p = p_{th}$, ΔT is infinite, i.e. no intercalation takes place.

Mass increase. In case of the interface-controlled process, eqns (6) and (11) can be combined to yield the relation between the edge expansion and the corresponding mass increase. Thus, for small time, we obtain a parabolic relation:

$$\frac{M_t}{M_\infty} \sim \frac{t_N}{t_G}\left(\frac{h_E}{h_\infty}\right)^2. \tag{12}$$

Figure 4 shows good agreement up to about 80% of the expansion between the theoretical curve [eqn (12)] and the experimental data for Br_2 intercalation reported in Fig. 2 of Ref. [4]. The value of t_N/t_G used is 0.24. In the absence of relevant data, it is difficult to calculate t_N/t_G for the sample used. However, we can use the ratio to calculate v and compare with that corresponding to HOPG (Grade ZYA) [18], as described below. We have $\Delta T = 7 \times 10^{-2}$ sec [8]. For the sample of size 4 × 4 × 1 mm and carbon layer separation of 3.35 Å, $N = 0.1/(2 \times 3.35 \times 10^{-8}) = 1.5 \times 10^6$ for a stage 2 compound. Thus, $t_N = (1/2)N\Delta T = 5.2 \times 10^4$ sec and hence $t_G = 2.2 \times 10^5$ sec. Therefore, $v = 0.2/t_G = 9.2 \times 10^{-7}$ cm/sec. This value is less than that (~5×10^{-6} cm/sec) [18] obtained with HOPG by a factor of ~5 and is consistent with the fact that samples used by Saunders *et al.* are much less well aligned than HOPG. It is of interest to note that the experimental curve for ICl intercalation also shows similar curvature [4].

As mentioned before, depending on the ratio of the time to finish the edge expansion (t_N) and that to finish the mass increase (t_l), or, in other words, depending on the value of M_{t_N}/M_∞ compared to 1, the shape of the curve of mass uptake vs time varies for Case 1 of the interface-controlled intercalation model. This is clearly demonstrated by comparing gravimetric and expansion data for samples of varying degrees of crystallite alignment. The following data of Hooley *et al.*[6] are particularly illustrative. The sample PG1 of thickness 1.2 mm took ~400 min to complete edge expansion (Fig. 1) at which point the mass uptake was about half of the maximum

$(M_{t_N}/M_\infty \simeq 0.5)$ (Fig. 5); the sample PG3 of thickness 6 mm took ~20 min at which point the fractional bromine uptake was only 0.1; the corresponding numbers of PG6 were 5 min and 0.03. The samples PG1, PG3 and PG6 are in order of increasing degree of crystallite alignment. Thus, it is evident that, the more well-oriented are the crystallites, the less is the fractional mass uptake during edge expansion (t_N). Consequently, according to the model, the parabolic part of the mass increase curve becomes insignificant. One case where t_N is not small has already been discussed in the previous paragraph. All curves of bromine weight uptake vs $t^{1/2}$ in the early part of intercalation, as obtained with sample PG1 [6], were convex and thereby lend further support to the model, although the curves seem to rise less rapidly than a t^2-dependence.

The gravimetric curves obtained during Br_2 intercalation by Marchand *et al.*[15] are all linear in time initially and accordingly indicate that t_N is negligible, as is true for all HOPG samples. Putting t_N equal to zero in eqn (9.2) reduces this equation to the one used by Marchand *et al.*, provided that one uses f appropriate for a rectangular sample of sides l_1 and l_2, i.e.

$$f(t) = \left(\frac{1}{t_{G_1}} + \frac{1}{t_{G_2}}\right)\frac{t^2}{t_N}\left(1 - \frac{4}{3}\frac{t}{t_{G_1} + t_{G_2}}\right), \quad (13)$$

where $t_{G_1} = l_1/v$ and $t_{G_2} = l_2/v$. Hence, eqn (9.2) reduces to

$$\frac{M_t}{M_\infty} = 2\left(\frac{1}{t_{G_1}} + \frac{1}{t_{G_2}}\right)t - \frac{4t^2}{t_{G_1}t_{G_2}}. \quad (14)$$

