QUANTUM-CHEMICAL CALCULATION OF SOME THERMODYNAMIC PROPERTIES OF GASEOUS AND HYDROTHERMAL SYSTEMS

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The ab-initio calculations of equilibrium geometry, vibrational frequencies, thermodynamic properties of unusual molecule Si_2O_2 (a product of impact process, as O.I.Jacovlev, GEOHI, has reported) also as calculation of full energy of crystalline silica and thermodynamic properties of aqua species HF, HCl, Cl^-, F^- and dissociation constants of HF and HCl acids were performed.

All calculations were done by the use of GAMESS programs [1, 2]. The restricted Hartry-Fock level and Møller-Plesset second order perturbation theory (except a full energy calculations of silica) were selected for our calculation. The basis DH+G** was used.

For the Si_2O_2 and SiO molecules the full energy of molecules including the Gibbs free energy $E^G{}_T = E_{form} + G^T$ was calculated at temperatures 298K and 2000K. These values allowed to obtain the Gibbs free energy $\Delta_r G^o{}_T$ for reaction **$2SiO = Si_2O_2$** and Gibbs free energy $\Delta_f G^o{}_{298}$ of formation Si_2O_2 in standard condition. We obtained (in kcal/mol):

for SiO $E^G{}_{298} = -228473.5$, $E^G{}_{298} = -228576.5$
for Si_2O_2 $E^G{}_{298} = -456946.2$, $E^G{}_{2000} = -457124.8$
Hence, $\boldsymbol{\Delta_r G^o{}_{298} = +0.8 kcal/mol;}$ $\boldsymbol{\Delta_r G^o{}_{2000} = +28.2 kcal/mol}$

The usage of Gibbs free energy of formation of SiO: $\Delta_f G^o{}_{298} = -30.45 \pm 2$ kcal/mol [3] allowed us to obtain the free energy of formation for previously unstudied Si_2O_2 molecule: $\boldsymbol{\Delta_f G^o{}_{298} = -60.9 \pm 4 + 0.8 = -60.1 \pm 4}$ ***kcal/mol.***

The usage of the value of $\Delta_f G^o{}_{298}(SiO)$ and of the full energy of O_2 molecule allowed us to calculate the full energy of crystalline silica at 298K following the equations **$Si_{cr} + (1/2) \cdot O_2 = SiO$** and $\Delta_r G^o{}_{298} = \Delta_f G^o{}_{298}(SiO)$: $\boldsymbol{E^G{}_{298}(Si_{cr})} = E^G(SiO) - (1/2) \cdot E^G(O_2) - \Delta_f G^o(SiO) = \boldsymbol{-181310.8}$ ***kcal/mol.***

Thermodynamic properties of aqueous species were obtained via combination of two methods [4]. At the first stage the studied molecule is inserted into a cluster of 20 water molecules – a "hard" effective fragments of media described with interaction potentials. That is EFP method [5]. The EFP model describes electrostatic, van der Waals, interchange, hydrogen-bond forces. The electrostatic interaction of central particle (especially of ion or charged cluster) with continuous media outside the cluster is estimated by means of method SCRF (Self Consistent Reaction Field [6]), which is the quantum mechanical implementation of Onsager's reaction field model.

This scheme was applied for calculation Gibbs free energy of hydration of HF and HCl, F^- and Cl^-, entropy of these aquaspecies and Gibbs free energy of dissociation reaction of HF and HCl in water (table 1).

The Gibbs free energy of hydration of species was calculated after equation (all values for 298K): $\Delta_h G^o(sp) = E^G(sp+20H_2O) - E^G(20H_2O) - E^G(sp.gas)$

The entropy of aquaspecies in conventional scale is given by equation: $\boldsymbol{S^o{}_{298}(sp^{-z}{}_{aq})} = S^o{}_{298}(sp+20H_2O) - S^o{}_{298}(20H_2O) - (-z) \cdot S^o{}_{298}(H^+{}_{aq})$, where $S^o{}_{298}(H^+{}_{aq}) = -5.3 cal/mol \cdot K$ [7]. It is necessary to mention, that not only the value, but also the sign of entropy corresponds to experimental data, and that this would be impossible, if SCRF method had been used alone.

The Gibbs free energy of dissociation reaction **$HX = H^+ + X^-$**, where **$X = F, Cl$** was calculated (for 298K) after equation: $\boldsymbol{\Delta_{diss} G^o{}_{298}} = E^G{}_{298}(X^- + 20H_2O) + E^G{}_{298}(H^+{}_{aq}) - E^G{}_{298}(HX+20H_2O)$.

The full energy of solvated proton equals to $E^G{}_{298}(H^+{}_{aq}) = E^G{}_{298}(H^+gas) + \Delta_h G(H^+{}_{gas})$. Here $E^G{}_{298}(H^+{}_{gas})$ - is the full energy of the proton in gas phase, $E^G{}_{298}(H^+{}_{gas}) = E_{form}(H^+{}_{gas}) + G^o{}_{298}(H^+{}_{gas}) = G^o{}_{298}(H^+{}_{gas})$, since in quantum chemistry $E_{form}(H^+{}_{gas}) = 0$. The Gibbs free energy of $H^+{}_{gas}$ in a gaseous fase is: $G^o{}_{298}(H^+{}_{gas}) = H^o{}_{298}(H^+{}_{gas}) - T \cdot S^o{}_{298}(H^+{}_{gas})$, where $H^o{}_{298}(H^+{}_{gas}) = 1.48$ kcal/mol and $S^o{}_{298}(H^+{}_{gas}) = 26.01 cal/(mol \cdot K)$ [8]. Hence: $E^G{}_{298}(H^+{}_{gas}) = -6.27$ kcal/mol. The Gibbs free energy of hydration of proton $\Delta_h G^o{}_{298}(H^+) = -263.98$ kcal/mol [9]. Hence: the full energy $E^G{}_{298}(H^+{}_{aq}) = -270.25$ kcal/mol.

The Gibbs free energy of dissociation HF was found to be well consistent with experimental data (table 1). It was then a reason for calculating in the same basis a Gibbs free energy of dissociation of

HCl, since it is known [10], that the uncertainty for the constant of dissociation of HCl attains 7 orders.

Table 1

ΔG - in kcal/mol, S - in cal/mol·K.

central species	calcul. $\Delta_h G^o_{298}$	literature $\Delta_h G^o_{298}$	calcul. $S^o_{298,aq}$	literature $S^o_{298,aq}$	calcul. $\Delta_{dis} G^o_{298}$	literature $\Delta_{dis} G^o_{298}$
HF	-1.0	-7.84 [11]	15.7	21.93 [7]	4.7	4.33 [11]
F^-	-94.6	-102.49 [9]	-4.7	-3.31 [11]		
HCl	1.6	-1.80 [12]	22.7		-0.7	-0.7 ÷ -10 [10]
Cl^-	-63.1	-72.71 [9]	7.5	13.52 [11]		

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