KINETICS AND THERMODYNAMICS OF INTERCALATION OF BROMINE IN GRAPHITE—I. EXPERIMENTAL

S. H. ANDERSON AXDAL and D. D. L. CHUNG†
Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213, U.S.A.

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Abstract—The intercalation of bromine in highly oriented pyrolytic graphite was performed at various combinations of temperature $T$ (20–160°C) and bromine vapor pressure $P$ (0.01 – 20 atm). The phase diagram ($\log P$ vs $1/T$) for the formation of various stages showed that the enthalpies of reaction were $-10.0$, $-10.8$ and $-11.0$ kcal mol$^{-1}$ Br$_2$ for stages 2, 3 and 4, respectively, and that the entropies of reaction were $-29.9$, $-30.8$ and $-30.6$ cal mol$^{-1}$ Br$_2$ K$^{-1}$ for stages 2, 3 and 4, respectively. The progress of intercalation was monitored in situ by optical measurements and ex situ by gravimetry, X-ray absorption and X-ray diffraction. The kinetic data yielded the first time-temperature-transformation diagram for intercalation. In particular, the rate of formation of stage 2 or 3 was found to first increase and then decrease as the reaction temperature increased and the thermal phase boundary (70°C for stage 2, 120°C for stage 3) was approached. In addition, the intercalation rate was determined as a function of the bromine potential, thereby yielding a time-concentration-transformation diagram.

Key Words—Intercalation, bromine.

1. INTRODUCTION

Accompanying the use of intercalated graphite as electrical conductors, catalysts, electrodes, etc., is the need for understanding the kinetics of the intercalation of graphite. This understanding is also important for elucidating the mechanism of intercalation and the process of stage formation.

The intercalation of graphite is a process that forms an intercalation compound, which contains the intercalate in the form of layers between the graphite layers. Sasa et al.[1] and Aronson[2] had reported thermodynamic information for the formation of graphite–bromine and graphite–alkali metal compounds, but without kinetic information. More recently, work had been reported concerning the kinetics of intercalation of alkali metals[3–6], metal halides[7–10], sulfuric acid[11] and bromine[12–14] and the chemistry involved in the intercalation of nitric acid[15–17] and arsenic pentfluoride[18,19]. There had also been theoretical modeling done on the staging reaction[20–30]. Nonetheless, there had not been a study of the concentration and temperature dependence of a diffusion-controlled intercalation reaction. Bromine is one of the most well-known intercalates in graphite and has attracted much recent scientific[13,31,32] and technological interest[33]. This paper presents an extensive experimental investigation of the kinetics and thermodynamics of intercalation of bromine in graphite. In particular, by measuring the dependence of the intercalation rate on the reaction temperature, it has provided the first determination of a time-temperature-transformation diagram for the intercalation of graphite. Detailed theoretical fits to the experimental data are presented in the accompanying paper[34].

2. EXPERIMENTAL METHODS

The intercalation of bromine in highly oriented pyrolytic graphite (HOPG) was performed at various combinations of temperatures and bromine vapor pressures. The progress of intercalation was monitored in situ by optical measurements and ex situ by gravimetry, X-ray absorption and X-ray diffraction.

2.1 Intercalation methods

The graphite used in this work was largely ZYA grade HOPG kindly provided by Union Carbide Corporation. Bromine reacts readily with graphite at room temperature at partial pressures above about 20 Torr. The graphite can be exposed to the bromine vapor or immersed in a bromine solution. Samples which were intercalated in vapor fell into two categories—samples for gravimetric studies or samples for study by optical microscopy. All other samples were intercalated in liquid.

Unless otherwise stated, the samples used for the kinetic and thermodynamic studies were cut from a single piece of HOPG to samples $4 \times 12$ mm$^2$ with thickness ranging from 0.1 to 0.3 mm. This sample shape allows approximation to one-dimensional diffusion, in contrast to the radial diffusion considered by others[35,36]. When intercalation occurred at room temperature, samples were held in glass vials containing bromine solutions. The samples were removed for analysis by weighing, X-ray diffraction and X-ray absorption.

†Present address: Dept. of Mechanical and Aeronautical Engineering, 613 Furnas Hall, S.U.N.Y./Buffalo, Buffalo, NY 14260.
Pure bromine was used to study the reaction rate at elevated temperatures. Samples were sealed in glass or monel tubes with liquid bromine and immersed in heated triethylene glycol. The tube was then removed, quenched in water, and opened to remove the HOPG sample. Typically it took about a minute from the removal of the sample from the bath to the time when it was mounted for analysis. The sample was then analyzed by X-ray diffraction and absorption. The time required for analysis was typically 25 min. A separate sample was used for each individual time at temperature.

Br2–CCl4 solutions of various compositions as well as pure bromine were used to determine the phase diagram. Each sample was initially intercalated to second or third stage in pure bromine at a controlled temperature. The sample was then transferred to a Br2–CCl4 solution and raised to a constant temperature so that stage changes, if any, would occur by desorption. Each sample was immersed in 5 ml of solution in a sealed glass tube. The sealed tubes were held at temperature for 1 day in a water bath, then removed and quenched in cold water. The tubes were then broken and X-ray diffraction and absorption patterns were taken. The equilibrium stage was taken to be the highest stage present, since a phase change should form a higher stage. In practice, it was rarely the case that more than one stage was observed. In particular, stage 4 was observed at the edges of samples intercalated above 150°C. In this case however, the amount of stage 4 at the sample edge was independent of the length of time at temperature, but depended on the quench rate. The presence of the stage 4 in these samples was attributed to fast reaction kinetics below the nominal reaction temperature. Experiments were also undertaken to ascertain the effect of hydrostatic pressure on the reaction rate.

To investigate the effect of pressure on intercalation, a pressure cell was constructed out of copper lined with teflon. Pressure was applied by insertion of a teflon tipped copper piston. The cell was sealed by deformable teflon gaskets. A 6 × 7 × 0.3 mm3 HOPG sample was placed in pure bromine in the cell. The vice and cell were placed in the waterbath at 113°C for 10 min. After this, the vice and cell were removed and quenched in cold water. Then the pressure on the cell was released and the cell was dismantled to obtain the HOPG sample. The sample was then analyzed by X-ray diffraction and absorption. The pressure applied to the cell was monitored by the change in the resistance of a strain gage cemented to the outside of the cell. Calibration of the pressure readings was performed by measuring the strain induced by the vapor pressure of water, bromine, or tetrafluoromethane sealed in the cell at 113°C.

