THERMODYNAMICS OF INTERCALATION OF BROMINE IN GRAPHITE*

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ABSTRACT

The thermodynamics of intercalation of bromine in highly oriented pyrolytic graphite had been studied by determining the pressure-temperature equilibrium diagram for stages 2-4. The standard heat and entropy of reaction for the transformation from stage n to stage n-1 (n=5, 4, 3) were found to be roughly the same, though the enthalpy of reaction became slightly more negative as the stage number increased. The heat and entropy of formation from pure graphite were thus found to be -10.9 kcal mol^{-1} Br_2 and -30.4 cal mol^{-1} Br_2 K^{-1} respectively for stage 2, -11.3 kcal mol^{-1} Br_2 and -30.6 cal mol^{-1} Br_2 K^{-1} respectively for stage 3, and -11.5 kcal mol^{-1} Br_2 and -30.6 cal mol^{-1} Br_2 K^{-1} respectively for stage 4.

INTRODUCTION

The thermodynamics of intercalation of alkali metals in graphite had been studied for stages 1-5 by vapor pressure measurement [1-4], solid-state emf measurement [5], calorimetry [6] and stage-2-to-stage-1 transformation temperature measurement [7]. On the other hand, the thermodynamics of intercalation of bromine in graphite had only been studied by decomposition vapor pressure measurement of stage 2 [8-10], which gave the standard heat of reaction of -10.2 ± 0.3 kcal mol^{-1} and the standard entropy of reaction of -29.9 ± 1.2 cal mol^{-1} K^{-1} for the stage-3-to-stage-2 transformation [10]. In this paper, by determining the pressure-temperature equilibrium diagram for stages 2-4 of graphite-bromine, we have obtained the standard heats of reaction and the standard entropies of reaction for the transformations from stage 5 to stage 4, from stage 4 to stage 3, and from stage 3 to stage 2. Using these data, the heats of formation of stages 2-4 were calculated.

INTERCALATION METHODS

Four methods of intercalation have been investigated. They differ in the parameter(s) used to control the eventual stage, as listed in Table 1 and also described below.

1. <u>Temperature method (two-bulb)</u>. In this method, the sample temperature is varied to control the eventual stage, while the intercalate vapor pressure resulting from a reservoir of pure intercalate is fixed. The sample temperature should be kept higher than the intercalate reservoir temperature to avoid condensation of the intercalate on the sample. This method is popular and was originally developed for the intercalation of alkali metals [7].

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TABLE I
Intercalation Methods

Method	Parameters	
	Intercalate vapor pressure	Sample temperature
Temperature method (two-bulb)	-	X
Temperature method (one-bulb)	X	X
Solution method	X	-
Temperature-solution method	X	X

X Varied to control the stage   - Not varied

2. Temperature method (one-bulb). In this method, the sample and the pure intercalate are at the same temperature. Thus an increase in sample temperature necessarily increases the intercalate vapor pressure. This method is experimentally simpler than the two-bulb method because it requires only one temperature. It was used by Bach et al. to prepare various stages of graphite-bromine, as shown by weight measurement [11].

3. Solution method. In this method, the intercalate is dissolved in a certain solvent which does not intercalate. The concentration of the intercalate in the solvent is used to control the eventual stage. Intercalation takes place at room temperature. This method was first used by Hennig to prepare graphite-Br_2 with Br_2-CCl_4 solution [12]; it was also used by Saunders et al. [13].

4. Temperature-solution method. In this method, the intercalate is dissolved in a solvent as in the solution method, but the temperature method (one-bulb) is also involved. In other words, the sample and the intercalate solution are at the same temperature, such that this temperature and the intercalate concentration in the solution are both varied to achieve a given eventual stage. In this work, this method was used for the first time to prepare graphite-bromine.

It should be noted that the temperature method (one-bulb) and the solution method are special cases of the temperature-solution method. In this paper, the use of the temperature-solution method enabled the determination of the pressure-temperature equilibrium diagram for various stages of graphite-bromine. The temperature method (two-bulb) was also used for the same purpose, though to a smaller extent. The consistency of the pressure-temperature data obtained by the two methods gave additional support for the validity of the temperature-solution method. Shown in Fig. 1 are 00ℓ x-ray diffraction patterns obtained with CuKα radiation on stage 4 highly oriented pyrolytic graphite (HOPG) samples prepared by (a) the temperature method (two-bulb), (b) the temperature method (one-bulb), (c) the solution method, and (d) the temperature-solution method. These diffraction patterns show that all four methods yield well-staged compounds.

