How well do we know the Diamond–Graphite Equilibrium?

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The transition from diamond to graphite is one of the key equilibria for interpreting mineral assemblages in ultrahigh pressure metamorphic rocks.   Despite widespread interest in the transition and numerous studies, there remain significant systematic differences between experimental determinations and thermodynamic calculations of the transition. Several thermodynamic treatments suggest a steeper P-T slope than the experiments. A "best" calculated Dmd – Gr transition has a slope similar to the experiments of Kennedy and Kennedy (1976), but is systematically lower than the determined transition by about 2 kbar.

Published determinations of the equilibrium lie in the temperature interval 1400 K – 2300 K. Most workers rely heavily on the results of Kennedy and Kennedy (1976) who provided a linear equation that has been used to estimate the transition pressure at lower and higher temperatures.   Numerous workers have made thermodynamic calculations of the equilibrium with variable results. At temperatures similar to those of the experiments, most thermodynamic data yield equilibrium pressures lower than the experiments by as much as 2 kbar. At lower temperatures, calculated pressures are systematically lower by as much as 5 kbar. Calculated pressures at 3000 K vary from more than 8 kbar above to almost 20 kbar below the position of the transition extrapolated from the experiments.   Possible sources of these discrepancies include: (1) systematic errors in the determination of the standard state enthalpy and entropy of diamond and graphite; (2) uncertainty in the character and thermodynamic properties of graphite; (3) inappropriate extrapolation of the experiments; (4) systematic errors in the experiments; (5) unreliable extrapolation of heat capacity determinations.

It is likely that several sources of uncertainty contribute to the observed discrepancies. At temperatures below about 1100 K, the thermodynamic properties of both Dmd and Gr are reasonably well known and the calculated pressure of the transition at 298 K is 16.1 $\pm$ 0.5 kbar. There remains the possibility that variation in the properties of graphite among various calorimetric and experimental studies may contribute to the observed discrepancies. The non-linearity of the calculated transition at low T and P suggest that linear extrapolation of the experiments to low T is inappropriate. Most experiments on the Dmd-Gr transition were conducted in a molten metal flux and graphite dissolves small amounts of those impurities. This suggests that the impurities may displace the determined transition to lower T and higher P. The large discrepancies at high temperature between the extrapolated experiments and the calculated equilibrium result from differences in the way that the heat capacity of diamond was extrapolated to high temperature.

A "best" calculated Dmd – Gr transition has a slope similar to the experiments of Kennedy and Kennedy, but is systematically lower than the determined transition by about 2 kbar. This result is sensitive to the way in which the heat capacities of diamond and graphite are extrapolated to high temperatures.

References

Kennedy, C.S. and Kennedy,G.C., 1976. The equilibrium boundary between graphite and diamond. Journal of Geophysical Research, 81, 2467-2470.