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Ternary graphite intercalation compounds (t-GIC's) have been the focus of considerable recent attention because they exhibit novel structural forms such as heterostructure stacking arrangements (e.g. for KC_8C_{16}). In addition, t-GIC's open up to investigation physical phenomena which cannot be conveniently explored with the more conventional binary GIC's such as MC_8 , $\text{M} = \text{K}, \text{Rb}, \text{Cs}$. For instance, the $\text{K}(\text{NH}_4)_x\text{C}_{24}$ system has been used extensively to study the free energy of staging in GIC's.

The synthesis and preparation t-GIC's is, like other ternary systems, complicated by the wide variety of pure and mixed phases which can be formed. Chemical physicists have long recognized the advantages of employing a triangular Gibbs phase diagram to describe ternary liquid systems. Recently, the Gibbs phase diagram approach has also been applied to ternary Chevrel compounds. The purpose of this brief note is to present and highlight the key features of the Gibbs triangle for $\text{K-NH}_3\text{-C}$, especially those features which are associated with staging phase transitions which GIC's are known to exhibit.

The full Gibbs triangle for K-NH₃-C is shown in Figure 1 and consists of several distinct regions, some of which are internally connected by tie lines (dashed lines + two-phase region) and some of which are empty triangles (three-phase regions). The straight lines from the NH₃ apex to the C-K axis are lines of constant composition KC_x. Also, horizontal lines (not shown) which were parallel to the C-K axis would be lines of constant NH₃ composition.

To illustrate the use of the K-NH₃-C Gibbs triangle consider what will occur if a binary KC₈ GIC is exposed to an increasing pressure of NH₃ gas. Such an exposure is equivalent to a trajectory along the line marked KC₈ and moving from the C-K base to the NH₃ apex. On exposure to low pressure NH₃ vapor the t-GIC composition would lie in the three-phase region labelled B in Figure 1. Thus, three materials corresponding to the corners of the B triangle would coexist, namely, KC₈,

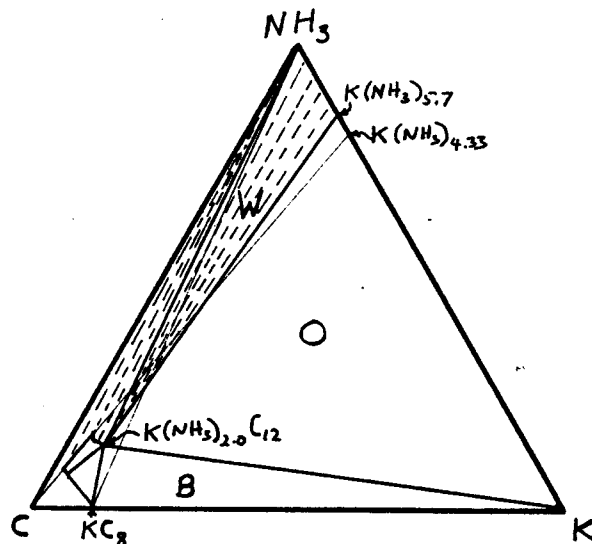


Figure 1. The Gibbs triangle for the K-NH₃-C system. Heavy solid lines represent phase boundaries. Light solid lines are constant composition paths. Light dashed lines are phase boundaries. The lettered regions are referred to in the text.

$\text{K}(\text{NH}_3)_2\text{C}_{12}$, and pure K. The relative proportions of the three phases would still yield a collective composition of $\text{K}(\text{NH}_3)_x\text{C}_{24}$ where x is determined by the pressure of the ammonia vapor.

As one increases ammonia pressure still farther, the total composition travels up the KC₂₄ line into the three-phase region labelled O and forms the t-GIC K(NH₃)_{3.2}C₁₂, pure potassium metal and a saturated gold¹⁰ K-NH₃ metal ammonia solution. As the ammonia pressure is increased even further, the system enters the two-phase composition region marked W in Figure 1. In this region, the two phases present are K(NH₃)_{3.2}C₁₂ and a metal ammonia solution K(NH₃)_y where $y < 5.7$. The relative amounts of the two phases are inversely proportional to their measured distances

from the intersection of the KC_{12} line with the dashed tie line of which they are the extremal points.

Notice that when ammonia is added to KC_8 , a new stage 1 $K(NH_3)_{2.0}C_{12}$ phase is immediately formed and persists for all ammonia pressures greater than some small minimum value. In contrast, dramatically different and much more interesting behavior is exhibited by stage-2 KC_{24} when it is ammoniated.⁵ To illustrate this, we refer to Figure 2 which shows an enlargement in the vicinity of the C apex of Figure 1.

The addition of NH_3 to KC_{24} corresponds to a trajectory along the KC_{24} line in Figure 2.

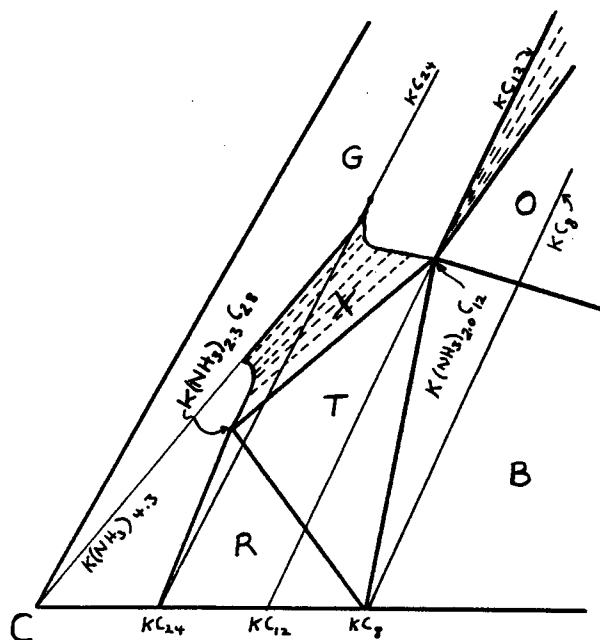


Figure 2. An enlargement of the region near the C apex of Figure 1. See also caption under Figure 1. Dots on KC_{24} line represent single phase region (see text).

Initial ammoniation at low pressure produces three distinct phases⁵ (R triangle) composed of KC_{24} , KC_8 , and $K(NH_3)_{2.3}C_{12}$. After crossing another three-phase region¹, the system enters a two-phase region, X, but now the two phases are stage-1 $K(NH_3)_{x_1}C_{y_1}$ and stage-2 $K(NH_3)_{x_2}C_{y_2}$. [The stages cited here have been determined from in situ x-ray measurements.⁵ The compositions have been established from x-ray intensity and weight uptake studies.] When the ammonia pressure exceeds ~6 atm., there is a staging phase transition⁵ and the system emerges into a pure stage-1 single phase

(between dots on KC_{24} line of Figure 2) with composition $K(NH_3)_xC_{24}$ where $4.1 < x < 4.33$ for 3 atm. $< P_{NH_3} < 9.5$ atm.²⁴ It is this single phase variable composition region which is of considerable scientific interest because the composition of binary GIC's cannot be conveniently⁸ varied over such a large range at constant stage.

Concluding Remarks

For t-GIC systems it would be an interminable project to accurately establish the complete Gibbs triangle since staging constitutes a relatively unwieldy complication. Thus, the diagrams of Figures 1 and 2 are approximations except in the X, T, and R regions. Moreover, certain rules, e.g. Schrienmakers rule, govern the intersections of two-phase boundaries with a three-phase internal triangle. Because we do not know the exact shape of most of the phase boundaries in Figures 1 and 2 we have represented them as straight lines even though doing so may locally violate the above mentioned rules.

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