Carbon Vol. 25, No. 2, pp. 211–218, 1987
Printed in Great Britain.

0008-6223/87 $3.00 + .00

KINETICS AND THERMODYNAMICS OF INTERCALATION OF BROMINE IN GRAPHITE—II. THEORY

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(*Received* 12 *May* 1986)

Abstract—A theory that describes the diffusion of an intercalate within graphite in a multiphase situation is presented. The theory was applied to the intercalation of bromine in graphite. Single-phase diffusion represents the intercalation of bromine in graphite as well as multiphase diffusion due to the dominance of the final stage.

Key Words—Intercalation, bromine.

1. INTRODUCTION

In estimating the dominant steps in the intercalation of bromine in graphite[1] and in the experimental results of the accompanying paper[2], it is evident that diffusion dominates the reaction kinetics of the graphite–bromine system. In describing diffusion in an intercalation compound, one might consider a rigorous description of diffusion in a multiphase system (Section 2.2) or a simple description of diffusion treating the entire intercalated region as a single phase (Section 2.1). Because of the common coexistence of stages during intercalation[2], a multiphase approach needs to be considered. The single phase approach was used by Dowell[3,4] to describe the intercalation of bromine, nitric acid and palladium chloride. This paper provides the first description of an intercalate diffusing in graphite using a multiphase approach. Both the single-phase and multiphase models are used in this work to fit the kinetic data obtained in the accompanying paper[2].

2. DIFFUSION OF AN INTERCALATE IN GRAPHITE

2.1 *Single-phase approach*

If a single stage were present during intercalation, the diffusion process could be represented using Fick's law to describe the flux balance at the interface between the intercalated region and the unintercalated graphite.

Although multiple stages are present during the intercalation of graphite by bromine, it can be useful to consider that the diffusion process can be represented by a single apparent diffusion coefficient. If this is done, the intercalation process can be likened to diffusion in a two-phase system with an interface between the "intercalated phase" and the pristine graphite. In this case the diffusion rate can be represented as the rate of motion of the interface between the two phases. If the position of the interface is represented by x, then the position of the interface as a function of time can be represented by[5]

$$x^2 = 4\eta^2 Dt, \tag{1}$$

where η accounts for the chemical potential gradient across the intercalated region and is defined as

$$\eta\ \mathrm{erf}(\eta)\ \exp(\eta^2)\pi^{-1/2} = [P_{\mathrm{ext}} - P_{\mathrm{eq}}], \tag{2}$$

where P_{ext} is the bromine vapor pressure external to the sample and P_{eq} is the equilibrium bromine pressure at the reaction interface.

2.2 *Multiphase approach*

Shatynski *et al.*[6] suggested a theory of multiphase binary diffusion which is used here for describing the diffusion occurring during an intercalation reaction. They considered a reaction of the form

$$aA + bB \longrightarrow A_\alpha B + cA_\beta B + dA_\gamma B + \cdots, \tag{3}$$

and described the reaction rates in terms of the thickening of the phases. The assumptions necessary for the application of the theory are that there is negligible terminal solid solubility of the reactants and that quasi-steady-state growth occurs. Quasi-steady-state growth is defined as in Jost[5]: (i) for constant cross section the fluxes of A and B atoms are inverse functions of the thickness of the phase and (ii) equilibrium boundary conditions are maintained at interphase interfaces. Condition (i) is met as long as the effect of the moving boundary conditions is small. Condition (ii) is approximately met when the compound has a narrow composition range and a nearly constant molar volume. In general, these conditions can apply to intercalation compounds. The samples are generally small and a given phase generally has narrow stoichiometric limits in the pure binary compounds. In particular this is the case for graphite–bromine intercalation compounds.

Several simplifications occur in dealing with intercalation compounds. First, the diffusivity of the carbon atoms comprising the graphite is negligible compared to the diffusivity of the intercalate. Hence only the flux of the intercalate need to be dealt with. Second, in the case of graphite–bromine compounds, the in-plane stoichiometry seems to be independent of stage so that terms involving the different stages can be written as ratios of the stage numbers without including corrections for stoichiometry changes.

