The Relative Thermodynamic Stability of Diamond and Graphite

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This work clarifies the question whether diamond or graphite is the most stable modification of carbon at ambient pressure in the temperature range from absolute zero to 400 K. The investigation of the transformation from graphite to diamond or vice versa has been subject of scientific research for a long time. Until now, contrary results were available especially regarding the stability at very low temperatures. We have ascertained and validated the Gibbs free energy of the thermodynamic cycle for the transformation of graphite to diamond based on entropies, heat capacities and enthalpies of reaction.

Two types of high-precision combustion calorimetry were performed in order to measure the standard molar enthalpies of combustion. Within the first method, the results were calculated based on the initially weighted mass of samples and within the second method, the calculations are based carbon dioxide capture. The heat capacities at constant pressure were determined with the thermal relaxation method of a Quantum Design Physical Property Measurement System (PMMS). Additionally, periodic-boundary DFT calculations based on Quantum ESPRESSO and the ABINIT code were used to calculate enthalpies, entropies, Gibbs energies and constant-volume heat capacities. Values for thermodynamic functions of graphite and diamond from the literature have been collected and evaluated.

The results from this work are in very good agreement with the literature and enable the assignment of more precise values in the region from absolute zero to 400 K. It was shown that at ambient pressure, graphite is more stable than diamond at all temperatures.

For details, see The Relative Thermodynamic Stability of Diamond and Graphite, M. A. White, S. Kahwaji, V. L. S. Freitas, R. Siewert, J. A. Weatherby, M. D. M. C. Ribeiro da Silva, S. P. Verevkin, E. R. Johnson and J. W. Zwanziger. Angew. Chemie Int. Ed. 60, 1546-1549 (2021). doi.org/10.1002/anie.202009897

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