2.2 X-ray absorption

Most intercalates may be readily measured by X-ray absorption because of the large difference between the mass absorption coefficient of carbon and that of the intercalate.

A description of the geometry of the absorption setup follows. A Siemens diffractometer with a graphite monochromator tuned to Cu Kα was set at a 26° value of 0°. The normal sample holder held a collimating slit 10 μm by 2 mm. The absorption sample was held with its basal plane perpendicular to the beam 2 cm from the collimating slit and 13 cm from a 0.1-mm receiving slit in front of the monochromator and scintillation detector. The dead time of the detector electronics was determined to be 10 μs. The sample was translated through the beam by a synchronous motor turning a micrometer. Although the sample moved continuously, the intensity was measured as the number of counts in periods of 1.6 s each. Counting was begun before the sample intercepted the beam and was continued until after the sample was fully out of the beam. The intensity measured before and after the sample intercepted the beam was averaged to serve as the incident beam intensity.

The absorbance of the transmitted beam may be calculated with the following equation:

\[
\left(\frac{I}{I_0}\right)^\lambda = \exp \left[ - \mu C x_b + \mu a x_a + \mu t x_t + \cdots \right],
\]

where \(I_0\) is the unabsorbed beam intensity, \(I\) is the transmitted beam intensity, \(\mu_a\) is the linear absorption coefficient of component \(a\) (\(a = C\) or \(Br2\)) at wavelength \(\lambda\) (Cu Kα or Mo Kα), and \(x_a\) is the thickness of component \(a\). When a single intercalate was present, a molecular weight weighted average of the absorption coefficient was used in the calculations. This is tantamount to assuming that the intercalate species is present in molecular form. The value of \(x_a\) is constant for \(a = \text{graphite}\), otherwise \(x_a\) is the thickness of the intercalate present. Hence the concentration of component \(a\) can be determined knowing the initial graphite thickness and the amount of expansion in the c-direction resulting from a given stage compound. Using the nominal expansion of a first stage compound as the expected expansion, higher stages can be represented as concentrations equal to the reciprocal of the stage number. Since the graphite layer thickness remained constant for a given sample, the intercalate composition could be determined if the absorption profile of the graphite was obtained before intercalation was begun. Table 1 lists the values used for the linear absorption coefficient.

2.3 X-ray diffraction

X-ray diffraction of intercalated HOPG was performed using either a Siemens or Rigaku 0-20 X-ray powder diffractometer. The 001 diffraction pattern was obtained from the basal plane, with the long edge of the sample mounted horizontally. A graphite monochromator was used with Cu Kα radiation. For diffraction at selected areas of a sample, a lead or tantalum foil was used to mask the area at which
diffraction was not desired. For a typical sample of 4 mm width, the diffraction pattern of the central 2-mm-wide portion of the sample was obtained by masking off 1 mm of the two long edges of the sample. Similarly, the diffraction pattern of the two edge regions (each edge region being 1 mm wide) was obtained by masking the central 2-mm-wide portion of the sample. Diffraction patterns were typically taken for a 2θ range of 15°–25°. This range allowed the diffraction run to be obtained in a reasonable length of time while showing the strongest superlattice lines not coincident with the graphite lines. Although a monochromator was used, the graphite (002) line due to the Cu Kα radiation was quite pronounced. Generally no attempt was made to measure the graphite (002) Kα line because at the normal beam intensity the (002) diffracted intensity was so large that it overloaded the detector.

To indicate the relative depths from the basal surface of different stages present within a sample during intercalation, diffraction patterns were obtained with both Cu Kα and Mo Kα radiation on a 12 × 12 × 0.15 mm³ HOPG sample, which was intercalated in pure bromine at room temperature and intermittently removed for analysis. As the mass absorption coefficient of bromine for Mo Kα radiation is smaller than that for Cu Kα, Mo radiation has a greater effective penetration distance. Hence phases farther from the surface can contribute more to the diffraction pattern obtained with Mo Kα than is the case with Cu Kα. Selected area X-ray diffraction was also done on this sample; masking was such as to allow observation of either 4 mm in the center region or 4 mm total from the two edge regions combined (i.e., 2 mm of each edge region).

2.4 Weight measurements

The gravimetric samples were either Madagascar flake sized by screening, or HOPG cut to form square blocks, 4 × 4 × 0.5 mm³. The graphite was placed on a glass pan suspended on a glass hang-down wire from the beam of a Cahn electrobalance (Model RG). The balance was located within a glass bell jar and nitrogen was used as a blanketing gas to prevent contamination of the balance mechanism by bromine. Weight gain measurements were carried out at room temperature.

A sample was placed on the weight pan and an empty closed-end tube was attached. After the sample weight had stabilized, the sample weight was noted. The empty closed-end tube was then replaced by another closed tube filled with bromine so that the level of the bromine was 1 cm below the balance pan. This time was noted as the beginning of the gravimetry run. The purpose of changing tubes was to allow a temporally well-defined transition between the sample hanging in bromine-free air to the sample hanging in bromine saturated air. This arrangement was used so that an essentially saturated bromine atmosphere could be raised up around the sample at a known time without requiring an evacuated system or needing to be concerned with diffusion time through a surrounding atmosphere.

When intercalation was complete, as indicated by a constant sample weight, the bromine-containing tube was removed and replaced by a flow-through tube so that the nitrogen blanketing gas served as carrier gas sweeping desorbed bromine away from the sample. The weight change during desorption was monitored until a constant sample weight had been attained.

2.5 Optical measurements

In the optical measurements, the motion of the intercalate front on the basal surface was measured. HOPG samples used for the optical profilometry studies were cut to a size of 2 × 6 mm² (0.5 mm thick). An intercalating vessel was made of glass, with a center glass post for support of the sample. The vessel was sealed with wax and a microscope cover slide. This arrangement allowed the sample to be placed under a microscope and the top surface viewed under low magnification during the intercalation reaction.

In the profilometry measurements, the basal surface was observed. On intercalation the surface was deformed by the expansion within the sample and incident light perpendicular to the surface was reflected away from the microscope objective producing a dark region on an otherwise bright field. The motion of the intercalation front was monitored by the progress of the leading edge of the black zone on the sample surface. Photomicrographs were obtained in situ during intercalation of samples over pure Br₂ and several Br₂–CCl₄ solutions. The position of the intercalate front as a function of time was
determined by measurement on the photomicrograph negatives.

