COMPENSATION RELATIONSHIP IN THERMODYNAMICS OF GAS-PHASE MOLECULAR COMPLEXATION

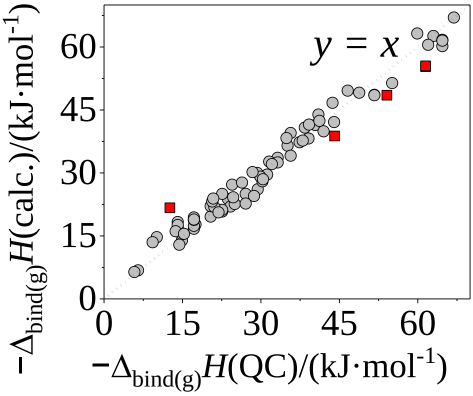
Khisamiev M.B., Solomonov B.N., Sokolov A.A., Yagofarov M.I.
Kazan Federal University, Department of Physical Chemistry
420008, Kazan, Kremlevskaya st., 18

The phenomenon of compensation between changes in enthalpy and entropy in various physicochemical processes has been a subject of interest for scientists for over 90 years. In previous works, linear relationships were obtained between the changes in Gibbs energies and enthalpies for solvation and solution-phase complexation processes, which share the same slope [1].

The common slope in these dependences allows deriving a similar equation for complexation in the gas phase:

$$\Delta_{\mathrm{bind(g)}}G\ /\ (\mathrm{kJ{\cdot}mol^{-1}}) = 0{,}660 \cdot \Delta_{\mathrm{bind(g)}}H\ /\ (\mathrm{kJ{\cdot}mol^{-1}}) + 17{,}0 + 2{,}5{\cdot}n$$

In the present work, a comparison was made between the enthalpy values calculated using the obtained relationship from experimental Gibbs energy values and the values computed by quantum-chemical methods for 67 donor-acceptor pairs (graphical representation of this comparison is given in fig. below) [2].



The relationship obtained in present work allows creating an approach for determining binding enthalpies in the gas phase from a single value of the equilibrium constant at 298.15 K. Furthermore, the obtained results mean that, in each case, the compensation relationships have a common origin, which is beyond experimental artifacts, group additivity in homologous series, or solvent reorganization effects.

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2. Sokolov A.A., Khisamiev M.B., Solomonov B.N., Yagofarov M.I. // Phys. Chem. Chem. Phys. 2025. Vol. 27, P. 26139–26151. https://doi.org/10.1039/D5CP04241K

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