

Thermal Gravimetric Analysis of Graphite-Bromine Compounds

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SUMMARY

Thermal gravimetric analysis was applied for the first time to the study of graphite intercalation compounds. The gravimetric measurements were carried out on graphite-bromine compounds in the temperature range from room temperature to 140 °C. Intercalate desorption was found to be thermally activated. Its rate is anomalously high near the intralayer intercalate position order-disorder transformation temperature (100 °C) and the exfoliation temperature. This rate was also found to increase with increasing intercalate concentration. The mechanism of desorption depends on the intercalate concentration. At high intercalate concentrations, desorption appears to be dominated by a diffusion process and has an activation energy of 14 kcal (mol Br₂)⁻¹, in good agreement with the activation energy for the diffusion of bromine in graphite. As desorption ends, the intercalate concentration approaches a minimum value which depends on the desorption temperature. Much of the retained intercalate is ordered. Below the intralayer order-disorder transformation temperature an initially saturated graphite-bromine sample has a minimum concentration of 18 - 19 wt.% Br₂. Above the order-disorder transformation temperature the minimum concentration is smaller. The energy of the desorption process is utilized mainly for the vaporization of the intercalate, as suggested by our differential scanning calorimetry results.

1. INTRODUCTION

The recent impetus in the study of graphite intercalation compounds is centered on the

use of optical [1 - 9] and electrical [7, 10] measurements. Although considerable information on the electronic and lattice properties has been gained by these measurements, numerous issues essential to the practical application and fundamental understanding of graphite intercalation compounds remain to be investigated. These issues include the thermal stability of the compounds, the interaction between the defects and the intercalate, and the kinetics of intercalation. In order to study these problems, we performed a thermal gravimetric analysis (TGA) on graphite intercalated with bromine, which is the most thoroughly studied acceptor intercalate species.

Gravimetry is a sensitive and direct experimental technique for studying intercalate sorption and desorption. This is because carbon is a relatively light element, so that intercalation generally causes a significant increase in the weight of the sample. For bromine intercalation the saturated lamellar compound is second stage and weighs 83% more than the parent pristine graphite. Another technique for studying intercalate desorption is the detection of the effluent gas during desorption. This technique serves to complement and confirm the gravimetric results, although it is not as sensitive as the gravimetric technique. In this work both gravimetry and effluent gas detection were used to study the intercalate desorption process.

Graphite intercalation compounds can be formed by exposing pristine graphite to the external intercalate vapor. During the intercalation process, sorption of the intercalate by the graphite occurs and continues until equilibrium is reached between the sample

and the external intercalate vapor. The resulting compound is known as a lamellar compound [11]. Applications involving lamellar compounds are attractive because relatively high concentration lamellar compounds can possess electrical conductivities considerably greater than those of less concentrated residue compounds [12]. However, one of the difficulties in using lamellar compounds in practical applications is that they tend to desorb their intercalates once they are not in equilibrium with the external intercalate vapor [11] unless they are maintained below a certain temperature, which varies with the intercalate species. Johnson *et al.* [13] recently observed that desorption of graphite-bromine (stage 2) caused a significant decrease in the *a* axis electrical conductivity at about 80 °C. The problem of intercalate desorption occurs with almost all intercalate species, including SbF_5 and AsF_5 [14].

The intercalate desorption process can be observed by using differential scanning calorimetry (DSC). The rate of enthalpy change of graphite-bromine during heating at a constant rate of 10 K min^{-1} is shown in Fig. 1. Prior to the temperature scan the sample contained 61.3 wt.% Br_2 . As the temperature increased, an increasing amount of endothermic heat was required. This increase began at about 80 °C and reached its maxi-

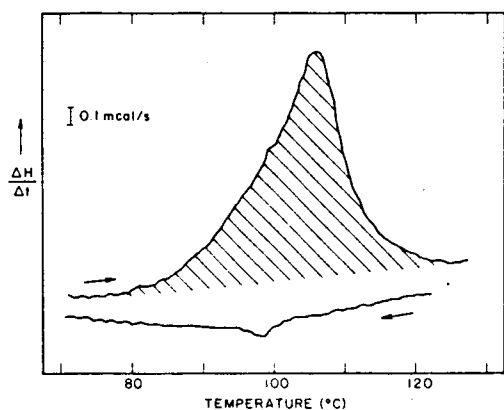


Fig. 1. The DSC spectrum of a concentrated graphite-bromine lamellar compound. The upper trace was taken during heating at a rate of 10 °C min^{-1} ; the lower trace was taken during cooling at a rate of 10 °C min^{-1} .