Marchand *et al.* already noted that there is good agreement up to ~75% of the mass uptake between the experimental data and the theoretical curves shown as heavy lines in Fig. 5. However the rate of intercalation beyond 75% seems to be much lower than the predicted curve. This can be accounted for by making the assumption that the initial velocity drops to a lower value after a certain period of time which can be found by fitting the curve. The results are shown by the dashed lines in Fig. 5. In this way, the agreement is extended to about 95% of the mass uptake. This assumption has indeed some experimental basis, being a result of edge effect, as found in the direct measurement of the velocity in surface profilometry [18]. The initial velocities used in Fig. 5 are 7.3×10^{-7} cm/sec (curve *I*) and 8.6×10^{-7} cm/sec (curve *II*); the values at later times are respectively 0.65 and 0.7 of the initial values. The time when the velocities change is about the same for the two curves (3300 min or 55 hr). Thus, the time period before the velocity change is close to 44 hr, which was when the edge effect was found to be dominant [18]. The magnitude of the velocity for intercalation at 20°C and 176 mm of Hg of Br_2 was calculated from the data to be about 5.6×10^{-6} cm/sec, which compares very favorably with the initial value $(\sim 5 \times 10^{-6}$ cm/sec) of the velocity obtained with HOPG disc at room temperature (22°C) and the saturated vapor pressure of Br_2 [18].

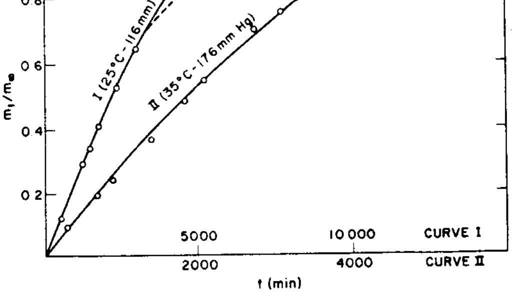

Fig. 5. Comparison between theory and experimental data of mass increase vs time during Br_2 intercalation. Each solid curve was calculated by using a single value of v; each dashed curved was calculated by using two values of v. (Experimental data after Marchand *et al.*[15] with permission of authors.)

Using a different experimental set-up, Dowell *et al.*[12] obtained gravimetric data during Br_2 intercalation. They have noted that the mass vs time curve cannot be fitted well with the usual diffusion theory. Furthermore, all their curves show a convex portion in the early part of intercalation. In our opinion, this convex portion probably results from the particular experimental set-up used and consequently prevents the data from being analyzed with the proposed model [29].

The increase in $FeCl_3$ content in the intercalation of graphite has also been reported to be linear with time at the beginning [16]. If the intercalation mechanism does depend on the intralayer order–disorder transformation temperature, the above results mean that the $FeCl_3$ layers are still ordered within the layers at least up to the highest temperature used (360°C). To test the validity of this implication, we have used differential scanning calorimetry which indeed did not show the existence of a transformation between room temperature and 360°C in graphite-$FeCl_3$. It would be interesting to know if there is any difference in behavior of mass absorption during intercalation below and above the intralayer order–disorder transformation temperature. For this purpose, an intercalate species like ICl might be a good choice for experimental investigation because the intralayer order–disorder transformation temperature (41°C) is not very far from room temperature [3, 30].

The assumption that nucleation starts at the edge of a layer permits one to draw the following qualitative conclusion about the geometric effect of sample shape on the rate of intercalation. Given two samples of the same thickness and basal plane surface area at the same temperature and pressure, the sample with the larger basal plane perimeter will be intercalated faster than the other. For example, a rectangular shaped sample is expected to be intercalated faster than a circular sample under the above conditions [31].