Normally the stoichiometry of graphite–bromine compounds can be written as $C_{7i}Br_2$, where i is the stage number, greater than or equal to 2. However, since bromine is the mobile species, it is more convenient to refer to the stoichiometry as $C(Br_2)_{1/7i}$. Then using B to replace Br_2, we may refer to the general intercalation reaction as

$$aC + bB \longrightarrow CB_{1/(7)(2)} + cCB_{1/(7)(3)} + \cdots + x_i CB_{1/(7)(i)} + \cdots, \quad (4)$$

where the x_i's are mass balance coefficients with x_2 arbitrarily chosen to be equal to 1.

We can consider the rate of expansion of the ith stage in this reaction. On one side there exists an interface between the $(i - 1)$th and ith stage; on the other side of the phase there exists the interface between the ith and $(i + 1)$th stage. The reaction at the $(i - 1) : i$ interface may be written as

$$7i(i - 1)CB_{1/7(i-1)} \longrightarrow 7i(i - 1)CB_{1/7i} + B, \quad (5)$$

and at the $i : (i + 1)$ interface as

$$7i(i + 1)CB_{1/7i} \longrightarrow 7i(i + 1)CB_{1/7(i+1)} + B. \quad (6)$$

Hence the formation of $7(i - 1)i$ moles of ith stage involves $7(i - 1)i$ moles of $(i - 1)$th stage per mole of bromine released and the formation of $7i(i + 1)$ moles of ith stage involves $7i(i + 1)$ moles of $(i + 1)$th stage per mole of bromine absorbed. The phase between the two interfaces will grow at a rate which is the difference between the velocities of the bounding interfaces. The velocity of an interface, for example, between $(i - 1)$th stage and ith stage, is the difference between the flux of bromine across the $(i - 1)$th stage to form the $(i - 1)$th stage from the ith stage at the $(i - 1)$th side of the interface, and the flux of bromine across the ith stage due to the formation of ith stage from $(i - 1)$th stage on the ith side of the interface. This may be written for the first interface (x_1) as

$$\frac{dx_1}{dt} = -7i(i - 1)\Omega_{i-1}D_{i-1}\frac{\partial c_{i-1}}{\partial x} + 7i(i - 1)\Omega_{i-1}D_i\frac{\partial c_i}{\partial x}, \quad (7)$$

and similarly for the interface (x_2) between the ith and $(i + 1)$th stages:

$$\frac{dx_2}{dt} = -7i(i + 1)\Omega_i D_i\frac{\partial c_i}{\partial x} + 7i(i + 1)\Omega_i D_{i+1}\frac{\partial c_{i+1}}{\partial x}. \quad (8)$$

Then the change in thickness of the ith stage can be written as

$$\begin{aligned}\frac{dX_i}{dt} &= \frac{dx_2}{dt} - \frac{dx_1}{dt}\\ &= -[7i(i - 1)\Omega_{i-1} + 7i(i + 1)\Omega_i]\left(D_i\frac{\partial c_i}{\partial x}\right)\\ &\quad + 7i(i - 1)\Omega_{i-1}\left(D_{i-1}\frac{\partial c_{i-1}}{\partial x}\right)\\ &\quad + 7i(i + 1)\Omega_i\left(D_{i+1}\frac{\partial c_{i+1}}{\partial x}\right) \quad (9)\end{aligned}$$

X_i is the thickness of the ith stage, Ω_i is the molar volume of the ith stage, c_i is the concentration of bromine in moles/per unit volume in the ith stage and D_i is the intrinsic diffusivity of bromine in the ith stage. The change in thickness of the ith stage can also be related to a parabolic rate constant k_i:

$$\frac{dX_i}{dt} = \frac{k_i}{X_i}. \quad (10)$$

After rearrangement of the molar volume terms the general equation may be written as

$$\begin{aligned}\frac{k_i}{X_i} &= -7i\left[(i - 1)\left(\frac{\Omega_{i-1}}{\Omega_i}\right) + (i + 1)\right]\left(\Omega_i D_i\frac{\partial c_i}{\partial x}\right)\\ &\quad + 7i(i - 1)\left(\Omega_{i-1}D_{i-1}\frac{\partial c_{i-1}}{\partial x}\right)\\ &\quad + 7i(i + 1)\left(\frac{\Omega_i}{\Omega_{i+1}}\right)\left(\Omega_{i+1}D_{i+1}\frac{\partial c_{i+1}}{\partial x}\right). \quad (11)\end{aligned}$$