3. RESULTS AND DISCUSSION

3.1 Phase diagram of the graphite–bromine system

A phase diagram was constructed by mapping the final stage formed during intercalation of bromine in HOPG at a variety of temperatures and bromine vapor pressures. The HOPG samples were immersed in bromine liquid or Br₂–CCl₄ solution, sealed and then heated at various temperatures. The stage was determined by X-ray diffraction. Analysis of the slopes and intercepts of the phase boundaries provided a determination of the enthalpies and entropies of the changes of stage.

3.1.1 Stage determination using X-ray diffraction. Figure 1 shows X-ray diffraction patterns obtained on graphite–bromine samples produced by immersing HOPG in pure bromine liquid at various temperatures. Figure 2 shows X-ray diffraction patterns obtained on graphite–bromine samples produced by immersing HOPG in Br₂–CCl₄ solutions of various concentrations at room temperature. Numerous other combinations of temperatures and Br₂–CCl₄ concentrations were used to make individual samples.

Figure 3 gives the diffraction pattern of one of these samples; this sample was produced by immersion of HOPG in Br₂–CCl₄ solution of 50 mol % Br₂ at 105°C. Figures 1–3 illustrate the quality of staging produced by intercalation with various Br₂ concentrations in CCl₄ and at various temperatures. All diffraction patterns were obtained from the basal plane and only show 00l lines. The following notation is used in this paper to label a particular 00l line:

![Diffraction pattern](image)

Fig. 1. Diffraction patterns produced by intercalating graphite in pure bromine at (a) 23°C, (b) 105°C and (c) 126°C. Each diffraction peak is labeled by the l index of the 00l Miller indices.

The line is referred to by the l index with a subscript indicating the stage of the compound (a subscript G is used to indicate a graphite peak), and a superscript β if it is a line due to Kβ radiation. The absence of a superscript implies that the line is due to Kα radiation.

Figure 1 illustrates the effect of temperature on staging in graphite–bromine. As the temperature was increased, stage 2 became unstable with respect to stage 3, so that intercalation in pure bromine produced stage 3 at 105°C [Fig 1(b)]. At still higher temperatures stage 3 also became unstable and the final stage produced in pure bromine was stage 4 at 126°C [Fig 1(c)].

A decrease in the bromine concentration in Br₃–CCl₄ solutions had a similar effect as that of an increase in temperature (Fig. 2). At room temperature stage 2 was formed [Fig. 2(a)], but with a decrease in Br₃–CCl₄ concentration to 20 mol % Br₃, the final stage became 3 [Fig 2(b)], and with a still lower concentration (10 mol % Br₃) the final stage was 4 [Fig 2(c)].

Under the conditions of both elevated temperatures and low bromine concentrations in Br₃–CCl₄, high stages also tended to form. For example, the sample of Fig. 3 was made by immersing the sample in Br₃–CCl₄ solution (50 mol % Br₃) at 105°C and was stage 4.

The diffraction patterns indicated a high degree of staging under all of the intercalating conditions. Diffraction peaks from coexisting stages were not observed even at close examination of the background areas between the principal peaks, and the peaks were quite narrow, indicating little mixing of stages. Typically the full width half maximum (FWHM) of a peak was 0.4° ± 0.2° compared to the value of 0.1° ± 0.2° for the 002 line of pristine HOPG.

3.1.2 Calculation of bromine vapor pressure. The vapor pressure of bromine was calculated for solutions of bromine and carbon tetrachloride using the equation published by Barthel and Dode[38,39],

\[ \ln \left( \frac{P}{P_c} \right) = 1.197 \left( 1 - x \right)^2 - 0.493 \left( 1 - x \right)^3, \]

where \( P \) is the vapor pressure of bromine above the Br₃–CCl₄ solution, \( P_c \) is the vapor pressure of pure bromine and \( x \) is the mole fraction of bromine in carbon tetrachloride. The vapor pressure for pure bromine was calculated as a function of temperature using the relations given in the compilation of Ohel[40], where

\[ \log(P) = A - B/(T + C). \]

\( P \) is the pressure in atmospheres and \( T \) is the temperature in °C. The values of \( A, B \) and \( C \) are 2.940, 638.3 and 158.0, respectively, up to the boiling point of bromine at 1 atm (58.2°C); they are 4.703, 1562
Fig. 2. Diffraction patterns produced by intercalating graphite at 23°C in (a) pure bromine, (b) 20% bromine–carbon tetrachloride and (c) 15% bromine–carbon tetrachloride. Each diffraction peak is labeled by the l index of the 00l Miller indices.

Fig. 3. Diffraction pattern produced from graphite intercalated at 105°C in 50% bromine–carbon tetrachloride. Each diffraction peak is labeled by the l index of the 00l Miller indices.
and 273.4, respectively, above the boiling point. The assumption was made that the data of Barthel and Dode can be extrapolated to higher temperature regimes without too much error. Furthermore, it was assumed that bromine can be considered close enough to an ideal gas that the vapor pressure of bromine in atmospheres was numerically equal to the fugacity of bromine. At the maximum temperature investigated, a 10% deviation from ideality actually exits.

### 3.1.3 Determination of entropy and enthalpy of reaction

The final stage attained was plotted as a function of the logarithm of the bromine vapor pressure (in atm) and 1/T (K⁻¹) (Fig. 4). In the diagram, a phase boundary was approximated as a straight line; the slope of the line is the enthalpy of the change of stage and the intercept of the line is the entropy of the change of stage. In the phase diagram, each phase boundary was calculated as a least square fit of the activity-temperature points which bordered the phase boundary between them. For example, at room temperature stage 2 was observed at 40 mol \% Br₂, but stage 3 was observed at 30 mol \%. Consequently, both (30\%, 273 K⁻¹) and (40\%, 293 K⁻¹) were used as coordinate pairs in the least square fitting.

In this manner enthalpies and entropies of reaction were found for the transformation of one stage to the next lower stage (Table 2). The values of ΔH° and ΔS° for the change from stage 3 to stage 2 are in close agreement with those reported by Sasa[41] (ΔH° = -10.2 kcal mol⁻¹ Br₂, ΔS° = -29.0 cal mol⁻¹ K⁻¹). Table 2 indicates that ΔH° increases slightly with increasing stage, while the variation in ΔS° is much less marked. These characteristics are similar to those reported for graphite–alkali metals[2].