EQUILIBRIUM DIAGRAM

Figure 2 shows the equilibrium diagram, which is a map of the pressure-temperature combinations that yield a given eventual stage. The pressure refers to the bromine vapor pressure; the temperature refers to the sample temperature. The vapor pressure P_{sol} above the Br_2-CCl_4 solution is related to the vapor pressure P_{Br2} of pure bromine and the mole fraction X of Br_2 in the solution by the relation [14]

$$\ln\left(\frac{P_{sol}}{P_{Br_2}\,X}\right) = 1.197\,(1-X)^2 - 0.493\,(1-X)^3, \qquad (1)$$

where P_{Br2} is pressure in mm Hg. The validity of Eq. (1) is confirmed by the consistency between data points obtained by the temperature-solution method and those obtained by the two-bulb temperature method. The vapor pressure P_{Br_2} of pure bromine is given by [15]

$$\log_{10} P_{Br_2} = \begin{cases} 5.82 - \dfrac{638.25}{T+158.006} & -48°C<T<58.2°C \\ 7.583 - \dfrac{1562.26}{T+273.78} & 70°C<T<110°C \end{cases} \qquad (2)$$

where T is temperature in °C .

The intercalation reaction between bromine and pure graphite for a final stage of n can be written as

$$7n\ C(s) + Br_2\ (g) = C_{7n}\ Br_2\ (s)\ . \qquad (3)$$

The transformation from stage n+1 to stage n can be written as

$$n\ C_{7(n+1)}\ Br_2\ (s) + Br_2\ (g) = (n+1)\ C_{7n}\ Br_2 \qquad (4)$$

In Eq. (3) and (4), the in-plane stoichiometry is such that stage 2 is C_7Br (or $C_{14}Br_2$), as indicated by the recently determined in-plane structure of stage 2 [16]. For either reaction (Eq.(3) or (4)), the equilibrium bromine vapor pressure P (in atmospheres) is related to the change in free energy of the reaction by the relation

$$\ln P = \Delta H°/RT \ - \ \Delta S°/R, \qquad (5)$$

where ΔH° is the standard heat of reaction and ΔS° is the standard entropy of reaction. Hence, the slope of the straight line separating regions of different final stages in the ln P vs. 1/T diagram gives ΔH° for the change from one stage to the next, whereas the intercept gives ΔS°. Such boundaries between stages 4 and 5, 3 and 4, and 2 and 3 are shown in Fig. 2, which was obtained by allowing intercalation to occur under conditions represented by a number of pressure-temperature combinations and then determining the final stage for each combination by x-ray diffraction. The values of ΔH° and ΔS° for the change of one stage to the next lower one are listed in Table 2. It may be pointed out that these values are independent of the actual in-plane stoichiometry used in writing Eq. (4).

The values of ΔH° and ΔS° for the change from stage 3 to stage 2 are in close agreement with those reported by Sasa [10]. 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 on graphite-alkali metals [5].

Salzano and Aronson [17] 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

$$\Delta H° = -aH + M + I\left(\frac{n_1}{n_2} - \frac{n_2}{n_1}\right), \qquad (6)$$

where a indicates the in-plane stoichiometry (a=7 for $C_{7n}Br_2$), H is the interlayer bonding energy between two adjacent carbon 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 interaction 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 [1], we have calculated the standard heats and entropies of formation of various stages from pure graphite (i.e., Eq. (3)), as listed in Table 3. The standard heat of formation $\Delta H_f°$ of stage 4 was approximated by plotting the experimental values of ΔH° versus $[(n_1/n_2) - (n_2/n_1)]$, thereby obtaining $-aH + M$ as the intercept and I as the slope, and then taking $\Delta H_f°$ as $-aH + M + \frac{I}{n}$, where n = 4. The standard entropy of formation $\Delta S_f°$ of stage 4 was taken as equal to the value of ΔS° for the change of stage 5 to stage 4. The values of $\Delta H_f°$ and ΔS° 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 ΔS° from stage to stage. This stage independence of ΔS° was also observed in alkali metal compounds [5]. While the ΔS° value of ∿30 cal mol^{-1} Br_2 K^{-1} seems large compared to

TABLE 2
Heats and Entropies of Changes of Stage

Change of Stage	Equilibrium Reaction	ΔH° (kcal mol^{-1} Br$_2$)	ΔS° (cal mol^{-1} Br$_2$ K^{-1})
3→2	$2C_{21}Br_2(s) + Br_2(g) \rightarrow 3C_{14}Br_2(s)$	-10.0 ± 0.5	-29.9 ± 0.5
4→3	$3C_{28}Br_2(s) + Br_2(g) \rightarrow 4C_{21}Br_2(s)$	-10.8 ± 0.2	-30.8 ± 0.3
5→4	$4C_{35}Br_2(s) + Br_2(g) \rightarrow 5C_{28}Br_2(s)$	-11.0 ± 0.2	-30.6 ± 0.3

the value of ∼−20 cal mol^{-1} M K^{-1} observed in alkali metals (M); in both cases the entropy change is approximately that for the condensation of the vapor phase to the solid phase.