mum at about 106 °C. The trace then returned to its baseline at 120 °C. It should be noted that the endothermic peak associated with the intralayer intercalate position order-disorder transformation [15] was not clearly resolved during heating. This order-disorder transformation was first observed by electron diffraction at $106 \pm 10 \text{ °C}$ [16, 17] and was later confirmed by DSC at $102 \pm 2 \text{ °C}$ [15]. Recent X-ray diffraction work yielded a transformation temperature of 100.5 °C [18]. During cooling a small exothermic peak associated with the intralayer intercalate position order-disorder transformation was observed. When cooled to room temperature again, the sample contained 24.1 wt.% Br_2 , i.e. more than 60% of the starting intercalate was lost on heating briefly to 130 °C. The DSC peak area, which is related to the enthalpy change of the process, indicates that the reaction required at least $110 \pm 11 \text{ mcal}$, the uncertainty being due to the area integration and ordinate calibration. The heat of vaporization for the mass of intercalate lost is $135 \pm 14 \text{ mcal}$, the uncertainty being due to continued weight loss (at a slow rate) after the initial large peak. Hence it appears that a significant portion of the intercalate in a high concentration graphite-bromine compound vaporizes at temperatures greater than 80 °C (350 K). This behavior was not observed in samples of bromine concentration less than about 30 wt.%. In contrast with compounds of high intercalate concentrations the peak associated with the intralayer intercalate position order-disorder transformation was observed in these samples during both heating and cooling. This indicates that the stability problem becomes more serious as the intercalate concentration increases.

Exfoliation, the large-scale expansion of the intercalated graphite in the *c* direction, also plays an important role in the thermal stability of graphite intercalation compounds. Exfoliation generally occurs when the compound is heated to a critical temperature. This critical temperature tends to decrease with increasing intercalate concentration. High concentration samples (greater than 75 wt.% Br_2) were found to exfoliate at temperatures as low as 80 °C, which is well below the critical temperatures for dilute compounds (approximately 150 - 170 °C).

2. GAS DETECTION

2.1. Technique

The detection of desorbed intercalate from a sample on heating was achieved by using an effluent gas analyzer incorporated in a differential scanning calorimeter (Perkin-Elmer DSC-1B). The analyzer consisted of a two-thermistor bridge circuit which monitored the thermal conductivity of the DSC sample holder purge gas relative to the gas which bypassed the sample holder. The system was purged at $30 \text{ cm}^3 \text{ min}^{-1}$ with dry nitrogen. A weighed graphite-bromine sample was placed in a platinum pan and mounted in the DSC sample holder which was purged for about 10 min at room temperature. The sample temperature was increased at a rate of either 5 or $10 \text{ }^\circ\text{C min}^{-1}$. A Columbia Scientific Industries integrator was used to record the effluent analyzer output; the acquisition rate was 5 or 10 min^{-1} .

2.2. Results

Typical effluent gas analyzer responses are shown in Figs. 2 and 3. A graphite-bromine sample, which had been allowed to desorb at room temperature from 83 to $43.4 \text{ wt.}\%$ Br_2 , was heated from room temperature to $107 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, as shown in Fig. 2. Little evolved bromine was detected until $101 \text{ }^\circ\text{C}$. At this point a considerable amount of intercalate was detected and is interpreted as an effect of intralayer intercalate position disordering at $100 \text{ }^\circ\text{C}$.

Figure 3 shows the effluent gas analyzer response for a less concentrated graphite-

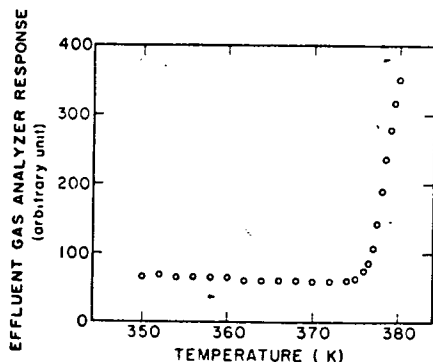


Fig. 2. The effluent gas detector response as a function of the temperature (at a heating rate of 10 K min^{-1}), showing desorption commencing at the intralayer order-disorder transformation temperature in a graphite-bromine compound ($100 \text{ }^\circ\text{C}$). The sample contained $43.3 \text{ wt.}\%$ Br_2 before heating.

