p–T–x–y Phase Diagram of the C_{60}–F_2–K System

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Abstract—Heterogeneous transformations in the C_{60}–F_2 system are for the first time analyzed in terms of phase equilibria. Consistent topological models are developed for the heterogeneous equilibria in the binary systems C_{60}–F_2 and C_{60}–K and in the ternary system C_{60}–F_2–K. The reliability of the proposed model phase diagrams is assessed thermodynamically.

INTRODUCTION

Among exohedral adducts of buckminsterfullerene, its fluorides are of particular interest. Fluorofullerenes can readily be prepared by exposing C_{60} to a number of fluorination agents [1–5]. They are stable in air [6–8] and at relatively high temperatures [9, 10] and are, therefore, convenient model systems for studying the structure and properties of compounds in the family in question. Moreover, C_{60} fluoroadducts offer unusual reactivity with oxidizers and nucleophilic reagents [11, 12], which makes them attractive precursors for the chemistry of fullerenes. In this context, a challenging problem is to devise techniques for preparing individual fluorinated derivatives of C_{60} since such an approach may ensure the preparation of products with controlled structure and properties.

Since molecules with a large number of π-bonds have a specific structure, fullerenes are potentially capable of forming a wide variety of adducts differing both in composition and in the arrangement of fluorine atoms. Indeed, the entire range of C_{60}F_n (n = 1–60) fluorides could be obtained in the gas phase over the C_{60}–ClF_3 system [10]. At the same time, in spite of the considerable experimental effort in this direction, only three groups of products based on fluoroadducts (C_{60}F_{18±2}, C_{60}F_{36±2}, and C_{60}F_{48±4}) [1–5, 13–15] and the group of C_{60}F_{2–8} compounds [16] have been prepared to date in the crystalline state and in macroscopic amounts. C_{60}F_{2n≤36} fluorofullerenes are commonly synthesized by reacting fullerenes with higher fluorides of some metals [1, 2, 13, 17, 18]. Highly fluorinated fullerenes (C_{60}F_{48±4}) are usually prepared by exposing C_{60} to fluorine gas [3, 5]. Individual components of fluorofullerene mixtures close in C:F ratio can only be separated by the technique described by Lukonin et al. [13]. Using sublimation, one can separate only the above groups of fluoroadducts [4, 13, 14].

Clearly, knowledge of the C_{60}–F_2 and C_{60}–F_2–metal phase diagrams may be helpful in optimizing the search for conditions under which individual C_{60} fluorides could be prepared separately. However, no systematic studies devoted to heterogeneous equilibria involving fluorofullerenes have been reported to date. It might well be that detailed experimental data on the phase equilibria in the C_{60}–F_2 system are extremely difficult to obtain because of the high activation barrier to equilibration in this system.

In this work, we analyze and systematize a large body of experimental data on the chemical and physicochemical properties of C_{60}, its fluorides, and fullerenes. The results are presented in the form of a model for the p–T–x–y phase diagram of a C_{60}–F_2–M system.

The p–T–x–y model for the heterogeneous equilibria in this ternary system was developed using topological transformation of the p–T–x phase diagrams of the constituent binary systems by the method of pseudobinary joins [19] in line with the Schreinemakers rules [20, 21] and based on Kurnakov’s continuity and one-to-one correspondence principles [22]. The total phase diagrams of the C_{60}–F_2 and C_{60}–K systems were inferred from incomplete experimental data [1–5, 10, 13–18, 23–25] using the basic concepts of geometric thermodynamics [19–21, 26, 27].

p–T–x PHASE DIAGRAMS

A question of major importance in analyzing phase equilibria in fullerene-containing systems is whether C_{60} can be treated as an individual component of the system.

To ascertain whether or not a substance is a component of a thermodynamic system, parameters of three phases in equilibrium have to be known [22].

As for buckminsterfullerene, there is currently no way to draw a unique conclusion because data on equilibrium states in broad temperature and pressure ranges
are missing. Analysis of the reported analytical models for the C$_{60}$ phase diagram demonstrates that the use of different model approximations, taking into account different contributions to intermolecular interactions in the system [28–35], leads to contradictory results regarding the stability of liquid C$_{60}$ and the existence of its ternary invariant. In our view, the most reliable modeling results have been reported in the recent work by Ferreira et al. [28], who used an intermolecular potential [36] ensuring an adequate description of the relationship between parameters of state at high pressures. Their model assumes the existence of a stable liquid C$_{60}$ phase in a narrow temperature range and allows the invariant parameters of the system to be evaluated: $T_t = 1881.2 \pm 0.1$ K, $\rho_t = 0.8447 \pm 0.0003$ nm$^{-3}$, $T_c = 2011.7 \pm 1.1$ K, and $\rho_c = 0.4676 \pm 0.0007$ nm$^{-3}$ (where subscripts “t” and “c” refer to the triple and critical points, respectively). In our opinion, this model for the equilibrium phase diagram of C$_{60}$ justifies the assumption that C$_{60}$ can be used as an individual component of thermodynamic systems.