Salzano and Aronson[42] proposed a model for the change in enthalpy during intercalation due to electrostatic interactions between the intercalate layer and the graphite layers. In this model, the change of enthalpy ΔH° for the transformation from stage \( n_2 \) to stage \( n_1 \) was given by

\[
\Delta H^o = -aH + M + I \left( \frac{n_2}{n_1} - \frac{n_1}{n_2} \right),
\]

where \( a \) indicates the in-plane stoichiometry (\( a = 7 \) for \( C_nBr_3 \)), \( H \) is the interlayer bonding energy between two adjacent graphitic layers in graphite less the interlayer bonding energy between two adjacent graphitic layers with the same spacing as in the compound, \( M \) is the attractive interactive energy between the graphite layers and adjacent intercalate layers and \( I \) is a measure of the repulsive interaction between adjacent intercalate layers. Following their analysis[43], the standard heats and entropies of formation of various stages from pure graphite were calculated and listed in Table 3. The standard heat of formation ΔH° of stage 4 was approximated by plotting the experimental values of ΔH° vs \( n_1/n_2 - n_2/n_1 \), thereby obtaining \(-aH + M\) as the intercept.

### Table 2. Enthalpies and entropies of reaction for bromine–graphite

<table>
<thead>
<tr>
<th>Stage</th>
<th>Reaction</th>
<th>ΔH° kcal mol⁻¹ Br₂</th>
<th>ΔS° cal mol⁻¹ Br₂ K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 ↔ 2</td>
<td>(2C_{21}Br_{2(s)} + Br_{2(g)} = 3C_{14}Br_{2(s)} )</td>
<td>-10.0 ± 0.5</td>
<td>-29.9 ± 0.5</td>
</tr>
<tr>
<td>4 ↔ 3</td>
<td>(3C_{28}Br_{2(s)} + Br_{2(g)} = 4C_{21}Br_{2(s)} )</td>
<td>-10.8 ± 0.2</td>
<td>-30.8 ± 0.3</td>
</tr>
<tr>
<td>5 ↔ 4</td>
<td>(4C_{28}Br_{2(s)} + Br_{2(g)} = 5C_{28}Br_{2(s)} )</td>
<td>-11.0 ± 0.2</td>
<td>-30.6 ± 0.3</td>
</tr>
</tbody>
</table>

Fig. 4. A phase diagram of the graphite bromine system, plotted as log(PBr) (in atm) vs. 1/T. The upper boundary was the vapor pressure of bromine, the lower lines were a least square fit to the data.
Table 3. Enthalpies and entropies of formation for bromine–graphite

<table>
<thead>
<tr>
<th>Stage</th>
<th>Reaction</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kcal mol$^{-1}$Br$_2$</td>
<td>cal mol$^{-1}$Br$_2$K$^{-1}$</td>
</tr>
<tr>
<td>C ↔ 2</td>
<td>14 C$<em>s$ + Br$<em>2$$</em>{2\text{g}}$ = C$</em>{14}$Br$_{2s}$</td>
<td>$-10.9 \pm 0.5$</td>
<td>$-30.4 \pm 0.5$</td>
</tr>
<tr>
<td>C ↔ 3</td>
<td>21 C$<em>s$ + Br$<em>2$$</em>{2\text{g}}$ = C$</em>{21}$Br$_{2s}$</td>
<td>$-11.3 \pm 0.2$</td>
<td>$-30.6 \pm 0.3$</td>
</tr>
<tr>
<td>C ↔ 4</td>
<td>28 C$<em>s$ + Br$<em>2$$</em>{2\text{g}}$ = C$</em>{28}$Br$_{2s}$</td>
<td>$-11.5 \pm 0.2$</td>
<td>$-30.6 \pm 0.3$</td>
</tr>
</tbody>
</table>

and $I$ as the slope, and then taking $\Delta H^\circ_I$ as $-aH + M + \ln n$, where $n$ = stage. The standard entropy of formation $\Delta S^\circ_I$ of stage 4 was taken as equal to the value of $\Delta S^\circ$ for the change of stage 5 to stage 4. The values of $\Delta H^\circ_I$ and $\Delta S^\circ_I$ for other stages were then calculated by summing the experimental heats and entropies of progressive stage changes.

Since the in-plane structure of graphite–bromine is the same for different stages, it is not surprising that there is little difference in $\Delta S^\circ$ from stage to stage. This stage independence of $\Delta S^\circ$ was also observed in alkali metal compounds[2]. While the $\Delta S^\circ$ value of $\approx -30$ cal mol$^{-1}$ Br$_2$ K$^{-1}$ seems large compared to the value of $\approx -20$ cal mol$^{-1}$ K$^{-1}$ observed in alkali metals, in both cases the entropy change is approximately that for the condensation of the vapor phase to the solid phase. $\Delta H^\circ_I$ in bromine are about a third less than those observed in the alkali metals, which suggests that there is less electrostatic interaction in graphite–Br$_2$.

3.2 Reaction kinetics in graphite–bromine

The reaction kinetics of the graphite–bromine system were studied using a variety of experimental techniques: weight gain measurements, surface profilometry using visible light reflection, concentration profilometry using X-ray absorption and X-ray diffraction.

3.2.1 Ex situ gravimetric study of intercalation. During the course of the intercalation of graphite samples at room temperature by immersion in Br$_2$–CCL$_4$ solutions, the samples were removed from the solutions at various times for weighing and X-ray analysis. Each removal lasted about 30 min, which was a short time compared to the total intercalation time (typically 1000 h). The weighing was performed using a Perkin-Elmer AD-22Z Autobalance which had a four and a half digit readout over a full-scale range of 1 mg to 1 g. Figure 5 is a plot of the fractional weight gain as a function of the square root of time for samples in Br$_2$–CCL$_4$ solutions of various concentrations from 5 to 50 mol % Br$_2$. Initially the curves are linear, indicating that at room temperature the reaction proceeded as a function of the square root of time. At long times the curves bend over because of the finite sample size and the completion of the reaction. The 40 and 50-mol % curves approach the weight gain for stage 2, 83% increase. The 30-, 25- and 15-mol % curves approach stage 3 at a 55% weight gain; 10 mol % approaches fourth stage at 42% weight gain; 5 mol % approaches stage 5 at 33% weight gain. As the concentration decreases, the reaction rate, i.e. the slope of the weight gain line, also decreases. An average diffusion coefficient can be obtained from the initial weight uptake rate using the following relation[44]:

$$D = \frac{\pi}{16} \left( \frac{d(M/M_s)}{d(t/\bar{t}^2)} \right)^2,$$

where $D$ is the average apparent diffusion coefficient, $M_t$ is the weight gain at time $t$, $M_s$ is the weight gain at infinity and $\bar{t}$ is the diffusion length.

