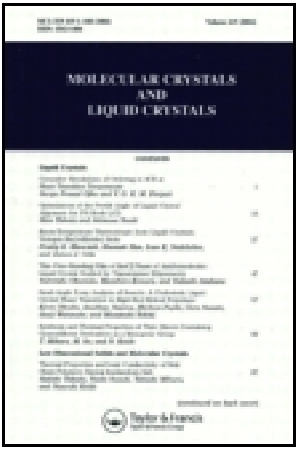

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Thermodynamic Model of Thermoexfoliation

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The equations that describe partial thermodynamic functions for graphite intercalation compounds (GIC) have been obtained. The derived equations determine the difference of chemical potentials between the intercalant in GIC layers and pure liquid intercalant in the first and the second order of approximation. The notion of T^* temperature have been formulated, that determines the boundary of thermal stability of GIC. The formulated physical model of thermoexfoliation process of GIC is in agreement with experimental data.

Keywords: thermodynamic theory; graphite intercalation compounds (GIC); thermoexfoliated graphite (TEG); saturating vapor pressure; chemical potentials of intercalant in different states

INTRODUCTION

Thermoexfoliated graphite is the material produced by quick heating of GIC and characterized by anomalous low density (nearly by two orders less than graphite density). It finds wide application in various field of modern engineering. The physical causes of thermoexfoliation process which is accompanied with intensive escape of intercalant from the graphite has not been fully investigated by now. The possibility and conditions of GIC existence have been considered in terms of thermodynamics insufficiently [1-3]. The aim of this work was to develop thermodynamic theory of stable and metastable state in GIC and to determine the conditions of appearance of thermoexfoliation process under non-equilibrium state of intercalant in GIC in terms of this theory. We shall consider two problems. First, we shall dwell upon stable and metastable states. First, we shall dwell upon stable and metastable states of intercalant in GIC. Second, we shall consider the causes of thermoexfoliation.

RESULTS AND DISCUSSION

In the thermodynamic theory of GIC existence the concentration C_2 of intercalant in GIC or gaseous phase is determined by equation

$$C_2 = n_2/(n_1 + n_2), \tag{1}$$

where n_1 is the number of moles of graphite, n_2 is the number of moles of intercalant. The peculiarity of GIC is the discrete character of variation of C_2 concentration in graphite, i.e. $C_2 = f(s)$, where s is a stage number. We denote chemical potentials of intercalant in GIC, pure liquid state and gaseous state with μ^1, μ^2, μ^3 respectively (here and further on the upper index indicates the state). Similarly we introduce the terms of heat content $H^1(T,C_2)$, $H^2(T,C_2=1)$, $H^3(T,C_2')$ and entropy $S^1(T,C_2)$, $S^2(T,C_2=1)$, $S^3(T,C_2')$, where C_2' is the concentration of intercalant in gaseous state $(C_2 \neq C_2')$. It is obvious, that $H^1(T,C_2)$, $S^1(T,C_2)$, $H^3(T,C_2')$ and $S^3(T,C_2')$ are partial molar quantities. Then we introduce the notion of standard state under condition that at T=0 the atoms (molecules) of intercalant are infinitely removed from one another (gas) and the heat content $H^3(0) = 0$. On account of above said we shall write

$$\mu^1(T,C_2) = H^1(0,C_2) + H^1(T,C) - TS^1(T,C_2); \tag{2}$$

$$\mu^2(T,C_2=1) = H^2(0,C_2=1) + H^2(T,C_2=1) - TS^2(T,C_2=1); \tag{3}$$

$$\mu^3(T,C_2') = H^3(T,C_2') - TS^3(T,C_2'). \tag{4}$$

Now we shall derive the equations to define T* temperature above which the intercalant in GIC is in metastable state in two approximations:

1. when $\Delta H^{3\text{-}1} = H^3 - H^1$ and $\Delta H^{3\text{-}2} = H^3 - H^2$ in a certain vicinity of T* are assumed constant;
2. in general case when $\Delta H^{3\text{-}1} = \Delta H^{3\text{-}1}(T,C_2)$ and $\Delta H^{3\text{-}2} = \Delta H^{3\text{-}2}(T,C_2)$.

Let's consider the first approximation of the theory [1].