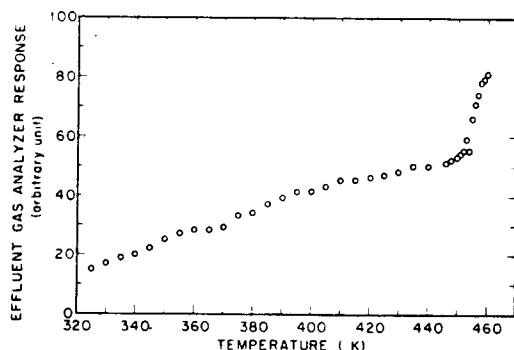


Fig. 3. The effluent gas detector response as a function of the temperature (at a heating rate of 5 K min^{-1}), showing desorption associated with exfoliation near $177 \text{ }^\circ\text{C}$. The sample contained $21.5 \text{ wt.}\%$ Br_2 before heating.

bromine sample at a higher temperature range and sensitivity. The sample was originally a saturated lamellar compound ($83 \text{ wt.}\%$ Br_2); prior to this temperature scan it had been desorbed at room temperature and by heating to about $117 \text{ }^\circ\text{C}$, and it contained $21.5 \text{ wt.}\%$ Br_2 . The temperature of the sample was scanned from room temperature to $187 \text{ }^\circ\text{C}$ at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. In Fig. 3 the analyzer trace increases slowly (probably because of baseline drift at this high sensitivity) until about $177 \text{ }^\circ\text{C}$ where the amount of desorbed intercalate increases sharply. This increase is attributed to extensive exfoliation, which was visually confirmed at $176 \text{ }^\circ\text{C}$ for this sample.

The amount of vapor desorbed near $101 \text{ }^\circ\text{C}$ was found to increase significantly with increasing intercalate concentration. At low intercalate concentrations, as for the sample of Fig. 3, this increase at about $102 \text{ }^\circ\text{C}$ was too small to be observed. In contrast, at relatively high intercalate concentrations, as for the sample of Fig. 2, a large increase was observed at about $102 \text{ }^\circ\text{C}$.

By using the gas detection technique we found that the intralayer order-disorder transformation and exfoliation markedly affect the rate of intercalate desorption. However, the effect of the order-disorder transformation on desorption is small at low intercalate concentrations. In order to study these effects more precisely and to obtain information on the kinetics of intercalate desorption, we used thermal gravimetry, as described in Section 3.

3. THERMAL GRAVIMETRY

3.1. Technique

The thermal gravimetric measurement was performed by using a Perkin-Elmer electronic microbalance (autobalance model AD-2Z), which has a maximum sensitivity of $0.1 \mu\text{g}$. The sample was placed on a Pyrex pan which was suspended by a Pyrex hangwire. A Pyrex tubing 19 mm in inside diameter enclosed the hangwire and the sample pan. During the measurement the tube was slowly purged with argon at a rate of approximately $20 \text{ cm}^3 \text{ min}^{-1}$. A low mass furnace surrounded the sample pan and was controlled by a Theall Engineering model TP-2000 temperature programmer which was capable of either isothermal or scanning temperature control. The sample temperature was measured by placing a chromel-alumel thermocouple immediately below (within 2 mm) the sample pan. During isothermal measurements the controller kept the sample temperature within 1°C from the programmed temperature. All temperature scans were performed at a heating rate of 2°C min^{-1} .

3.2. Results

3.2.1. Isothermal desorption

Isothermal desorption was studied on graphite-bromine samples prepared by exposing pristine highly oriented pyrolytic graphite to bromine vapor at room temperature for a sufficient amount of time to produce saturated second-stage graphite-bromine (83 wt.% Br_2) specimens. The samples were approximately $4 \text{ mm} \times 4 \text{ mm} \times 0.5 \text{ mm}$ in size and of mass between 9 and 18 mg before intercalation. The uncertainty in sample mass was $\pm 10 \mu\text{g}$.