Using eqn (5), diffusion coefficients were determined from the weight uptake data displayed in Fig. 5. These diffusion coefficients are displayed in Table 4, along with diffusion coefficients which had been reported in the literature[45–49]. The table is grouped in terms of the final stage formed, which was governed by the concentration of the Br$_2$–CCL$_4$ solution. Both the weight gain and X-ray diffraction results (see Section 3.2.3) indicated that intercalation of HOPG in a Br$_2$–CCL$_4$ solution containing 40–100-mol % Br$_2$ resulted in stage 2, a solution containing 15–30-mol % Br$_2$ resulted in stage 3, a solution containing 10-mol % Br$_2$ resulted in stage 4, and a solution containing 5-mol % Br$_2$ resulted in stage 5. The diffusion coefficients were found to be governed by the final stage. There was fairly little difference between the diffusion coefficient in pure bromine and that in 0.4-mol % bromine solution, but the diffusion coefficient was reduced by about half between bromine concentrations of 0.4 and 0.3 mol %. There was a similar reduction in the apparent value of the diffusion coefficient between 0.15 and 0.10 mol %.

The diffusion coefficients determined by ex situ weight gain indicate that the diffusion process was affected by the stage formed. However, since the contributions of different stages to the weight gain
cannot be separated, information on the amounts of individual stages cannot be extracted from the weight gain data.

3.2.2 In situ optical observation of intercalation. It has been observed that intercalation is often accompanied by the so-called “ash-tray” or “window-pane” effect, where the sample edges expand before the center of the sample. Bardhan et al. [12,51,52] used surface profilometry to investigate the propagation of the surface deformation in graphite–bromine, but the measurement intervals were fairly infrequent and ex situ measurements were required. We have used optical profilometry as an in situ method of observing the motion of the surface deformation.

In the in situ optical studies the intercalate front was taken to be delineated by the line between the region where light was reflected back into the eyepiece and the region where reflection was away from the eyepiece. The photographs in Fig. 6 indicate the appearance of the sample surface at short (13-h) and long (118-h) times during intercalation at room temperature in Br₂ vapor above a 15-mol % solution of Br₂–CCl₄. The surface deformation which was assumed to correspond to the intercalate front was clearly evident. At long times, the position of the front was still clear, but the surface of the region which had been intercalated showed other types of surface relief as well. These might be similar to the ledges reported by Bardhan et al. [12].

Figure 7 is a plot of the position of the intercalate front, as observed optically, versus the time the sample was exposed to the intercalate vapor. While a smooth curve can be drawn through the points, the curve is nonlinear. If the same data are plotted versus the square root of the time exposed to the intercalate (Fig. 8), the data can be fitted quite well by a straight line, which is consistent with the weight uptake results of Fig. 5. Neither Fig. 7 or Fig. 8 indicates an appreciable interval of time between the exposure to bromine and the start of intercalation. This was in contrast to the incubation times reported by some other investigators [13,36,53].

Surface profilometry is not much more specific than the weight gain measurements, in that it indicates only the position of the intercalate front and does not give information about the intercalated region. However, the consistency between the in situ data obtained by surface profilometry and the ex situ data obtained by weight gain measurements (Section 3.2.1), X-ray absorption and X-ray diffraction (Section 3.2.3) confirms the validity of the ex situ kinetic data.

3.2.3 Ex situ X-ray studies of intercalation. A combination of X-ray absorption and X-ray diffraction was used to indicate the extent of reaction and
Intercalation of bromine in graphite

Table 4. Diffusion coefficients determined from weight gain experiments

<table>
<thead>
<tr>
<th>Bromine Mol %</th>
<th>Diffusion Coefficient $cm^2/sec \times 10^8$</th>
<th>Temperature ($^\circ$C)</th>
<th>Final Stage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.30</td>
<td>30</td>
<td>2</td>
<td>PG powder [47]</td>
</tr>
<tr>
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13 hours

118 hours

Fig. 6. In situ optical micrographs and schematic surface profiles of an HOPG sample during intercalation of bromine at 22°C (sample width = 2 mm).
the stages present during the reaction. As a result of the large difference in the mass absorption coefficients of bromine and graphite, measurement of X-ray absorption was quite sensitive to the presence of bromine in the graphite. A representative concentration profile is shown in Fig. 9. On the left-hand side of the figure the concentration is given in terms of the weight percent of bromine present; on the right-hand side of the figure the corresponding nominal stage number is indicated.

The change in concentration at the sample edge was not a step function because of the experimental conditions. Since the X-ray beam had a finite width, the observation of the sample edge was broadened by the time needed for the sample to completely intercept the beam.

The concentration profile was fairly symmetrical about the center of the sample, and several shoulders were apparent between the center of the sample and either edge. These shoulders were typically found in the concentration profiles and were observed at positions which approximated second, third and fourth stages. The presence of the shoulders suggests that staging in the graphite-bromine reaction occurs in a progression of stages from high to low stages.

This interpretation of the shoulders in a concentration profile is supported by X-ray diffraction patterns obtained during intercalation. Figure 10 illustrates the volume fraction of each stage present during intercalation in 40-mol% Br2–CCL4, as determined by X-ray diffraction. Initially stages 3–5 were observed, but the amount of the higher stages present decreased as the final stage was formed (stage 2). There was agreement between the amount of a given stage as determined from the diffraction patterns and from the X-ray absorption results. Figures 11 and 12 illustrate, respectively, the volume percents of stages 2 and 3 present as a function of the square root of time during the intercalation of graphite in 40-mol% Br2–CCL4, calculated from concentration profiles and from diffraction patterns. In the calculation using the concentration profiles, the shoulders were assumed to delineate regions of various stages. Calculations based on concentration profiles and diffraction patterns were consistent, thereby supporting the above interpretation of the shoulders in the concentration profiles. Minor differences between the two calculations arose from the error in locating the second and third shoulders on the concentration profile, and from the error in measuring the area under each diffraction peak when overlapping diffraction peaks were present.

