Polish chemist explains stability of graphite – with unexpected outcome

Carbon, the element crucial to the development of organic life, exhibits a particular richness of its forms in the solid state, with graphite, **G**, and diamond, **D**, (and now also fullerenes, nanotubes and graphene) being the prototypical exemplifications of what is known as *allotropy* or *polymorphism* as taught to every elementary school pupil worldwide (Figure 1). Indeed, it was in 1772 that Lavoisier showed in an elegant (but quite expensive!) experiment that the only product of the diamond's combustion was carbon dioxide, thus proving that diamond is simply another form of carbon. A quarter century later, Tennant expanded that experiment; by demonstrating that burning **D** and **G** releases the same amount of gas he unequivocally established the chemical equivalence of these substances. It has been well known that these two prototypic forms of carbon have remarkably different properties – but which of them is more stable?

The received textbook dictum is that graphite is the thermodynamically favoured form of elemental carbon in the solid state, while diamond is metastable at ambient pressure and temperature conditions and may be formed only at elevated pressures exceeding 4.5 GPa. But it now turns out that the story is much more complex than that.

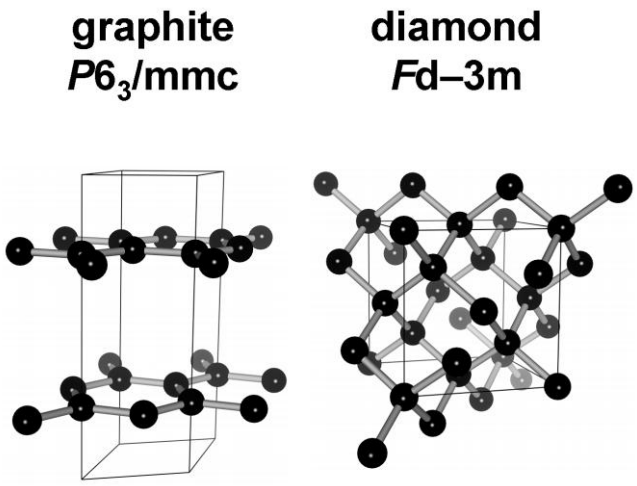

Fig. 1. Crystal structures of graphite and diamond.

In his short communication Prof. Wojciech Grochala from the University of Warsaw (Poland) described the most precise calculations carried up to date for the two polymorphic forms of carbon. Grochala has used very large "chunks" of solid (so called supercells) of up to 64 carbon atoms for his study and employed very precise but computer power–demanding hybrid density functional theory calculations. To the researcher's great surprise diamond has proved to be more stable than graphite as far as electronic contribution to the total energy is concerned (Figure 2). The preference for diamond is very small, some 1.1 kJ/mol, or 0.3% of the heat produced when one mol of coal is combusted in air.

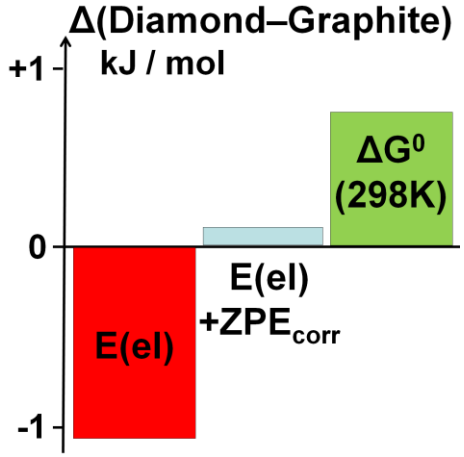

*Fig. 2. The components of relative stability of **D** versus **G**. The electronic energy term, E(el), favours **D**, while the vibrational and entropy corrections reverse the stability order.*

It turns out, however, that the small "electronic preference" for diamond over graphite is outweighed by the contributions from vibrations of solids' lattice (aka "phonons") as well as other terms influencing the thermodynamic parameters of both forms of carbon. As a result, graphite is indeed more stable than diamond at ambient pressure and temperature conditions. But the relative contributions to its stability are similar to what has recently been found for various polymorphs of elemental boron – an element neighbouring carbon in the Periodic Table.

According to Grochala, the "electronic preference" for diamond could be viewed as a spectacular manifestation of what is known as the Maximum Hardness Principle (by R. G. Pearson).

The article "*Diamond is the electronic ground state of carbon at temperatures approaching 0 K*" will be published in *Angewandte Chemie*. The calculations were carried out at the Interdisciplinary Center for Mathematical and Computational Modeling of the University of Warsaw (ICM) and took nearly one and a half year.