

# THE DETERMINATION OF THERMODYNAMIC POTENTIALS OF SUBSTANCES BY AB-INITIO CALCULATIONS

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The quantum-chemical calculations of the thermodynamic properties of substances are at present time quite useful for the studying of the chemical reactions.

In opposite to the conventional thermodynamic scale of energy there is a common zero level of energy for all substances for the ab-initio calculations. It is a such state of the system when all electrons and nuclei are separated from each other to the infinity. The energy equilibrium of the reaction takes into account the rebuilding of the external atomic and molecular orbitals of all molecules and atoms participating in the reaction. Besides the thermodynamic potentials it maintains the energy  $E$  of all electron-nuclear interactions. Taking into account the full energy, the enthalpy of the formation of any substance may be expressed as:

$$\Delta H_r = \Sigma(E+H)_{\text{fin}} + \Sigma(E+H)_{\text{init}} \quad (1)$$

The enthalpy of formation of some gaseous compound can be established in the usual conventional thermodynamical scale if the quantum-chemical calculations of the full energy  $(E+H)$  of all initial simple related substances forming this compound is possible. In this case anyone has  $\Delta H_f = \Delta H_r$ .

The study of the enthalpy of formation of some mercury complexes accomplished by J.Tossell [1] is a good illustration of this possibilities. In his study the difference between the experimental and calculated data is only 1÷10 kcal/mol. It must be mentioned that the value of the items in equation (1) is nearly  $10^5$  kcal/mol.

The great difficulties arise when some simple substances in the reaction are the crystal, for example C, W and others. The full energy of the crystal is the sum of its atomisation energy and the energy of atoms themselves. These calculations are not the routine procedure. But if one considers the reaction with known value of  $\Delta H_r$  and with the only one crystalline matter, its full energy can be determined by means of calculating the full energies of the other simple substances of the reaction:

$$(E+H)_{\text{cryst}} = \Sigma(E+H)_{\text{fin}} - \Sigma(E+H)_{\text{init-1}} - \Delta H_r$$

The crystal full energy obtained such way can be used for calculation of another reactions with participation of this crystalline substance. For example, one may consider the reaction  $C_{\text{graphite}} + O_2 = CO_2$  with known enthalpy  $\Delta H_r^{\circ}_{298.15} = -94.1$  kcal/mol [2]. In accordance to quantum-chemical calculation  $(E+H^{\circ}_{298.15})_{CO_2} = -117774$  kcal/mol,  $(E+H^{\circ}_{298.15})_{O_2} = -93904$  kcal/mol. Then the full energy of the crystalline graphite is  $(E+H^{\circ}_{298.15})_{\text{graphite}} = (-117774 + 93904 + 94)$  kcal/mol =  $-23776$  kcal/mol.

In this way the reactions of formation  $C_2$ ,  $C_3$ ,  $C_5$ , CO,  $CO_2$ ,  $C_2O$ , CH,  $CH_2$ ,  $CH_4$  and  $CH_3$  participating graphite were studied. Finally the mean value of the full energy of graphite was  $(E+H^{\circ}_{298.15})_{\text{graphite}} = -(23780 \pm 13)$  kcal/mol.

In a same manner the energy of a crystalline tungsten  $(E^*+H^{\circ}_{298.15})$  was calculated using the reaction  $W_{\text{cryst}} + 2O_2 + H_2 = H_2WO_4$ , the known value  $\Delta H_f^{\circ}_{298.15} = -216.707$  kcal/mol [3] and the effective core potential SBK [4] for tungsten. Ab initio calculation gives  $(E+H^{\circ}_{298.15})_{H_2} = -696$  kcal/mol,  $(E+H^{\circ}_{298.15})_{O_2} = -93904$  kcal/mol and  $(E^*+H^{\circ}_{298.15})_{H_2WO_4} = -230830$  kcal/mol. Consequently the SBK-energy of tungsten  $(E^*+H^{\circ}_{298.15})_W = -42109$  kcal/mol.

This result was applied for calculation of the unknown thermodynamic properties of gas  $WF_4$  described by the reaction  $W_{\text{cr}} + 2F_2 = WF_4$ . It was obtained for the free molecule  $WF_4$ :  $\Delta H_f^{\circ}_{298.15} = -317$  kcal/mol in the conventional thermodynamic scale. Consuming the value of entropy calculated for  $WF_4$  in this study ( $S^{\circ}_{298.15} = 83$  cal/mol·K) and published data for  $W_{\text{cryst}}$  (7.81 cal/mol·K [2]) and  $F_2$  (48.51 cal/mol·K [2]) we obtained for  $WF_4$ :  $\Delta S_f^{\circ}_{298.15} = 27$  cal/mol·K. Consequently the Gibbs free energy of formation of  $WF_4$  is  $\Delta G_f^{\circ}_{298.15} = -325$  kcal/mol.

Our calculations were made at the restricted Hartree-Fock level by means of quantum-chemical GAMESS computer programs. The equilibrium structures were calculated at base electron state. For tungsten we used SBK effective core potential. The atoms of oxygen, chlorine and hydrogen were calculated with the triple zeta valence basis sets with the adjusted polarization orbitals d-type at oxygen and chlorine and p-type at hydrogen.

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