If it is assumed that the concentration of a given stage is constant across the stage, and the diffusion coefficient is independent of the chemical potential, it is possible to replace the concentration gradient with the chemical potential gradient in the following manner

$$D_i\frac{\partial c_i}{\partial x} = \frac{D_i^* c_i}{RT}\frac{\partial \mu_i}{\partial x} = \frac{D_i^*}{7i\Omega_i\,RT}\frac{\partial \mu_i}{\partial x}, \quad (12)$$

where μ_i is the chemical potential per mole of bromine in stage i and D_i^* is the mobility of bromine in the ith stage. Furthermore we can relate the molar volume to the molar concentration. The molar volume of a stage i compound is the volume of the compound per mole of the compound. The molar concentration is the number of moles of bromine per unit volume of the compound. Then the relation between the molar volume and molar concentration is the number of moles of bromine per mole of compound, which is evident from the stoichiometry of the compound. Hence for a reaction of the form

$$C + \frac{1}{7i} B \longrightarrow CB_{1/7i}\,, \tag{13}$$

a dimensional analysis shows that

$$\frac{\Omega_i \mathrm{cm}^3\, CB_{1/7i}}{\mathrm{mol}\ CB_{1/7i}} = \frac{\mathrm{cm}^3\, CB_{1/7i}}{c_i\ \mathrm{mol}\ B}\,\frac{1/7i\ \mathrm{mol}\ B}{\mathrm{mol}\ CB_{1/7i}}\,. \tag{14}$$

or after cancelling equivalent terms,

$$\Omega_i = 1/[7ic_i]. \tag{15}$$

Then we can write

$$\frac{k_i}{X_i} = -\left[(i-1)\left(\frac{\Omega_{i-1}}{\Omega_i}\right) + (i+1)\right]\left(\frac{D_i^* \partial\mu_i}{\mathrm{RT}\ \partial x}\right) + i\left(\frac{D_{i-1}^*}{\mathrm{RT}}\frac{\partial\mu_{i-1}}{\partial x}\right) + i\left(\frac{\Omega_i}{\Omega_{i+1}}\right)\left(\frac{D_{i+1}^*}{\mathrm{RT}}\frac{\partial\mu_{i+1}}{\partial x}\right). \tag{16}$$

At this point it is convenient to introduce a single term to represent similar portions of the equation. Following the nomenclature of Shatynski *et al.*, we can define

$$h_i = \frac{D_i^* X_i}{\mathrm{RT}}\frac{\partial\mu_i}{\partial x}\,. \tag{17}$$

Then we can write the following expression for the rate constant of the *i*th stage:

$$k_i = -\left[(i-1)\left(\frac{\Omega_{i-1}}{\Omega_i}\right) + (i+1)\right]h_i + i\left(\frac{X_i}{X_{i-1}}\right)h_{i-1} + i\left(\frac{\Omega_i X_i}{\Omega_{i+1}X_{i+1}}\right)h_{i+1}. \tag{18}$$

if we assume that the k's are constant, then since $X = \sqrt{2kt}$, the ratio X_i/X_j is also constant.

The rate constant must be considered specially at the boundaries of the intercalated region, i.e., at the sample edge and at the interface with pure graphite. At the edge, the location of the phase boundary between the intercalation compound and the atmosphere is fixed by the physical edge of the graphite lattice, which may be considered to be fixed in space. As a consequence the rate of growth of the stage at the sample edge is just the rate of motion of the interface between the edge stage and the preceding (inner) stage. If j is the edge stage, then

$$k_j = -(j+1)h_j + j\left(\frac{\Omega_j X_j}{\Omega_{j+1}X_{j+1}}\right)h_{j+1}. \tag{19}$$

At the interface with pure graphite, it is reasonable to assume that the flux of intercalate is so low as to be negligible since the solid solubility of bromine in graphite is much less than the concentration of bromine within the intercalate layer. In that case, if p is the initial stage formed,

$$k_p = -\left[1 + \left(\frac{\Omega_{p-1}}{\Omega_p}\right)(p-1)\right]h_p + p\left(\frac{X_p}{X_{p-1}}\right)h_{p-1}. \tag{20}$$