Figure 4 shows the intercalate concentration as a function of time for samples desorbed at 50, 60, 70, 80 and 90°C . During the early part of the desorption process the desorption rate increases as the temperature increases. However, complete desorption does not occur, because a significant portion of the original intercalate (18 - 19 wt.% of the parent graphite) is retained by the parent graphite even after a long desorption time. This behavior is clearly shown by the 90°C desorption curve. In a similar manner the samples desorbed at lower temperatures also approached this minimum concentration if

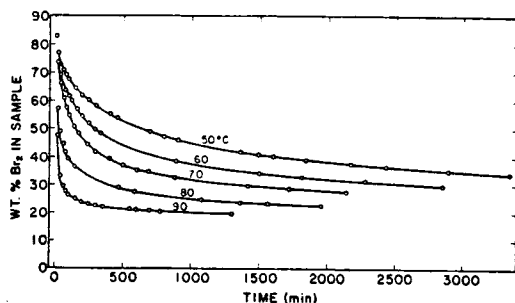


Fig. 4. Isothermal desorption curves of initially saturated graphite-bromine samples at temperature below the intralayer order-disorder transformation temperature.

sufficient time was allowed. Since 18 - 19 wt.% Br_2 is strongly retained by the graphite at these temperatures (for desorption below 100°C), this amount is subtracted from the total amount intercalated to yield the "desorbable" portion of the intercalate. The desorbable bromine concentration c^* for desorption at temperatures below the intralayer order-disorder transformation temperature (100°C) is defined as

$$c^* = \frac{M_{\text{Br}_2} - M_{19}}{M_c} \quad (1)$$

where M_{Br_2} is the mass of intercalated bromine at a given time, M_{19} is the mass of bromine at 19 wt.% and M_c is the mass of the parent graphite. The desorbable bromine concentration is plotted semilogarithmically against the time in Fig. 5. The variation in c^* is of interest during the period between 20 and 100 min from the start of desorption. During this time the intercalate concentration is high and a large concentration gradient

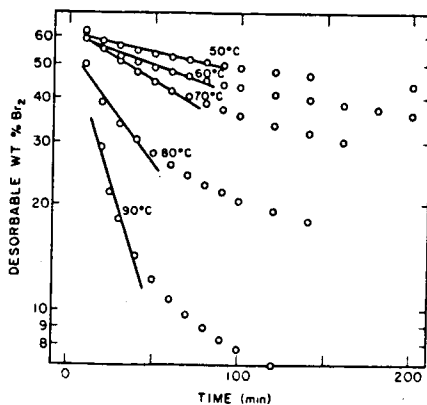


Fig. 5. The desorbable bromine concentration as a function of the time.

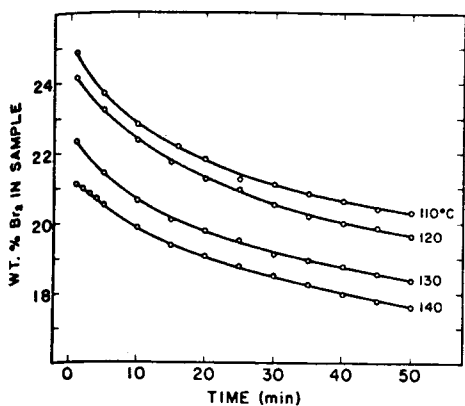


Fig. 6. Isothermal desorption curves of relatively dilute graphite-bromine samples at temperatures above the intralayer order-disorder transformation temperature.

exists between the sample and its surroundings. Thus the desorption process during this period is probably diffusion controlled.

Desorption curves for desorption at temperatures above the intralayer order-disorder transformation temperature are shown in Fig. 6. Owing to the anomalously high desorption rate at the intralayer order-disorder transformation temperature it was impossible to maintain a high intercalate concentration above the order-disorder transformation temperature. As a result, measurements above the order-disorder transformation temperature could only be performed on relatively dilute compounds. The temperatures chosen for the isothermal measurements were 110, 120, 130 and 140 °C. As shown in Fig. 6, desorption at these temperatures led to intercalate concentrations of less than 18 wt.% Br₂. However, the minimum concentration was not determined and the effect of the order-disorder transformation on the concentration was not quantitatively studied. Nevertheless, the desorption rate above the order-disorder transformation temperature increases as the temperature increases, similarly to desorption below the order-disorder transformation temperature.