To the extent that an electrostatic model is suitable for bromine, it is interesting to compare the enthalpies obtained in bromine with those observed in the alkali metals. ΔH_f° in bromine are about a third less than those observed in the alkali metals, suggesting that there is much less electrostatic interaction in graphite-bromine.

CONCLUSION

The thermochemical data for the intercalation of bromine in HOPG have been determined. The standard heats and entropies of reaction reported are expected to be of use to graphite-bromine concentration cells [18].

TABLE 3
Heats and Entropies of Formation

Stage	Reaction	ΔH_f° (kcal mol^{-1} Br$_2$)	ΔS_f° (cal mol^{-1} Br$_2$ K^{-1})
2	$14C(s) + Br_2(g) \rightarrow C_{14}Br_2(s)$	-10.9	-30.4
3	$21C(s) + Br_2(g) \rightarrow C_{21}Br_2(s)$	-11.3	-30.6
4	$28C(s) + Br_2(g) \rightarrow C_{28}Br_2(s)$	-11.5	-30.6

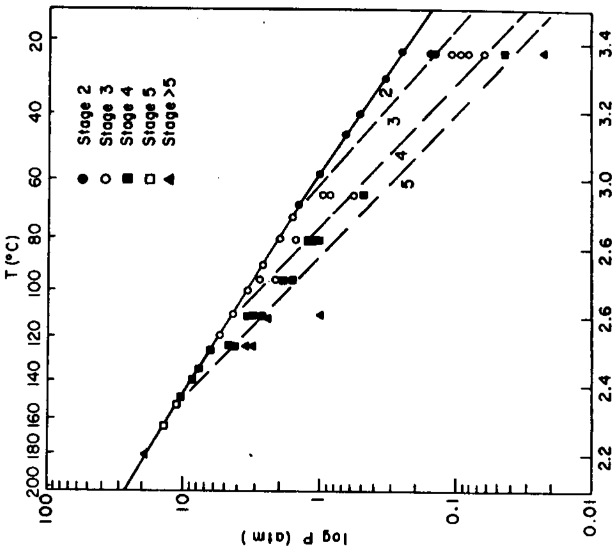

Fig. 2. Equilibrium diagram of bromine vapor pressure P vs. 1/T.

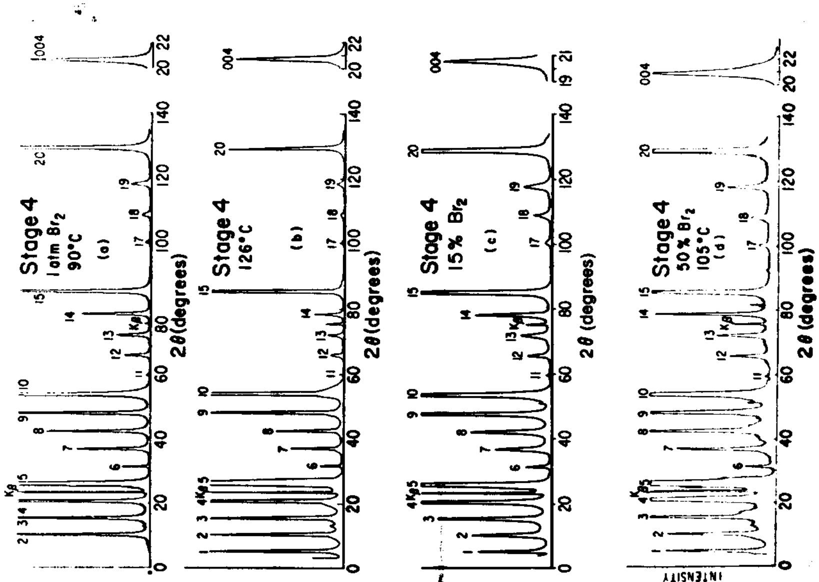

Fig. 1. 00ℓ x-ray diffraction patterns of stage 4 prepared by (a) two-bulb temperature method, (b) one-bulb temperature method, (c) solution method, and (d) [illegible]