Within the constraints of our assumption that the diffusion coefficient and concentration are constant within a stage it is possible to write

$$h_i = \frac{D_i^*}{\mathrm{RT}}\int \mathrm{d}\mu, \tag{21}$$

where the integral is performed across the stage. If it is assumed that bromine can be treated as an ideal gas, which is not a bad assumption at low reduced temperatures and pressures (when T and P are not near the critical temperature, 302°C, and critical pressure, 126 atm, of bromine[7]), the change in chemical potential for the reaction can be expressed in terms of the partial pressure of bromine. That is, for the reaction at the interface between stage i and stage $i-1$,

$$\mathrm{Br}_{2(g)} + (i-1)\mathrm{C}_{7i}\mathrm{Br}_{2(s)} = i\,\mathrm{C}_{7(i-1)}\mathrm{Br}_{2(s)},$$

the change in free energy for the reaction can be written as

$$\Delta G = \Delta H - T\Delta S = \mathrm{RT}\ln\left(\frac{a_{i-1}}{a_i a_{\mathrm{Br}_2}}\right), \tag{22}$$

and the change in the chemical potential of the bromine can be written as

$$\Delta\mu_{i-1:i} = \mathrm{RT}\ln(1/P_{i-1:i}), \tag{23}$$

where $P_{i-1:i}$ is the bromine pressure at which stage i and stage $i-1$ are in equilibrium. Then the change in chemical potential of bromine across a given stage is

$$\begin{aligned}\Delta\mu_{i:i+1} - \Delta\mu_{i-1:i} &= \mathrm{RT}[\ln(1/P_{i:i+1}) - \ln(1/P_{i-1:i})]\\ &= \mathrm{RT}\ln(P_{i-1:i}/P_{i:i+1}),\end{aligned} \tag{24}$$

and

$$h_i = D_i^*\ln(P_{i-1:i}/P_{i:i+1}). \tag{25}$$

If conditions can be established where transport within the graphite is the rate-controlling step, and only two stages are present, then the diffusion coefficient for one stage (the stage being formed) may be determined. Alternately, if multiple stages are present, an overall rate constant exists and may be defined as

$$\frac{k_T}{X_T} = \sum_{i=j}^{p} \frac{k_i}{X_i}. \qquad (26)$$

Then the amount of graphite left after intercalation for time t is $1 - x$, where x is the intercalated width and can be represented as

$$t = x^2/k_T. \qquad (27)$$

In this form it is evident that using either the simple approximation given by eqn (1) or eqn (27), the square of the width of the intercalate front can be expected to be proportional to the intercalation time.

3. COMPARISON OF THEORY AND EXPERIMENT

3.1 *Calculation methods*

In order to test the single-phase and multiphase approaches, five methods were used to calculate time-temperature-transformation (TTT) and time-concentration-transformation (TCT) curves for the intercalation of graphite with bromine. These curves had been determined experimentally[2]. Specifically, the length of time necessary to intercalate a fraction of the sample to a particular stage was calculated. The calculations were made without including terms representing bromine transport outside the graphite sample. This was justified on the basis of the calculations of reaction step times[1], and more importantly, on the basis of the weight gain and intercalate front position as a function of time[2]. Both the weight gain and the intercalate front position could be extrapolated back to zero time without indicating incubation times or other reaction steps external to the sample. Consequently, the reaction time was represented by the final two terms of eqn (1) of Ref. 1,

$$t = x^2/K + x/v, \qquad (28)$$

where t is the intercalation time, x is the intercalated length, v is the reaction velocity for the staging reaction and K is a term incorporating the diffusion coefficient.

It was assumed that the staging reaction was first order with respect to the bromine concentration so that the staging reaction velocity could be written in the form

$$v = A_0 \exp[-E_s/\mathrm{RT}][P_{\mathrm{surface}} - P_{\mathrm{interface}}], \qquad (29)$$

where A_0 can be considered a proportionality constant, E_s is the activation energy for the staging reaction, P_{surface} is the vapor pressure of bromine at the sample surface and $P_{\mathrm{interface}}$ is the vapor pressure of the bromine at the staging interface.