3.2.2. Scanning thermal gravimetric analysis

Because the desorption rate is very high at high temperatures for high concentration samples, measurement during temperature scanning was performed on samples with an initial concentration of less than 30 wt.% Br₂. The uncertainty in the sample mass was

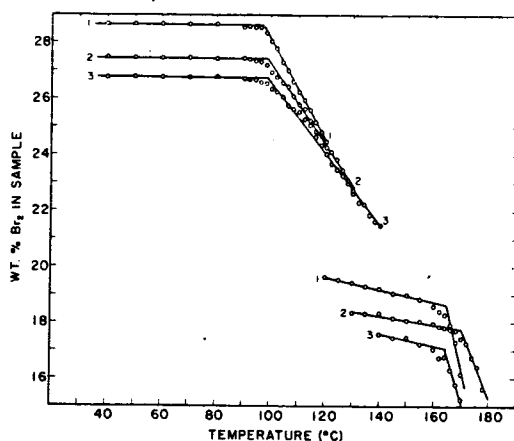


Fig. 7. Scanning TGA curves taken at a rate of 2 °C min⁻¹ for three relatively dilute graphite-bromine samples. The scan was interrupted for 50 min at 120 °C for sample 1 (curve 1), at 130 °C for sample 2 (curve 2) and at 140 °C for sample 3 (curve 3).

±10 µg at low temperatures and increased as the temperature increased, since disturbance caused by violent desorption or exfoliation occurred at high temperatures.

Figure 7 is a plot of the intercalate concentration against the temperature for three samples which were obtained by desorbing saturated graphite-bromine compounds at various temperatures to the starting concentration. The samples were heated at a rate of 2 °C min⁻¹ and were held isothermally at 120, 130 or 140 °C for 50 min before being heated to higher temperatures. The sample associated with curve 1 was initially desorbed at 60 °C and was held at 120 °C. The samples yielding curves 2 and 3 were desorbed at 50 and 70 °C respectively and were held at 130 and 140 °C respectively.

As shown in Fig. 7, the bromine weight percentage decreases sharply at two distinct temperatures. The first decrease occurs at approximately 98 °C and corresponds closely to the temperature associated with the intralayer intercalate position order-disorder transformation. The desorption rate below this temperature is negligible compared with that above this temperature. The second decrease occurs at about 165 - 170 °C and is associated with exfoliation. The desorption rate and the equilibrium intercalate concentration above the exfoliation temperature were not determined in this work. However, it was observed that the bromine weight percentage in the sample did not decrease

smoothly but jumped, indicating perhaps that desorption above the exfoliation temperature occurred in spurts. Moreover, the exfoliation temperature appears to depend on the desorption temperature prior to the temperature scan in such a manner that, the lower the initial desorption temperature, the higher is the exfoliation temperature. These observations on exfoliation are consistent with our thermal mechanical analysis results [19].

4. ANALYSIS

It should be emphasized that the desorption process for high intercalate concentrations could be studied only at temperatures below the intralayer order-disorder transformation temperature because of the significant desorption at the transformation temperature. The desorption process for high intercalate concentrations is probably diffusion controlled, since a considerable concentration gradient exists between the sample and its surrounding ambient. The concentration remaining in the parent graphite is then approximately proportional to $\exp(-kt)$ where k is the rate constant for the process [20]. The rate constant can be determined from the slope of the plot of the concentration against the time (Fig. 5) by using the relation

$$k = \frac{d(\ln c^*)}{dt} \quad (2)$$

where c^* is the desorbable bromine concentration, as defined in eqn. (1), for samples desorbed below the intralayer order-disorder transformation temperature. For a diffusion process the rate constant varies with temperature as

$$k = k_0 \exp\left(-\frac{E_D}{k_B T}\right) \quad (3)$$

where k_0 is a constant of proportionality, E_D is the activation energy of the desorption process and k_B is Boltzmann's constant. A plot of k against $1/T$ is shown in Fig. 8. The slope of this plot is equal to $-E_D/k$ and hence yields an activation energy of 14 kcal (mol Br_2) $^{-1}$; this closely agrees with the activation energy of 11 - 14 kcal mol $^{-1}$ obtained by