In the topological models described below, the polymeric transformations of C$_{60}$ and its derivatives are left out of consideration because these transformations occur at rather low temperatures and have no significant effect on the phase relations of practical interest.

In describing phase equilibria, we use standard designations: $S_L$ represents a crystalline phase based on substance A, and L and V designate liquid and vapor phases, respectively. In figures, the surfaces and sections of crystalline phase regions are hatched. The melt compositions in SLV equilibria are shown by solid lines; the melt compositions in SSL equilibria are not shown in $T_x$ projections in order not to clutter the figure. The vapor compositions in SLV and SSL equilibria are represented by dashed lines.

Each topological model for heterogeneous equilibria with the participation of fullerenes is represented by a $p-T-x$ phase diagram, which provides an unambiguous description of all the phase states in the system and its $T-x$ and $p-T$ projections. If data cannot be conveniently presented using a single scale on account of a large spread in the parameters of equilibria, we use nonlinear, discontinuous temperature and pressure axes. To avoid severe distortions of graphic representation, the low-temperature region of the ternary invariant for F$_2$ is not shown in the $p-T-x$ phase diagrams of F-containing systems.

**System C$_{60}$–F$_2$.** As mentioned above, no systematic studies of phase equilibria in this system have been reported to date. The physicochemical properties of C$_{60}$ and its fluorides have been studied in only a small $p-T-x$ region. The available information often refers to nonequilibrium processes and can be interpreted in different ways. In connection with this, by analyzing the entire set of experimental data we initially developed several, equally probable models of the $p-T-x$ phase diagram. The plausibility of each model was assessed according to the principles of geometric thermodynamics: the invariant equilibria in the constituent binary systems must be compatible in the $p-T-x-y$ space (below, this issue will be discussed in greater detail). A consistent topological model for phase equilibria in the C$_{60}$–F$_2$ system is displayed in Fig. 1.

In constructing the $p-T-x$ phase diagram, we proceeded from the fact that the system contains only three crystalline intermediate phases, those based on C$_{60}$F$_{18}$, C$_{60}$F$_{36}$, and C$_{60}$F$_{48}$, with limited mutual solubility. This assumption can be substantiated as follows: The existence of only three crystalline phases (only these compounds have been obtained to date in macroscopic amounts and have been shown by x-ray diffraction to have distinct crystal structures [37, 38]) cannot be accounted for in terms of the relative thermodynamic stability of the fluorides in question since the C–F bond energy depends very little on the C : F ratio in fluorofullerene molecules [4, 10, 39]. Chilingarov et al. [40] interpreted the predominant formation of these adducts in terms of the kinetic competition between fluorination and desorption processes. It remains, however, unclear why the rate ratio $v_{\text{desorption}}/v_{\text{fluorination}}$ for the compounds with F : C$_{60}$ = 18, 36, and 48 is much larger than that for other, similar fluorides under the same conditions.

In our opinion, a simple and reasonable explanation for this selectivity is offered by the model proposed in this work, which is supported by the fact that, according to earlier results [15], C$_{60}$ cannot be in equilibrium with its highly fluorinated derivatives. In this approach, intermediate products are regarded as phases of variable composition. This is suggested primarily by the results reported in [14], which prove the formation of solid solutions between higher fluorofullerenes close in C : F ratio. To extrapolate these results to lower fluorine contents, we analyzed a large body of experimental data, according to which (1) all the main products of C$_{60}$ fluorination (C$_{60}$F$_{18}$, C$_{60}$F$_{36}$, and C$_{60}$F$_{48}$) contain an amount of impurities close in composition to the major phase [1–5, 13–15, 18], (2) such “mixtures” cannot be separated into individual components by sublimation [4, 5, 13, 14], and (3) the components of such polycrystalline mixtures have reduced activities [13].

Characteristically, the “nonstoichiometry index” depends directly on the composition region of our model phase diagram. For example, mass spectrometric analysis of the gaseous products of the reaction between C$_{60}$ and Pb$_2$F$_6$ [18] indicated the presence of a significant amount of C$_{60}$F$_{34}$, along with the main products C$_{60}$F$_{18}$ and C$_{60}$F$_{36}$, whereas C$_{60}$F$_{38}$ was not detected in the gas phase. According to our model, this can be accounted for by deviations from the C$_{60}$F$_{36}$ stoichiometry to a higher fullerene content via the formation of a solid solution of C$_{60}$F$_{18}$ in C$_{60}$F$_{36}$.