The diffusion term K can represent either the $4\eta^2 D$ term in the simple diffusion approximation of Section 2.1 or it can represent a rate constant developed in Section 2.2 [either the total rate constant, k_T, eqn (26) or a rate constant, k_i, for a given stage i, eqn (18)]. In either case, a diffusion coefficient, D, can be represented as

$$D = D_0 \exp[(-E_D + P_{\mathrm{surface}}V_a)/\mathrm{RT}], \qquad (30)$$

where D_0 is the proportionality constant, E_D is the activation energy for diffusion and V_a is the activation volume[2].

Five methods were taken to model the intercalation reaction in the bromine–graphite system. The adjustable parameters used in the modelling were the activation energy, E_s, and preexponential factor, A_0, for the staging reaction, and the activation energy, E_D, and preexponential factor, D_0, for the diffusion coefficient(s). The final parameters obtained are listed in Table 1.

(1) The first method was to treat diffusion as though the intercalate was a single phase (Section 2.1) using an activation energy for diffusion of 18 kcal/mol and a diffusion premultiplier of 1.1×10^5 cm^2/sec. These values were obtained by a recalculation of the gravimetric desorption data of Bardhan *et al.*[8]. The activation energy for the staging reaction was taken to be the activation energy for motion of an interstitial in graphite, reported by Thrower and Loader[9] as 0.69 kcal/mol. The staging velocity premultiplier was varied to fit the intercalation times measured as a function of temperature. (Fig. 21 of Ref. 2).

(2) The second method was to model diffusion in a multiphase system (Section 2.2). In this method the activation energy for diffusion and the staging reaction were assumed to be the same, i.e., the adjustable parameters were A_0, D_0 and $E_{S,D}$. The values of the coefficients were determined by using a simplex optimization method of curve fitting for this and the remaining methods.

(3) The third method was to model diffusion in a multiphase system, but allowing the activation energy for diffusion and staging to differ in the fitting process. The adjustable parameters were A_0, D_0 E_s and E_D.

(4) The fourth method was to use the multiphase diffusion model, using the same activation energy for diffusion and staging, but allowing the diffusion premultiplier to vary with stage. The adjustable parameters were A_0, D_0 (stage 2), D_0 (stage 3), D_0 (stage 4) and $E_{S,D}$.

(5) The final method was to use the multiphase diffusion model, allowing the activation energies to vary, and also allowing the diffusion premultipliers to vary with stage. In this method all six parameters were varied, namely A_0, D_0 (stage 2), D_0 (stage 3), D_0 (stage 4), E_s and E_D.

3.2 *Experimental parameters*

The dependent experimental parameters used for the fitting were the positions of the stage-2 shoulder

Table 1. Parameters used to calculate time-temperature-transformation curves

Method 1:
Single Phase Model

E_S[9]	A_0	E_D[8]	D_0 [8]
kcal/mol	cm/sec	kcal/mol	cm^2/sec
0.69	1×10^{-3}	18	1×10^5

Method 2:
Multi-Phase Model (One Activation energy, One D_0)

E_S	A_0	E_D	D_0
kcal/mol	cm/sec	kcal/mol	cm^2/sec
18	9×10^8	18	1×10^5

Method 3:
Multi-Phase Model (Two Activation energies, One D_0)

E_S	A_0	E_D	D_0
kcal/mol	cm/sec	kcal/mol	cm^2/sec
14	8×10^5	21	1×10^7

Method 4:
Multi-Phase Model (One Activation Energy, Stage Dependent D_0)

E_S	A_0	E_D	D_0		
			Stage 2	Stage 3	Stage 4
kcal/mol	cm/sec	kcal/mol	cm^2/sec	cm^2/sec	cm^2/sec
21	7	21	7×10^7	6×10^6	6×10^6

Method 5:
Multi-Phase Model (Two Activation Energies, Stage Dependent D_0)

E_S	A_0	E_D	D_0		
			Stage 2	Stage 3	Stage 4
kcal/mol	cm/sec	kcal/mol	cm^2/sec	cm^2/sec	cm^2/sec
15	2×10^8	22	7×10^7	1×10^7	1×10^7

(where it existed), the stage-3 shoulder, and the position of the initial (leading) intercalate front as determined by X-ray absorption. The independent experimental parameters were the reaction temperature, the bromine concentration and the intercalation time. The reason for using the X-ray absorption profiles for fitting was that in an infinite diffusion couple, the position of a plane of constant concentration should vary as a function of the square root of time. The X-ray absorption data provided a means of locating a plane of constant concentration, even though the intercalate front might not be perpendicular to the basal plane, or a shoulder on the absorption curves might not exactly correspond to the interface between phases. The X-ray diffraction results should indicate the fraction of a given stage which is present, but may be too dependent on the distribution of stages near the sample surface. Optical profilometry would give information about the position of a constant concentration interface, but would only give information about the leading edge of the surface deformation. Weight uptake would only give composite information about the overall intercalation rate without allowing information concerning individual stages to be discerned.