X-ray absorption and diffraction provided information which neither weight gain nor surface pro-

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Fig. 7. The width of the intercalated edge of a graphite sample exposed to 15% bromine–carbon tetrachloride vapor plotted as a function of the square root of time (h^{1/2}).

Fig. 8. The width of the intercalated edge of a graphite sample exposed to 15% bromine–carbon tetrachloride vapor plotted as a function of time (h).

Fig. 9. Concentration profile of bromine in graphite obtained by X-ray absorption of Cu Kα radiation after 308 h of exposure of HOPG to a 40-mol% solution of Br2 in CCL4.
filometry was able to give, namely, the distribution and quantities of the stages present during the intercalation process.

Figure 13 illustrates the changes in X-ray absorption and diffraction results observed during the reaction of graphite with 50-mol % Br$_2$-CCl$_4$ at room temperature. The panels in the leftmost column are concentration profiles of bromine obtained by X-ray absorption. The bromine concentration in these profiles was calculated [eqn (1)] in terms of the weight fraction of bromine, which is inversely proportional to the nominal stage number of the intercalation compound. In Fig. 13, the nominal stage number is used as the scale for the concentration axis. The two right columns of Fig. 13 show the corresponding diffraction patterns, which indicate progressive stage changes during intercalation. Diffraction patterns were obtained from both the center and edge of the sample to help clarify the distribution of the stages during the intercalation process.

The diffraction patterns in Fig. 13 were obtained between 2θ angles of 15° and 25° with Cu Kα radiation; each pattern includes the nth stage 00n diffraction peaks. The 00n peaks were selected because they had reasonably high intensities and offered resolvable separations between the peaks because of different stages. A mixture of stages was quite evident in the diffraction pattern taken from the edge of the sample at 34 h. The final stage, stage 2, as well as stages 3 and 4, were present and the peak at the position of the graphite Kβ 002 line indicated
pristine graphite. The superlattice peaks appeared to emerge from a broad high background peak. This was the result of multiple stages being formed more or less simultaneously. When two stages are intermixed, the effect of the partial long-range ordering is to increase the apparent background and broaden the peaks, with a shift in peak position also possible[54]. Although the 00(n + 1) peaks of an nth stage bromine compound would be much more intense than the 00n peak, the 00(n + 1) peaks of different stages are much less resolvable as can be seen in the superposition of the Kβ peaks at 2θ = 23°.

The diffraction pattern from the center of the sample at 34 h indicated that intercalation compounds were present, despite the negligible amount of intercalate in the center of the concentration profile. These diffraction peaks might arise from incompletely masking the edges, but might also arise from intercalation into ledges on the surface of the sample; these ledges do not show up in the concentration profiles because of statistical uncertainties. There is also a possibility of some intercalation starting at the crystallite boundaries[42], but we have observed no evidence to support this. (Both diffraction and absorption were sensitive to the presence of about 1 wt. % Br₂ in the volume of the sample in the beam.)

At 210 h the intercalation reaction had proceeded to the point where the intercalate fronts had met in the center of the sample. The pattern from the edges indicated principally stage 2, some stage 3 and a negligible amount of stage 4. The center of the sample was still a mixture of stages, with stage 4 predominating. At the center there was still a small graphite 002 Kβ peak visible in the diffraction pattern, indicating that some pristine graphite was still present. The shoulder and slow tailing off to high angles of the 004 stage 4 peak was probably due to the presence of stage 5 and/or stage 6. Finally, at 1187 h, the concentration profile was flat, with a concentration consistent with stage 2, and both diffraction patterns showed only stage 2 to be present.

The effect of decreasing the bromine concentration in the Br₂–CCL₄ solution on the intercalation process can be seen in Fig. 14, which shows X-ray absorption and diffraction results for Br₂–CCL₄ solutions containing 15, 25 and 30-mol % Br₂. In all three cases, the final stage was 3, and the concent-
The intercalation profiles and diffraction patterns were all obtained after 600 h of intercalation. The sample in 30-mol % bromine is nearly completely intercalated to stage 3. The diffraction pattern from the edges showed only stage 3; the diffraction pattern from the center showed predominantly stage 3, although stage 4 was still present. The intercalate fronts had just met in the case of the sample in 25-mol % bromine. The diffraction patterns indicated that the edge was predominantly stage 3 while the center was predominantly stage 4. In the case of the sample in 15-mol % bromine, which was the Br₂-CCl₄ concentration corresponding nearly to the phase boundary between stage 3 and stage 4, the intercalate fronts had not met yet and even at the edge there was very little stage 3 present. In this case however, stage 5 was fairly prominent in the center of the sample.

Figure 15 shows plots of the square of the distance between the intercalate front and the sample edge versus time in h for samples exposed to several intercalate concentrations. As the intercalate concentration was decreased, the slope of the line became more shallow, indicating a decrease in the intercalation rate. The slope of each line, the change in the position of the intercalate front as a function of the square root of time, was used as a measure of the intercalation rate. In both the in situ (optical profilometry) and ex situ (X-ray absorption) cases, the intercalation rate was calculated as a least square fit of the average position squared and the exposure time, where the average position was the average of the position of the intercalate front on either side of the centerline of the sample.

Interpretation of the concentration profiles was complicated by the fact that the intercalate front was not parallel to the c-axis; instead intercalation ap-

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**Figure 14.** Concentration profiles and diffraction patterns from the edges and center of a sample after 600 h of intercalation in various concentrations of Br₂-CCl₄ solutions at 23°C.

**Figure 15.** Intercalate front position squared versus time during intercalation in Br₂-CCl₄ solutions of various concentrations. The intercalate front position was determined by X-ray absorption.
pears to proceed initially from the edges bounding the basal surfaces. This was probably the reason why the different stages were not more clearly delineated in the concentration profiles. This also affected the diffraction patterns. In particular, the lowest, most concentrated stage, tends to form near the basal surface, and so an 00l diffraction pattern tends to indicate a predominance of the stage closest to the surface. This tendency was further aggravated by the fact that the lower stages have higher absorption coefficients, so that the effective penetration distance of the diffracted beam was less. This results in further enhancement of the low stages near the surface.