$$\Delta\mu^{1-2} = \mu^1(T,C_2) - \mu^2(T,C_2=1) = RT\ln\frac{P^1(T,C_2)}{P^2(T,C_2=1)}, \tag{5}$$

where $P^1(T,C_2)$ is the pressure of saturating vapors of intercalant in GIC at the concentration C_2 of intercalant; $P^2(T,C_2=1)$ is the pressure of intercalant saturating vapors on pure liquid (or solid) intercalant. At ΔH^{3-1}, ΔH^{3-2}=const, $P^1(T,C_2)$ and $P^2(T,C_2=1)$ are usually expressed as follows

$$\lg P^1(T,C_2) = \frac{\Delta S_0^{3-1}(C_2)}{2.3R} - \frac{\Delta H^{3-1}}{2.3RT};\ \lg P^2(T) = \frac{\Delta S_0^{3-2}}{2.3R} - \frac{\Delta H^{3-2}}{2.3RT}, \tag{6}$$

where $\Delta S_0^{3-1}(C_2)$ and ΔS_0^{3-2} are the entropies of intercalant transition from gas into GIC and into pure intercalant in standard state, respectively, i.e. at $P^2(C_2=1) = P^1(C_2) = 1$ atm. Substituting (6) into (5) we receive

$$\Delta\mu^{1-2}(T,C_2) = T\cdot\left[\Delta S_0^{3-1}(C_2) - \Delta S_0^{3-2}\right] - \left[\Delta H^{3-1}(C_2) - \Delta H^{3-2}\right] \tag{7}$$

From (7) we obtain under condition $\Delta\mu^{1-2}(T^*,C_2)=0$

$$T^* = \left[\Delta H^{3-1} - \Delta H^{3-2}\right]\cdot\left[\Delta S_0^{3-1} - \Delta S_0^{3-2}\right]^{-1} \tag{8}$$

Equation (8) is convenient because in a number of works (for example in [3]) the quantities ΔH^{3-1}, ΔH^{3-2}, ΔS_0^{3-1}, ΔS_0^{3-2} were found experimentally. Thus, we have obtained, that at $T<T^*$ intercalant in GIC is in stable state and at $T>T^*$ it is in metastable (non-equilibrium) state.

Now we derive a formula for T^* in general case, i.e. keeping in mind that ΔH^{3-1}, ΔH^{3-2} depend on temperature. From (2) and (3) it follows:

$$\begin{aligned}\Delta\mu^{1-2}(T,C_2) = T\cdot\left[S^2(T,C_2=1) - S^1(T,C_2)\right] - \\ -\left[H^2(0,C_2=1) + H^2(T,C_2=1) - H^1(0,C_2) - H^1(T,C_2)\right]\end{aligned} \tag{9}$$

Let's perform the necessary transformations in (9)

$$H^2(0,C_2=1) + H^2(T,C_2=1) - H^1(0,C_2) - H^1(T,C_2) = \Delta H^{2-1}(T,C_2) \tag{10}$$

Since $\Delta H^{2-1}(T,C_2)$ is difficult to determine experimentally it is useful to write $\Delta H^{2-1}(T,C_2)$ in the form

$$\Delta H^{2-1}(T,C_2) = \Delta H^{3-1}(T,C_2) - \Delta H^{3-2}(T) \qquad (11)$$

The values of ΔH^{3-1} and ΔH^{3-2} may be determined from the temperature dependencies of pressure of intercalant saturating vapor in GIC of stage $s(C_2)$ and on pure intercalant. The results of these measurements are presented in [2-6]. Therefore (9) can be written for convenience in the form

$$\Delta\mu^{1-2}(T,C_2) = T\cdot\left[S^2(T,C_2=1) - S^1(T,C_2)\right] - \left[\Delta H^{3-1}(T,C_2) - \Delta H^{3-2}(T)\right] \qquad (12)$$

The result of comparison (12) and (7) in the temperature range close to T* is

$$S^2(T,C_2=1) - S^1(T,C_2) = \Delta S^{3-1}(C_2) - \Delta S^{3-2} > 0 \qquad (13)$$

since usually $\Delta S_0^{3-1}(C_2) > \Delta S_0^{3-2}$ [3]. Consequently, the partial entropy decreases during intercalant transition from pure state into GIC of any stage. From (12) we obtain under condition that $\Delta\mu^{1-2}(T^*,C_2) = 0$

$$T^* = \left[\Delta H^{3-1}(T,C_2) - \Delta H^{3-2}(T)\right]\cdot\left[S^2(T) - S^1(T,C_2)\right]^{-1} \qquad (14)$$

Now we shall define $H^1(0,C_2)$ and $H^2(0,C_2=1)$. Taking into account the relations $H^1(0,C_2) < 0$, $H^2(0,C_2=1) < 0$ and our definitions $\Delta H^{3-1}(T,C_2) > 0$, $\Delta H^{3-2}(T) > 0$ we obtain at $T \to 0$

$$H^1(0,C_2) = -\lim_{T\to 0} \Delta H^{3-1}(T,C_2);\; H^2(0,C_2=1) = -\lim_{T\to 0} H^{3-2}(T) \qquad (15)$$