The six experimental parameters (time, temperature, bromine activity and the positions of the intercalate fronts for stages 2, 3 and 4) allow the use of up to six adjustable parameters in the model. In the actual fitting, the number of parameters adjusted varied from one (the staging velocity premultiplier) in method 1, to six in method 5, which had separate activation energies for the staging reaction and diffusion coefficient, and had stage-dependent diffusion coefficient premultipliers.

The data used in the fitting fell into two classes—(i) temperature dependent data and (ii) concentration (Br_2 concentration in Br_2–CCl_4 solution) dependent data. Except at room temperature, few samplings were done at any one temperature. The points in Fig. 21 of Ref. 2 were determined as the time at which a single stage had been formed, as observed by X-ray diffraction. This was used as the time necessary to intercalate to a position of half the sample width, yielding a time-temperature data pair for the TTT diagram. Each combination of time, temperature and position so determined was used as a data point in the curve fitting.

For graphite intercalated in Br_2–CCl_4 solutions at room temperature, the reaction rate was followed at more frequent time intervals and the use of X-ray absorption to determine concentration profiles allowed the motion of the interstage interfaces (i.e. the shoulders in the concentration profiles) to be followed. Consequently, time-position pairs for the stage-2 shoulder, stage-3 shoulder and the shoulder representing the leading edge of the intercalate front were used for curve fitting. The shoulder position

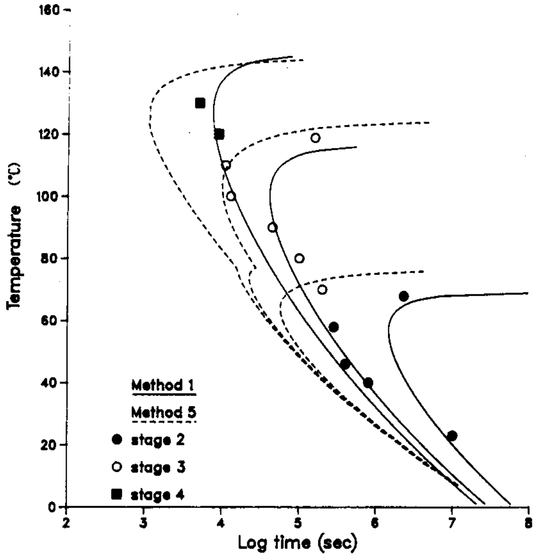

Fig. 1. Time-temperature-transformation curves calculated for graphite–bromine intercalation compounds. The solid lines were calculated using method 1; the dashed lines using method 5. The experimentally observed times to complete intercalation are given by filled circles for stage 2; open circles for stage 3; and filled squares for stage 4.

data were used preferentially to the diffraction data because the models were developed in terms of the motion of interfaces. They were used in preference to the weight gain information since the weight gain provided no information on individual stages. Furthermore, both the weight gain and the volume fraction of an individual stage can be calculated from the interstage interface positions from the concentration profile, while it would be difficult to obtain the interface positions from either the diffraction data or the weight gain data.

It is possible for a discrepancy to exist between the temperature dependent data and the concentration dependent data. The temperature dependent data were based on the times at which intercalation of a stage was complete, as indicated by X-ray diffraction. The concentration dependent data were based on the leading edge of the intercalate front, as indicated by X-ray absorption. If the intercalate front and the basal plane were perpendicular to each other, diffraction and absorption would be the same. However, the intercalate front tends to be not perpendicular to the basal surface, because the surface layers tend to intercalate before the center layers[10–12]. As a result, the leading edges of the intercalation fronts could indicate that intercalation is complete before the sample is actually a single stage.

3.3 *Agreement between theory and experiment*

Figure 1 illustrates how the TTT curves calculated by the different methods compare with the experimental data. The solid lines indicate curves calculated using method 1; the dashed lines were calculated using method 5. None of the models provides an excellent fit; method 1 and method 5 (Fig. 1) yield the best fit.