Although the exact layer sequence for a given stage has been assumed while describing the model (Fig. 1), this assumption is not necessary for the model to be applicable. In fact the consequences of the model are insensitive to the difference between the classical stage model and the domain model of Herold *et al.*[32]. The model is applicable even if some disorder is present in the stacking of the intercalate layers [33]. Of importance to the model is just the number of layers that eventually form.

We have not obtained experimental evidence for Case 2. This is not surprising in view of the dimensions of the samples used (thickness along the *c*-direction being much less than the basal plane dimensions). On the other hand, the use of graphite powders might yield evidence for Case 2. However, because of the experimental difficulty in performing surface profilometry on a powder particle, Case 2 can only be investigated by careful analysis of gravimetric results obtained during intercalation. The effect of the degree of graphitization is expected to be reflected in the values of the parameters in the model, to the extent that the basic mechanism described here still plays the leading role. Both catastrophic and non-catastrophic cracks, particularly the latter, are primarily responsible for much of the disagreement among the results of expansion and various other experiments. They are yet to be investigated systematically.

It is clear that the proposed model does not intend to explain the most fundamental aspect of intercalation, namely staging. Assuming the presence of staging, the model provides a phenomenological description of the kinetics. However it is apparent that a theoretical analysis of the elastic effects based on the picture given here would be of immense help for further understanding of the problem.

3.2 *Applicability of model to the intercalation of other materials*

It is known that materials such as the dichalcogenides and the layered silicates also form intercalation compounds through processes being described in general as topochemical [34]. It is of interest to consider the similarity among these materials and graphite in the kinetics of intercalation. The work of Chianelli[35] on the intercalation of lithuim into transition metal dichalcogenides brings out a picture which is very similar to the interface-controlled process described in this paper. Unfortunately, the lack of quantitative experimental data inhibits the direct test of the applicability of the proposed model to the intercalation of these materials.

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24. This assumption implies that the system does not progressively go through different stages on the way to a given stage. This implication is supported by X-ray diffraction results [25, 26] with bromine, which showed no evidence for any stage other than the saturated second stage and a virgin region in a sample undergoing vapor phase intercalation to a saturated compound. Marchand *et al.*[15] also came to the same conclusion from their study of the variation of the magnetic anisotrophy with temperature. However, this is known to be not true in the case of nitration [19, 26], where a given stage is reached through a succession of higher stages. In our opinion, this characteristic of HNO_3 intercalation complicates the description of the kinetics of intercalation in terms of simple diffusion.
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29. In using gravimetry to study the kinetics of intercalation in the presence of an inert atmosphere, it is important to consider the diffusion of the intercalate vapor through the inert gas atmosphere before the vapor reaches the sample. Of relevance in this consideration is the distance between the sample and the meniscus of the intercalate liquid reservoir. This distance is about 10 cm in Dowell's experimental set up [*Mater. Sci. Engng* **31.** 129 (1977)], which involves the Cahn Electro-balance. Dowell (private communication) believes that in his experiment the partial pressure of Br_2 became constant before intercalation had proceeded very far. However, by using a similar experimental set-up with the above-mentioned distance being small (~ 2 cm), Anderson and Chung (unpublished) did not observe any significant induction period, nor any initial convex portion in the mass absorption curve.
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31. This point needs further investigation as can be seen from the observed large difference in intercalation time for samples of approximately comparable dimensions and quality but of different shapes. In an unpublished work, Anderson and Chung observed that a circular disc of HOPG (diameter 4.5 mm), cut by a spark cutter, took about 10 days to be fully intercalated with Br_2, whereas a similar sample of rectangular shape took about 2 days only. A similar dependence of the intercalation time on sample shapes was observed with HNO_3 as the intercalate species. Measurements of Dowell [11] indicated that intercalation with HNO_3 took about 60 hr for a circular sample, whereas data of Forsman *et al.* (*Carbon* 16, 1978) showed that the corresponding time for a rectangular sample is about 5 hr only, although the latter had larger dimensions. The elastic state of a sample is probably influenced significantly by the shape and consequently affects the relevant kinetic parameters.
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