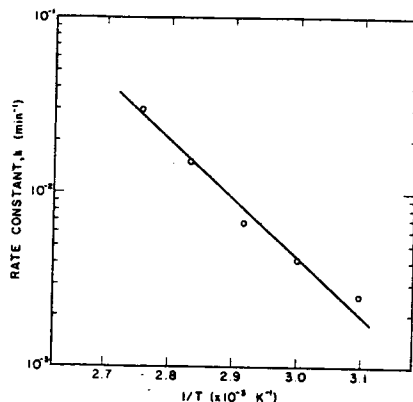


Fig. 8. A plot of the rate constant k against $1/T$ for desorption at high intercalate concentrations.

Aronson [21] for the diffusion of bromine in graphite.

The desorption rate increases with increasing intercalate concentration, in addition to increasing with increasing temperature. Therefore it is appropriate to compare the desorption rates measured at various temperatures for the same intercalate concentration. Desorption above the intralayer order-disorder transformation was analyzed by comparing the instantaneous desorption rates for a concentration of 20.5 wt.% Br_2 at temperatures of 110, 120, 130 and 140 °C, as shown in Fig. 9. This yields an activation energy of about 17 kcal (mol Br_2) $^{-1}$. Desorption of disordered intercalate can also be analyzed by plotting the desorption rate as a function of the bromine vapor pressure, as shown in Fig. 10, where the vapor pressure was that in equilibrium with bromine at the

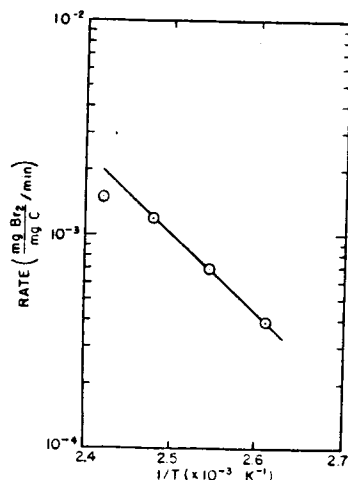


Fig. 9. A plot of the desorption rate against $1/T$ for the same intercalate concentration (20.5 wt.% Br_2).

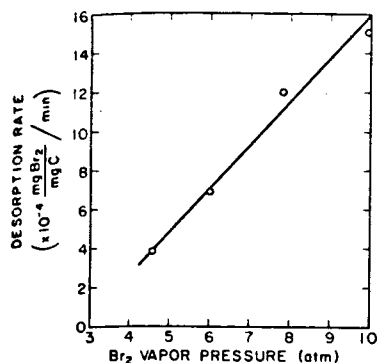


Fig. 10. A plot of the desorption rate against the bromine vapor pressure.

measured temperature, as calculated by using the Clapeyron equation. The desorption rate seems to be proportional to the intercalate vapor pressure for desorption above the intralayer intercalate order-disorder transformation temperature.

5. DISCUSSION

This work has clearly shown that graphite intercalation compounds are temperature sensitive. The thermal instability is due mainly to intercalate desorption which causes changes in the stage. The TGA indicated that the rate of intercalate desorption increases with increasing intercalate concentration and with increasing temperature. The instability is particularly severe at temperatures above the intralayer intercalate position order-disorder transformation temperature.

Because of the thermal instability it is difficult to perform experimental measurements as a function of temperature on samples of uniform and constant stage. This problem cannot be avoided by keeping the sample in a sealed ampoule because the external intercalate vapor pressure must be varied simultaneously with the sample temperature in order to maintain the stage. However, because of the lack of information on the pressure-temperature phase diagram, the pressure required at a given temperature for a given stage is not known at present. Such information will be extremely valuable for a basic understanding of the stability of graphite intercalation compounds.

The effect of thermal instability on the electrical conductivity can be appreciated by

noting the change in the α axis electrical conductivity of the second-stage graphite-bromine compound as it is heated. Johnson *et al.* [13] reported that a significant conductivity decrease occurred at about 80 °C and interpreted this as due to intercalate desorption, as observed by the formation of droplets of bromine on the glass encapsulation [14]. This is consistent with our DSC (Fig. 1) and TGA (Fig. 4) results which show that desorption starts to become significant at about 80 °C during heating for concentrated graphite-bromine samples.

