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Calorimetric study of the rate of the 277K phase transition in graphite-bromine

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Graphite intercalated with bromine exhibits a number of phase transitions. One of these occurs at 277K, as observed by differential scanning calorimetry (DSC)[1, 2] and X-ray diffraction[3]. The phase below 277K has a complex diffraction pattern of sharp spots, which corresponds to a superlattice that is seven times that of graphite in the a_G direction ($a = 17.22$ Å) and twenty times that of graphite in the $(110)_G$ direction ($b \simeq 42.6$ Å)[3]. DSC revealed this transition as an endothermic peak at 277K upon heating. However, a corresponding exothermic peak at the transition temperature was not observed by DSC upon cooling[1], which suggests that the transition during cooling is much slower than the corresponding transition upon heating. This paper describes additional DSC measurements of this phase transition which indicate that the enthalpy change of the phase transition at 277K upon heating is sensitive to the amount of time spent equilibrating the sample at a temperature below the transition temperature. This sensitivity to equilibration time and temperature was not observed for the 374K melting transition in the same material, indicating that the kinetics of the 277K transition are much slower than that of the 374K transition. We report here the first study of the rate of a phase transition in an intercalation compound of graphite.

These DSC measurements were made with a Perkin-Elmer DSC-2 differential scanning calorimeter. Temperature calibration was performed by using the melting points of indium and tin, scanning at 5 K/min; enthalpy change calibration was performed by heating a known mass of indium through its melting point. The heat of fusion of indium was taken as 6.79 cal/gm.

Samples were obtained by desorbing saturated graphite-bromine at room temperature in air. These saturated materials were prepared by vapor phase intercalation of highly-oriented pyrolytic graphite (HOPG), which had dimensions of 4 × 4 × 0.5 mm. Sample weight was obtained both before and after DSC measurement using a microbalance with an uncertainty of ± 0.002 mg. The sample was mounted in an unsealed platinum pan with a platinum cover; the sample holder was purged with dry argon at 20 cc/min.

The effect of the equilibration temperature and time on the enthalpy change of the 277K transition is shown in Fig. 1, where normalized enthalpy change ($\Delta H/\Delta H_{max}$) is plotted against equilibration time for different equilibration temperatures. The normalized enthalpy change is defined as the enthalpy change for a given equilibration time and temperature divided by the maximum enthalpy change expected for a given intercalate concentration, as determined by Fig. 8 of Ref. [2]. As the equilibration temperature decreased, less time was necessary to reach the maximum enthalpy change value. The enthalpy change of the transition was not sensitive to equilibration time for equilibration temperatures less than 220K due to the rapid equilibration which took place at these temperatures. However, equilibration at temperatures greater than 220K occurred only after tens of minutes at the equilibration temperature.

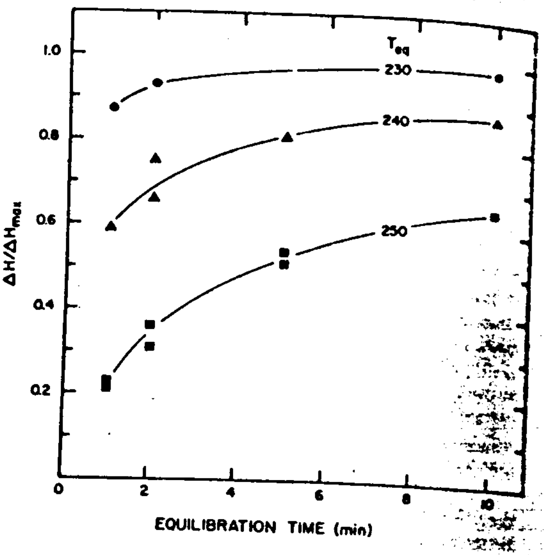

Fig. 1. The dependence of the normalized enthalpy of transformation on the equilibration time and temperature (T_{eq} in K). ΔH_{max} is the maximum enthalpy change.

The fraction $\Delta H/\Delta H_{max}$ is a measure of the degree of order achieved through equilibration at a particular temperature for a particular amount of time. This fraction is unity if the equilibration is carried out to completion. Figure 1 indicates that the rate of ordering increases with decreasing equilibration temperature; in the first minute of equilibration, the rate is $0.22\ s^{-1}$, $0.59\ s^{-1}$ and $0.87\ s^{-1}$ at 250, 240 and 230 K, respectively. This trend is expected since the rate of ordering increases with the increasing degree of supercooling of the high temperature phase. In addition, Fig. 1 indicates that, at a constant equilibration temperature, the rate of ordering decreases with increasing time. A plot of $\Delta H/\Delta H_{max}$ against the square root of time does not yield a straight line. More detailed rate measurements are needed to give quantitative information on the kinetics of the ordering.

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