

Partial Molar Enthalpy from Fluctuations at Small Scale

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Experimentally one of the most important quantities to measure during a transformation is the heat of transformation, which can be done directly in calorimeters. From a thermodynamic point of view, this heat can be calculated from the knowledge of partial molar enthalpies for constant pressure transformations or from the partial internal energy for transformations at constant volume. Despite the large interest in these quantities, their calculations from molecular simulations is still a challenge in particular for high density systems, cumbersome molecules, traces or for reacting systems. In the presentation it will be shown how looking at mass and energy fluctuations at small scales in open systems under equilibrium conditions gives a direct access to partial molar enthalpies [1]. This new method, called the small system method, will be applied to molecular dynamics simulations of a reacting system $H_2=2H$ at different temperatures for which the calculated heats of reaction agree with experimental data [2].

References

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- [2] R. Skorpa, J. M. Simon, D. Bedeaux, S. Kjelstrup, *Phys. Chem. Chem. Phys.* 16, 19681 (2014).