For high intercalate concentrations, desorption appears to be dominated by a diffusion mechanism and has an activation energy of 14 kcal (mol Br₂)⁻¹, in good agreement with the value reported by Aronson [21] for diffusion of bromine in graphite.

The mechanism of desorption appears to depend on the intercalate concentration. At high intercalate concentrations, desorption appears to be dominated by a diffusion process since a large intercalate concentration gradient exists. However, as desorption progresses and the concentration decreases, this gradient eventually disappears. Below the intralayer order-disorder transformation temperature the remaining intercalate, with a concentration of 18–19 wt.% for an initially saturated graphite-bromine sample, is strongly retained by the parent graphite. It should be emphasized that electron diffraction has shown that a significant portion of this remaining intercalate is ordered although a portion is at defects [17]. It is probable that the degree of ionization of the intercalate is different for the intercalate at the different types of sites. At temperatures above the order-disorder transformation temperature the disordered intercalate is able to continue to diffuse through the graphite matrix. At these temperatures the desorption rate, for a given intercalate concentration, is linearly related to the vapor pressure of the intercalate (which depends on the sample temperature), as shown in Fig. 10. This indicates that the driving force for desorption of low concentration graphite-bromine compounds above the intralayer order-disorder transformation temperature is the vapor pressure of the disordered intercalate.

For practical applications of graphite intercalation compounds it is useful to note

that the intercalate concentration approaches a minimum value as the desorption process ends, as shown in Fig. 4. This minimum value is a function of the temperature at which desorption occurs. For saturated graphite-bromine (83 wt.% Br₂) compounds, desorption at temperatures below the intralayer order-disorder transformation temperature (100 °C) leads to a minimum intercalate concentration of 18 - 19 wt.% Br₂. The time necessary to reach the minimum intercalate concentration decreases as the desorption temperature increases. Once the minimum intercalate concentration is reached, desorption is almost negligible and the sample can be considered to be "stable" at temperatures less than the order-disorder transformation temperature. However, if the sample is then heated to a temperature above the intralayer order-disorder transformation temperature, the stability is disturbed and desorption resumes until a lower minimum intercalate concentration is reached. Above the order-disorder transformation temperature the minimum concentration appears to decrease with increasing temperature. Hennig [11] reported that desorption at 2000 °C still does not decrease the intercalate concentration to zero. Therefore the minimum intercalate concentration does not decrease indefinitely as the desorption temperature increases. Rather, it appears to approach a limiting value at high temperatures. It would be interesting to extend the present work by obtaining quantitatively the variation of the minimum intercalate concentration with the desorption temperature.

From the DSC result of Fig. 1 it appears that the energy of the desorption process is utilized mainly for the vaporization of bromine and that DSC observation of the intralayer order-disorder transformation on heating is possible only in relatively dilute and stable compounds. We observed that violent desorption from concentrated samples is accompanied by crack formation, similar to exfoliation though on a smaller scale. This suggests that vaporization of the intercalate within the sample may be responsible for the crack formation. However, the amount of exfoliation is insufficient to account for the change in volume due to vaporization. Therefore it appears that vaporization does not occur simultaneously for all the

desorbable intercalate in the sample and that the pressure caused by vaporization is quickly dissipated by the diffusion of the intercalate.

Exfoliation, which significantly affects the *c* axis electrical conductivity and mechanical properties, also contributes to the thermal instability of graphite intercalation compounds, since exfoliation is accompanied by a substantial increase in the rate of intercalate desorption. A better understanding of the exfoliation process is needed for control of this instability and its effects.

In conclusion, considerable attention must be given to the stability problem in order to use graphite intercalation compounds in practice. This problem is serious because almost all the intercalates are corrosive, toxic or undesirable for the environment. A possible solution of this problem is the use of desorbed compounds with the minimum intercalate concentration for the operating temperature. Although these compounds are quite dilute, they contain the intercalate in ordered interplanar positions, as indicated by electron diffraction [17] for the graphite-bromine system. Furthermore, they are stable and so pose little danger to the environment. Much more work is needed to characterize desorbed compounds.

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