We shall analyze the agreement of the results predicted by theory and the experimental data keeping in mind that at T=T* the chemical potentials of intercalant in all three states are equal

$$\mu^1(T,C_2) = \mu^2(T,C_2=1) = \mu^3(T,C_2') \qquad (16)$$

The available detailed experimental data for Rb [5] make it possible to verify the validity of (16). Substituting tabular data into (2) - (4) at T=T* and taking into account (13) and (15) we obtain (in kJ/mole): $\mu^1(T^*, C_2) = -255.8$; $\mu^2(T^*) = -258.0$; $\mu^3(T^*) = -255.4$, which shows that (16) holds with high accuracy. The quantities for C_nRb and C_nCs system determined in [3] are used to calculate T* with formula (8). The analysis of these data shows that only for GIC C_8Rb (stage 1) $T^*=1670$ K < $T_{cr}=2100$ K. For all other donors systems [3] $T^*>T_{cr}$ and the thermoexfoliation process must not occur. C_nSbCl_5 system was discussed and studied in detail in [6] as well as by authors of this paper. The calculation on (8) for $C_{24}SbCl_5$ (stage 2) gives $T^*=630$ K ($T_{cr}=700$ K). Fig. 1 presents as the example $\Delta\mu^{1-2}(T, C_2)$ dependencies calculated with Eq. (7) The calculation with more precise formula (12) must not

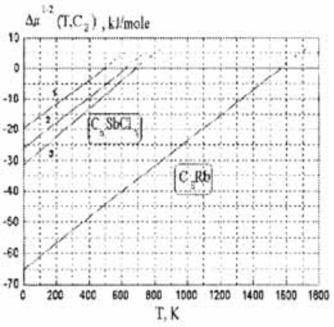

FIGURE 1. $\Delta\mu^{1-2}(T, C_2)$ dependences for C_nSbCl_5 systems (1,2,3 are stage numbers) and C_8Rb system of stage 1.

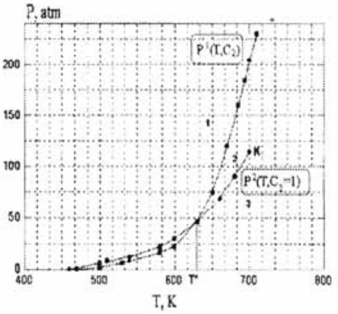

FIGURE 2. $P^1(T, C_2)$ and $P^2(T, C_2 = 1)$ dependences for $C_{24}SbCl_5$ system. **K** is the critical point (T_{cr}, P_{cr}); T* is the temperature at which $P^1(T, C_2)$ and $P^2(T, C_2 = 1)$ curves cross.

yield linear dependence of $\Delta\mu^{1-2}$ on T. However the analysis of (7), (8), (12) - (14) allows us to make a conclusion that at T=0 and T=T* the results of calculations made with (7) and (12) will practically coincide and the calculation with more precise formula (12) in the temperature range 0<T<T* will yield a deviation from the linear dependence. Fig. 2 presents $P^1(T, C_2)$ and $P^2(T, C_2 = 1)$ dependences for $C_{24}SbCl_5$ system. For this system we performed thorough experimental investigations in ther-

moexfoliation process when the heating temperature of GIC powder (d=400 μm) was increase from 2 K/sec to 400 K/sec; the beginning of thermoexfoliation process was found to be around 630 K which is in good agreement with theory. The analysis of reported in [7, 8] and our experimental data allowed us to estimate T* for the following GIC systems:

1. $C_{12}FeCl_3$ (stage-2) - $T^* \approx 600$ K;
2. C-ICl (stage-2) - $T^* \approx 350$ K;
3. C-H_2SO_4 (stage-2) - $T^* \approx 500$ K.

Let's formulate the main ideas of the physical model of GIC thermoexfoliation.

1. Thermoexfoliation process may occur in GIC systems for which $T^* < T_{cr}$ (T_{cr} is the critical temperature of pure intercalant). This condition does not hold for all GICs.
2. The condition of existence of T* is $P^1(T^*, C_2) = P^2(T^*, C_2' = 1)$ at the temperatures $T^* < T_{cr}$. In this case $\Delta\mu^{1-2}(T^*, C_2) = 0$ and in the temperature region from T* to T_{cr} the intercalant in GIC is thermodynamically unstable in comparison with pure intercalant.
3. GIC heating at $P < P^1(T, C_2)$ results in sublimation (or evaporation) of intercalant from GIC which takes place at $T < T^*$ and $T > T_{cr}$ from the sample's surface. In this case the process of thermoexfoliation does not occur.
4. The analysis of experimental data shows that the partials molar volume of intercalant in GIC is considerably smaller than the molar volume of pure intercalant. Since the transition from the condensed state "1" (intercalant in GIC layers) into the condensed state "2" (pure liquid intercalant) does not occur only on the surface but throughout the whole intercalant layer. Intercalate escapes from the space between graphite layers and the distance between the layers and consequently the volume of individual crystallites reduce to the volume of pure graphite. The intercalant accumulated in the cracks and cavities that have been formed and under conditions of fast heating transforms into gaseous state abruptly causing the exfoliation of graphite. The performed researches allow us to make the following conclusions.

CONCLUSIONS

1. **The equations for the definition of T* in the first and second order of an approximation are obtained.**
2. **The model of GIC thermoexfoliation process consistent with experimental data is developed.**

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