Figures 2 and 3 indicate the fit of the models for intercalation in Br_2–CCl_4 solutions at room temperature. Figure 2 is a comparison of the intercalate front positions for stages 2, 3 and 4 as a function of the square root of time for intercalation of graphite in a 50-mol % Br_2–CCl_4 solution at room temperature. Figure 3 is a comparison of the fit of the models to the intercalate front position of stage 4 in three Br_2–CCl_4 solutions, namely those containing 50-, 30- and 10-mol % Br_2. As was the case in Fig. 1, methods 1 and 5 provide the best fit for the concentration dependent data (Figs. 2 and 3). The fit is better for stage 4 (Fig. 3) in large part because the intercalate front position was more pronounced so that there was less scatter in the data.

Method 1 provided a surprisingly good fit to the data, especially considering that the staging velocity premultiplier (the only adjustable parameter) really only affects the position of the nose of the TTT curves. Methods 3 and 5 appeared to provide a better fit overall than did methods 2 and 4; this suggests that the staging process and diffusion are dissimilar enough to have different activation energies. This pairing of methods (see Table 1) also suggests that a difference in the activation energy between staging

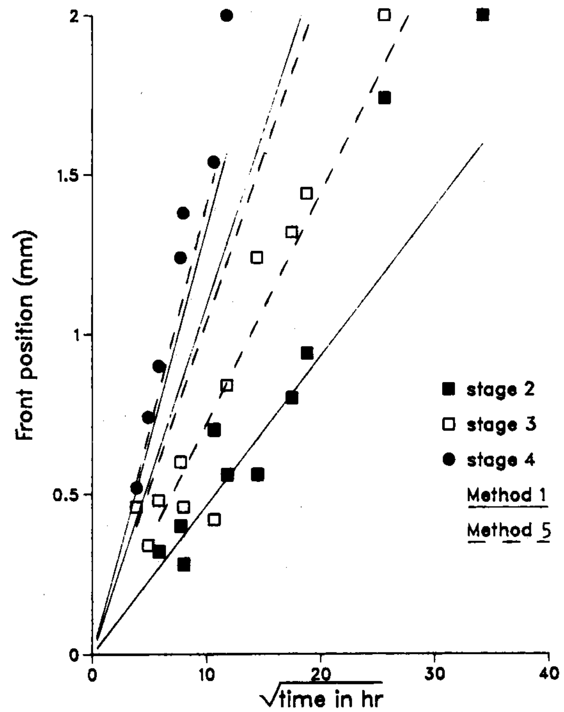

Fig. 2. Comparison of the calculated front position and the experimental front position for intercalation of 4-mm-wide graphite in 50-mol % Br_2 in CCl_4 at room temperature. The filled squares indicate the experimental front position of stage 2 as a function of the square root of time; open squares stage 3; filled circles stage 4. The solid lines were calculated using method 1; the dashed lines using method 5.

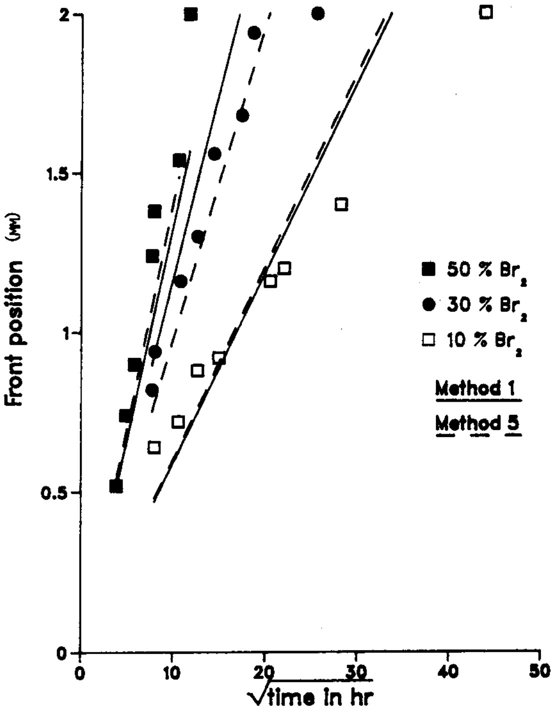

Fig. 3. Comparison of the calculated front position and the experimental front position for stage 4 during the intercalation of 4-mm-wide graphite in Br_2–CCl_4 at room temperature. The filled squares indicate intercalation in 50-mol % Br_2; filled circles 30-mol % Br_2; and open squares 10-mol % Br_2. The solid lines were calculated using method 1; the dashed lines using method 5.

and diffusion may be more important than the stage dependence of the diffusion coefficients.

