Ab initio Thermochemistry

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ABSTRACT

The Gibbs free energy G (p,T) can be obtained from quantum-chemical calculations based on Density-Functional Theory (DFT) by

$$G(p,T) = E(V) + F_{\text{ph}}(T,V) + pV + \left[F_{\text{el}}(T,V) - T \cdot S_{\text{conf}} \right]$$

Where E(V) is the ground state electronic energy at 0 K, F_{ph} is the temperature dependent phononic free energy due to lattice vibrations. If needed, the free energy caused by electronic excitations, F_{el}, and the configurational entropy S_{conf} can be taken into account.

Having obtained a reliable Gibbs function, one is able to calculate other thermochemical potentials as the entropy S, the enthalpy H and the heat capacity Cp by the well known relations: $S = -\left(\dfrac{\partial G}{\partial T} \right)_P$, $H = G + T \cdot S$ and $C_p = \left(\dfrac{\partial H}{\partial T} \right)_P$.

From those numerically calculated values one is able to obtain the parameters in the Gibbs energy equation $G = C_1 + C_2 T + C_3 T \ln T + C_4 T^2 + C_5 T^3 + \dfrac{C_6}{T}$ by a simple fitting procedure, which starts with Cp, then H and S and finally G. The theoretically obtained coefficients can be stored directly in the data base, when they are related to the elements.

If one wants to use the theoretical data in combination with experimental, the H-values must be related to the elements.

Some applications of the method to "real world" problems will be presented, e.g. formation free energies and transitions between different phases of compounds.