To test the effect of the X-ray penetration distance, an HOPG sample of size 12 × 12 mm² was intercalated in pure bromine at room temperature and then X-ray diffraction patterns were obtained with Cu Kα and Mo Kα radiation separately, as shown in Fig. 16. Since the mass absorption coefficient of Mo radiation by bromine was less than that of Cu, Mo radiation should, in a sense, produce a diffraction pattern from deeper within the sample. A comparison of the diffraction patterns does indicate this. For example, the copper radiation diffraction pattern from the edge of the sample [Fig. 16(b), on the left] showed predominantly the stage 2 002 peak, with small peaks from stages 3 and 4 and pristine graphite. The molybdenum radiation diffraction pattern from the sample edge [Fig. 16(c), on the left] also had a strong stage 2 009 peak. The graphite 006 peak in the molybdenum radiation diffraction pattern was much more pronounced at the edge of the sample than was the graphite 002 peak in the copper radiation diffraction pattern. The diffraction pattern from the center of the sample showed the same tendency. While the copper radiation diffraction patterns showed a strong stage 2 002 peak and a strong graphite 006 peak, the molybdenum radiation diffraction pattern was dominated by the graphite 006 peak. Table 1 gives a list of the adsorption coefficients of bromine for Cu and Mo radiation and the penetration depths accounting for 99% of the diffracted intensity from second, third and fourth stage graphite–bromine compounds as well as for graphite. From this table it can be seen that copper radiation can produce diffraction patterns which are much more sensitive to the stages present near the surface than within the sample.

3.2.4 Determination of TCT and TTT diagrams. Figure 17 illustrates how the intercalation rate varies with the bromine concentration in the Br₂–CCl₄ solution at room temperature. The filled symbols indicate data obtained by ex situ X-ray diffraction and absorption, while the open symbols indicate data obtained by optically following the intercalate front in situ. The in situ and ex situ rates agree with each other, indicating that the removal of the sample from the intercalate in the ex situ studies did not appreciably affect the intercalation rate. A linear extrapolation of the data to zero concentration indicated that the intercalation rate became zero before zero concentration was reached. This is in keeping with the observation of a threshold pressure below which intercalation of bromine does not occur and in fact, the observed threshold pressure (10 mm Hg[55]) is approximately the vapor pressure calculated for the concentration at which the extrapolated rate is zero (14 mm Hg).

The positions in the concentration profile corresponding to the concentrations of pure stages were also followed, as it was observed that shoulders in the concentration profiles were generally present at approximately those concentrations. This information, as well as the information from the peak areas from the X-ray diffraction patterns, was used to monitor the amount of each stage present as a function of the intercalation time. The diffraction patterns were used to indicate when a particular stage appeared in the course of intercalation; the concentration profiles from the absorption curves were taken to be more reliable indicators of the distribution of stages within the sample.
An indicator of the dependence of the reaction rate on the concentration of the Br$_2$–CCl$_4$ solution can be obtained by plotting the length of time needed to react a given size sample to a given stage as a function of the concentration of the Br$_2$–CCl$_4$ solution, i.e., time-concentration-transformation (TCT) curves (Fig. 18). The curves on the left side of the diagram indicate the times at which a given stage was first observed in the diffraction pattern during reaction at room temperature. At longer times a mixture of stages was observed. The curves on the right side of the diagram indicate the times at which the reactions were completed. The first line from the right corresponds to the time at which the sample first became only stage 2; the second line from the right corresponds to the time at which stage 4 vanished; the remaining line corresponds to the time at which pristine graphite vanished.

As shown in Fig. 18, stage 2 was the final stage for Br$_2$–CCl$_4$ solutions containing 40-mol % Br$_2$ or more; stage 3 was the final stage for Br$_2$–CCl$_4$ solutions containing 15–30-mol % Br$_2$; stage 4 was the final stage for the Br$_2$–CCl$_4$ solution containing 10-mol % Br$_2$. As the Br$_2$ concentration decreased, the intercalation rate also decreased.

The progression of the stages during the reaction can be seen more clearly in plots of the amount of each stage present as a function of time (Fig. 19). As mentioned earlier, diffraction patterns were obtained within the 2θ range of 15°–25°. This was done to minimize the amount of time required to obtain diffraction patterns from both the center and the edges of the material while including the staging peaks which were both the most intense and the most widely separated. The resulting loss in intensity precluded getting more separation by going to higher 2θ angles; the near superposition of the peaks precluded the use of the most intense peaks which occur at approximately the graphite 00l positions. The amount of a stage present was calculated from the area under the nth stage 00l peak in the diffraction pattern. Each diffraction peak was fitted to a Lorentzian curve.

The peak area was taken to be proportional to the peak height times sigma, the Lorentzian deviation. The relative amount of the nth stage was calculated as the height-sigma product of the 00l peak over the sum of the height-sigma products of the 00n peaks for all stages ($n = 2, 3, \ldots$, etc.) present. For describing the relative amount of pristine graphite remaining in the sample, the intensity of the graphite 002 Kβ peak was compared to the total intensity of the overlapping 00(n + 1) Kβ peaks for all stages. (The Kβ peaks were used for the latter comparison because the Kα peaks saturated the detector at the power settings necessary for reasonable intensities of the stage peaks.) When comparing the different peak areas, corrections were made for the change in wavelength, the change in θ and the difference in scattering factor between carbon and bromine (Table 1).

In general, the amounts of all stages increased until no graphite peak was observed. However, the maximum amount of a given stage occurred at the
Fig. 18. Time-concentration-transformation (TCT) curves for graphite exposed to bromine–carbon tetrachloride solutions of various concentrations at room temperature. The phases present are indicated by the stage numbers and the symbol G for graphite. The horizontal scale indicates the time divided by the square of the half-width of the sample.

time when that stage had reached the center of the sample. From then on, the amount of that stage decreased until only the final stage was left. The equilibrium stage was not necessarily the fastest stage to form. In particular, comparison between the plots of the relative amounts of stages present versus time for 50-mol % (Fig. 19) and 40-mol % (Fig. 20) Br₂–CCl₄ indicates that stage 2 was present immediately when 50-mol % Br₂–CCl₄ was used, while in 40-mol % Br₂–CCl₄ stage 2 did not appear until quite a bit of stage 3 was present. This can be accounted for by the fact that with dilution of the Br₂–CCl₄ solutions the change in free energy due to the formation of stage 2 approaches the change in free energy for the formation of stage 3. In fact, the phase diagram (Fig. 4) indicates that below 37-mol % Br₂–CCl₄, stage 2 is no longer stable with respect to stage 3.