The staging activation energy of method 1 was twenty times less than that used in the other methods, yet the quality of the fit was about the same. This was a very strong indicator of the dominance of diffusion in determining the reaction rate of graphite with bromine. This also indicated that the difference in the staging activation energy between methods 2 through 5 was not significant.

Generally speaking, none of the methods were particularly sensitive to the values used for the staging activation energy or the staging velocity premultiplier. This is to be expected if the diffusion step in the reaction is the rate controlling step. Furthermore, the stage with the greatest change in reaction free energy dominates the overall diffusion rate. For example, Fig. 1 indicates that stages 2, 3 and 4 finished intercalating within short times of each other below 50°C (36.6×10^{-4} K^{-1}) because stage 2 had the greatest change in reaction free energy and dominated the overall diffusion rate. In the curves drawn from method 5 (Fig. 1), the dominance of stage 2 at low temperatures is indicated in the behavior of the TTT curves near the temperature where stage 2 becomes unstable with respect to stage 3. The effect of this can be seen in Fig. 1 near the stage-2 temperature limit. If the diffusion coefficients of stages 2 and 3 were the same, the time for intercalation to stage 3 should be less than or equal to the times extrapolated from the stage-2 curve (the stage-2 and stage-3 curves drawn for method 1). What was observed was that the time needed to intercalate to stage 3 (near the stage-2 temperature limit) was about the same as the shortest time needed to intercalate to stage 2. This was a longer time than was extrapolated from the increase in the stage-2 intercalation rate with temperature. An explanation for this behavior can be obtained if the diffusion coefficient for stage 3 is less than that for stage 2. With this difference in diffusion coefficients, a discontinuity was produced in the stage-3 curve near the stage-2 temperature limit, as shown in the stage-3 curve for method 5 in Fig. 1.

The discontinuity can be understood by considering the intercalate flux above and below the stage-2 temperature limit. Below the stage-2 temperature limit, the flux across stage 3 will be proportional to the flux across stage 2, but also will be the product of the stage-3 diffusion coefficient and the concentration gradient across stage 3. If the diffusion coefficient for stage 3 is smaller than the diffusion coefficient for stage 2, the concentration gradient across stage 3 will increase until the stage-2 flux can be supported. This would be observed as a narrow band of stage 3 within the sample, which would migrate through the sample at approximately the same rate as the stage-2 front. As the stage-2 temperature limit is approached, the flux of intercalate across stage 2 will decrease and so too the concentration gradient across stage 3.

The overall reaction rate during bromine intercalation can be described fairly well by a single apparent diffusion coefficient, approximately 10^{-8} cm^2/sec for all methods. This value is in agreement with the room temperature diffusion coefficients reported previously for bromine intercalation[13,14,3,10,8]. Bardhan *et al.*[8] and Aronson[13,15] also reported activation energies for diffusion. Aronson *et al.* reported an activation energy of 11–14 kcal/mol for the desorption of bromine intercalated graphite powder in the temperature range of 30–48°C. Bardhan *et al.*[8] reported a value of 17 kcal/mol up to 100°C. The value of 21 or 22 kcal/mol which methods 3–5 indicate appears somewhat high in light of the previous values, and may indicate inadequacies in the algorithm to handle the nonlinear nature of the equations making up the multiphase model.

4. CONCLUSION

This paper provides the first description of the diffusion of an intercalate within graphite using a multiphase approach. The model of Shatynski *et al.*[6] was used for this purpose. Although multiple phases are certainly present during bromine intercalation[2], the fit between the experimental data for bromine intercalation[2] and the curves calculated with the multiphase approach was not significantly better than the fit obtained with the single-phase approach. In part this is due to imprecision in the data, but the goodness of fit of the single-phase approach also reflects the dominance of the diffusion coefficient of the final stage in the reaction kinetics.

Acknowledgements—This work is supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR-78-3536.

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