

FEATURES OF GIBBS EQUATION ($\Delta G = \Delta H - T\Delta S$) APPLICATION TO THERMODYNAMICS OF SOLVATION, VAPORIZATION, AND COMPLEX FORMATION IN SOLUTION AND GAS PHASES*Yagofarov M.I., Solomonov B.N.*Kazan Federal University
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Gibbs equation is probably the most utilized in chemical thermodynamics. For a long time, researchers wondered whether there is a connection between the Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes in various processes, apart from the Gibbs equation. In this work, based on a large amount of experimental data (more than 5000 measurements), we analyzed the ΔG vs. ΔH relationship for the four types of processes: solvation, vaporization, electron donor acceptor and hydrogen bonding in solutions and in the gas phase [1, 2]. The following conclusions were made:

1. Classification of the solute-solvent systems, considering hydrogen bonding tendency, enabled the generalization of the ΔG vs. ΔH relationship in solvation/vaporization thermodynamics. A common linear relationship with a slope of 0.66 was observed for the solvation in non-hydrogen-bonded systems, while the deviations associated with solute-solvent complexation and solvophobic effect contributed to intercept only.

2. The linear ΔG vs. ΔH relationships for the solution- and gas-phase complexation with the same slope were derived from the above considerations for the solvation/vaporization processes and validated against numerous measurements, proving its predictive capability.

Summarizing, ΔG vs. ΔH relationship for the processes considered in this work obeyed the common expression:

$$\Delta G = \Delta H - T\Delta S_{\text{comp}} - T\Delta S_{\text{noncomp}} = 0,660 \cdot \Delta H - T\Delta S_{\text{noncomp}}$$

where ΔS_{comp} and $\Delta S_{\text{noncomp}}$ are the compensated and noncompensated (i.e., enthalpy-independent) contributions to the process entropy, with $T\Delta S_{\text{comp}}$ being $0.34\Delta H$. The above expression remained unchanged, regardless the type of intermolecular interactions (pairwise/collective) or the structure of interacting molecules.

Furthermore, the above equation could be applied for the description and prediction of the thermodynamic parameters of cyclodextrines complexation, even though it implies multiple interactions, such as electrostatic repulsion/attraction, hydrogen bonding, hydrophobic effects, charge transfer, and conformational changes.

Given that manifold experimental data were summarized, covering the diverse processes, objects, and interaction types, we conclude that the regularities observed should be considered as the general feature in the studies of intermolecular interactions.

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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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