Fig. 19. The relative amounts of stages observed as functions of time, determined from peak areas of X-ray diffraction patterns. The graphite was exposed to 50-mol % bromine–carbon tetrachloride.
Time-temperature-transformation (TTT) curves (Fig. 21) were obtained for intercalation of 4-mm-wide HOPG in pure liquid bromine at various temperatures from 23 to 180°C. Because the tube containing the sample and the bromine was sealed, intercalation was performed with the sample immersed in liquid bromine throughout the temperature range. In this temperature range the vapor pressure of bromine varies from 0.3 to 20 atm. The phases present are indicated by the stage numbers and the symbol G for graphite. The horizontal scale indicates the time divided by the square of the half-width of the sample. Each curve in Fig. 21 corresponds to the time for either the start or the completion of the formation of a final stage. Stage 2 was the final stage from room temperature to 70°C; stage 3 was the final stage from 70 to 120°C; stage 4 was the final stage from 120 to 130°C. In other words, the final stage increased with increasing temperature.

The curves in Fig. 21 correspond to the times at which a certain stage finished forming. Each curve is C-shaped, as is typical of the TTT-curves which are commonly used to describe the kinetics of metallurgical transformations. For each TTT-curve in Fig. 21, the process is mainly staging reaction-controlled at temperatures above the nose of the C-shaped curve because the temperature limit (phase boundary) for the stability of that stage is approached, whereas the process is mainly diffusion-controlled at temperatures below the nose of the C-shaped curve because the rate of diffusion decreases with decreasing temperature. Thus the rate-controlling step depends both on the stage and the temperature. At the same temperature, it may be reaction-controlled for one stage and diffusion-controlled for another. However, for the vast majority of the temperature range over which a given stage is stable, the process is diffusion-controlled. This conclusion is consistent with the results of weight uptake measurement, optical profilometry and X-ray absorption, which show that the extent of intercalation is a function of the square root of the time of intercalation (Sections 3.2.1, 3.2.2, 3.2.3). It is not possible on the basis of the experimental data to determine the diffusing component. It is possible for the diffusing component to be either a bromine molecule (e.g., as in the bromine exchange observed by Aronson[47]), or the bromine islands (e.g., the "sliding" process suggested by Herold[56]).

Overall the reaction rate increased exponentially with increasing temperature up to about 130°C. Above this temperature there appeared to be a gradual decrease in reaction rate. This was indicated by an increase in the amount of time needed to completely intercalate the sample, as indicated by the disappearance of the pristine graphite X-ray diffraction peak. A complicating factor in the determination of the high-temperature kinetics arose from the presence of stage 4 at the edges of all samples intercalated above 130°C. However, the amount of stage 4 present (as indicated by diffraction peak area and concentration profile) was independent of the time spent at the reaction temperature. It was concluded that the stage 4 was forming either on heating to the reaction temperature or on quenching to room temperature, during which passage through the nose of the stage-4 C-curve might have occurred. The decrease in reaction rate at high temperatures indicates that diffusion is no longer the rate controlling step.

A possible contribution to the decrease in rate...
with increasing temperature is the effect of the hydrostatic pressure due to the bromine vapor pressure. Saunders et al. [57] observed that a uniaxial load of up to 300 atm applied to HOPG along the c-axis decreased the bromine intercalation rate. Moran et al. [58] observed in the intercalation of nitric acid that the intercalation rate was quite sensitive to an argon overpressure, with a reduction in the reaction rate by a factor of ≈50 in the presence of an argon pressure of 5 atm. This raised the question of the effect of pressure on the reaction rate observed in this work, since there was a rate decrease with increasing temperature and the bromine vapor pressure increased to tens of atmospheres, well above the pressures observed by Moran et al. To test the possibility that the decrease in reaction rate at high temperatures was due to the hydrostatic pressure of the bromine vapor, a pressure cell was constructed and the rate was measured for different pressures. The results (Fig. 22) indicated that the pressure dependence of the reaction rate was approximately linear, with a slope of $0.3 \pm 0.1$ cal/mol-atm. This value is in keeping with an estimated activation volume for the viscosity of bromine, but is far less than that required to account for the observed decrease in rate with temperature. Thus the decrease in rate with increasing temperature was attributed to the decrease in stability of the intercalation compounds relative to pure bromine and graphite at high temperatures. In effect, the decrease in rate with increasing temperature is equivalent to approaching the intercalation threshold pressure by dilution. As the temperature increases, the change in free energy due to the reaction becomes small with respect to the amount of energy needed to initiate intercalation and the reaction rate decreases.

![Fig. 22. Width of intercalate front as measured by X-ray absorption as a function of pressure. The HOPG was immersed in pure bromine and placed in an oil bath at 130°C for 10 min.](image)

4. CONCLUSION

A phase diagram was determined for the graphite-bromine system. Prior to this work, phase diagrams...
had been determined for the graphite–alkali metals[42] which are electron donor compounds. This work is the first determination of a phase diagram for an electron acceptor graphite intercalation compound. This is particularly significant in light of the theoretical predictions of phase diagrams which have been published[20,25,26,30]. From the phase diagram of the graphite–bromine system, and the enthalpies and entropies of reaction for stages 2–4 of graphite–bromine compounds were calculated. The enthalpies of reaction were found to be \(-10.0, -10.8\) and \(-11.0\) kcal mol\(^{-1}\) Br\(_2\); the entropies of reaction were found to be \(-29.9, -30.8\) and \(-30.6\) cal mol\(^{-1}\) Br\(_2\) K\(^{-1}\) for stages 2, 3 and 4, respectively. These are the first values to be reported for stages 3 and 4, and the values for stage 3 are in agreement with the previously published results of Sasa[1].

By measuring the intercalation rate as a function of the reaction temperature, this work provided the first determination of a TTT diagram for an intercalation compound. In particular it was demonstrated that the reaction rate for stage 2 or 3 first increased and then decreased as the reaction temperature was raised and the thermal phase boundary (70°C for stage 2, 120°C for stage 3) was approached. This was evidence that the staging reaction became the rate controlling step at temperatures just below the maximum stable temperature for that stage, whereas the diffusion of bromine within the graphite was the rate controlling step otherwise. In addition, the intercalation rate was determined as a function of the bromine potential, thereby yielding a TCT diagram.

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