6th International Conference on

Physical and Theoretical Chemistry

September 02-03, 2019 | Zurich, Switzerland

The unique chemical-equilibrium in nano-systems: Confinement & quasi-confinement effects

Leonid Rubinovich and **Micha Polak**
Ben-Gurion University of the Negev, Israel

Chemical-equilibrium involving a small number of molecules inside a confined nanospace can exhibit considerable deviations from the macroscopic thermodynamic limit due to reduced mixing entropy, as was predicted in several of our works using statistical-mechanics canonical partition-functions and the lattice-gas [1-3] as well as non-lattice [4] models. In particular, for exergonic addition and dimerization a considerable shift of the bimolecular reaction extent towards product formation is expected. This "nanoconfinement entropic effect on chemical-equilibrium" (NCECE) was verified by revised analysis [5] of reported measurements of DNA hybridization inside confined nano-fabricated chambers. More recently, we predicted enhancement of Ir dimerization inside Pd-Ir nanoparticles that can affect their catalytic properties [4].

Using the grand-canonical ensemble, the modeling has been recently extended to the more common "quasi-confined nanosystems" exchanging molecules with a macroscopic environment. As exemplified by dimerization of alkali metal vapors ($2Na=Na_2$) trapped inside pores by potential wells, the following conditions facilitate product-stabilizing NCECE effects under quasi-confinement (QNCECE): (i) limited nanospace capacity; (ii) significant host-guest interactions (deep potential wells); (iii) high-coverage of the nanospace (e.g., due to high external pressure or to low temperatures). In the case of low-coverage product destabilization is predicted because of monomer deficiency effects (opposite to the QNCECE).

The unique chemical-equilibria under confinement and quasi-confinement are anticipated for a wide range of nanospaces (nanopores, zeolites, nanotubes, fullerenes, micelles), and thus can have implications for the growing nanotechnological utilization of chemical syntheses conducted within nanoreactors.

Recent Publications

1. Polak M, Rubinovich L, (2008) Nanochemical Equilibrium Involving a Small Number of Molecules: A Prediction of a Distinct Confinement Effect. NanoLetters 8: 3543-3547.
2. M, Rubinovich L, (2011) Remarkable Nanoconfinement Effects on Chemical Equilibrium Manifested in Nucleotide Dimerization and H-D Exchange Reactions. Phys. Chem. Chem. Phys. 13: 16728-16734.
3. Polak M, Rubinovich L, (2015) Nanoconfined nitrogen hydrogenation on Ru (0001): Prediction of entropy related shifts in the reaction equilibria. Surf. Sci. 641: 294-299.
4. L, Polak M, (2018) Statistical-Mechanics Modeling Focused on Ir Dimerization Beneath Surface Sites in Pd–Ir Nanoparticles. Topics in Catalysis 61: 1237-1246.
5. Rubinovich L and Polak M, (2013) The Intrinsic Role of Nanoconfinement in Chemical Equilibrium: Evidence from DNA Hybridization. NanoLetters 13: 2247-2251.

Biography

Leonid Rubinovich completed his PhD from Tomsk University, Russia. He is Researcher under KAMEA program at the Chemistry Department of Ben-Gurion University of the Negev, ISRAEL. L. R. published over 60 scientific articles.

Polak has completed his PhD from Tel-Aviv University, ISRAEL, and postdoctoral studies from the University of Utah and from California Institute of Technology (CALTECH), USA. He is Professor Emeritus of Chemistry at Ben-Gurion University, ISRAEL, published over 110 scietific articles, a few chapters, and served as a Guest Editor.