A Remarkable Nano-Confinement Effect on Chemical Equilibrium: From Nucleotide Dimer Formation in Molecular Cages to Deuterium Exchange Reactions on Interstellar Dust Grain Surfaces

Micha Polak, Leonid Rubinovich
Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel
mpolak@bgu.ac.il

With current developments in nanoscience and nanotechnology, experimental studies of reactions in confined nanospaces have been emerged. Thus, a variety of tailor-made "nanoreactors" have been fabricated: (i) molecular capsules, held together either by covalent bonding or by self-assembly via weaker interactions such as metal coordination and hydrogen bonds, for organic and metal catalyzed synthesis; (ii) carbon nanotubes for the synthesis of nanowires, nanobeads, or polymeric chains, and more. In a related field, considerable research has been devoted to explain and/or reproduce observations of deuterium fractionation in interstellar molecules originally adsorbed on surfaces of tiny dust grains. Yet, while focusing mainly on reaction kinetics, the possible role of equilibration has not been explored in these studies. Since classical thermodynamics of macroscopically large systems is not fully applicable under such conditions, we recently developed a pertinent statistical-mechanical formulation for chemical equilibria, based on the canonical-ensemble and the ideal lattice gas model [1]. As shown, unique properties characterize a closed small system of reaction mixture molecules at equilibrium, including significant extra stabilization of exothermic reaction products, namely, the enhancement of the reaction extent or equilibrium constant. The origin of this remarkable deviation from the macroscopic thermodynamic limit (TL), which we name "The nano-confinement effect on chemical equilibrium" (NCCE), is elucidated. In a first implementation of the theory, the work focuses on experimentally explored artificial and natural confined reaction systems, representing widely divergent branches of chemistry.

First, the NCCE effect is studied for a most recently reported original experiment regarding nucleotide dimerization in molecular cages [2]. In particular, the predicted remarkable enhancement of equilibrium constants as compared to the TL, can contribute to the experimentally observed stabilization of hydrogen-bonded base pairs of mono- and dinucleotides in the cages (Fig.1).

Secondly, we treat H-D exchange reactions driven by zero-point energy differences as a model for equilibration on interstellar dust grain surfaces. In particular, the computations reveal that the equilibrium constants of the $H_2CO+D=HDCO+H$, $HDCO+D=D_2CO+H$ and $H_2+D=HD+H$ exothermic surface reactions are significantly enhanced (Fig.2), mainly due to doubling of the lnK vs. 1/T slope, and the overall effect of product stabilization increases for smaller numbers of reacting molecules. We suggest that the herein predicted astrochemical NCCE effect can be an amplifying source for the commonly observed enrichment of interstellar media in deuterated molecules. The universality of the new effect can have important implications in other situations when chemical equilibration is reached in a confined nanospace.

References:

[1] M. Polak, L. Rubinovich, Nano Letters **8** (2008) 3543.
[2] T. Sawada, M. Yoshizawa, S. Sato, M. Fujita, Nature Chemistry, **1** (2009) 53.

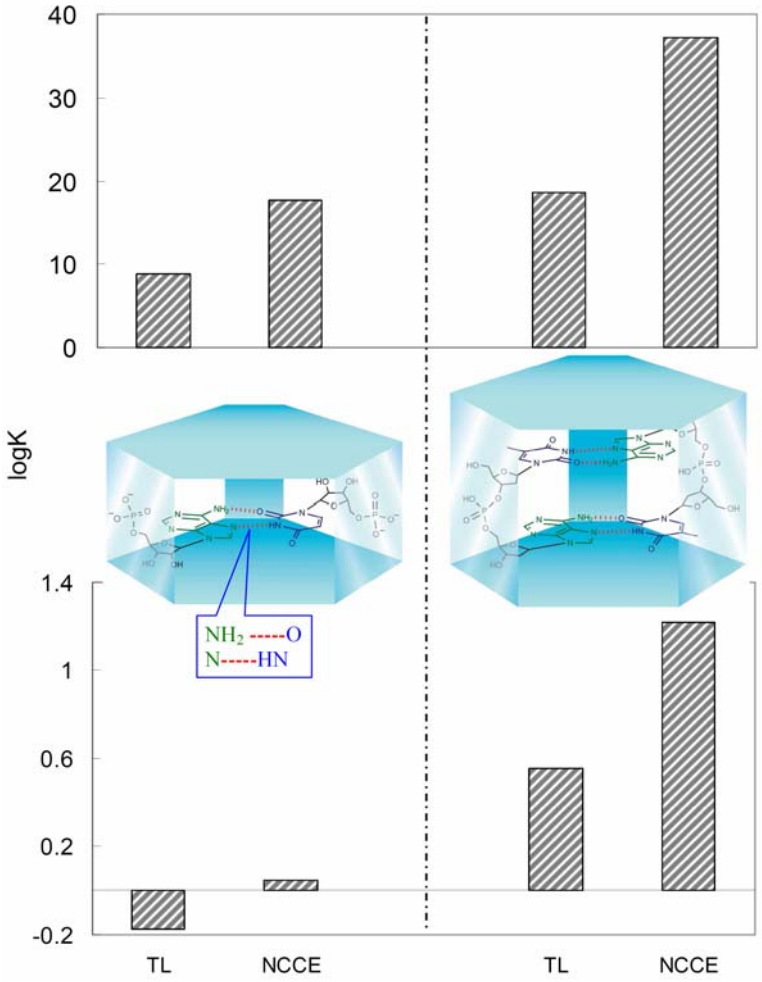

Fig.1. Nano-confinement effects relative to the thermodynamic limit: Equilibrium constants of mononucleotide (left) and dinucleotides (right) base pair formation computed (300 K) using estimated high (upper panel) and the low (lower panel) values of the reaction energy for each of the two reactions. Inset: Schematics of the mono- and dinucleotide base pairs encapsulated in self-assembled molecular cages and the hydrogen bonds formed (box).

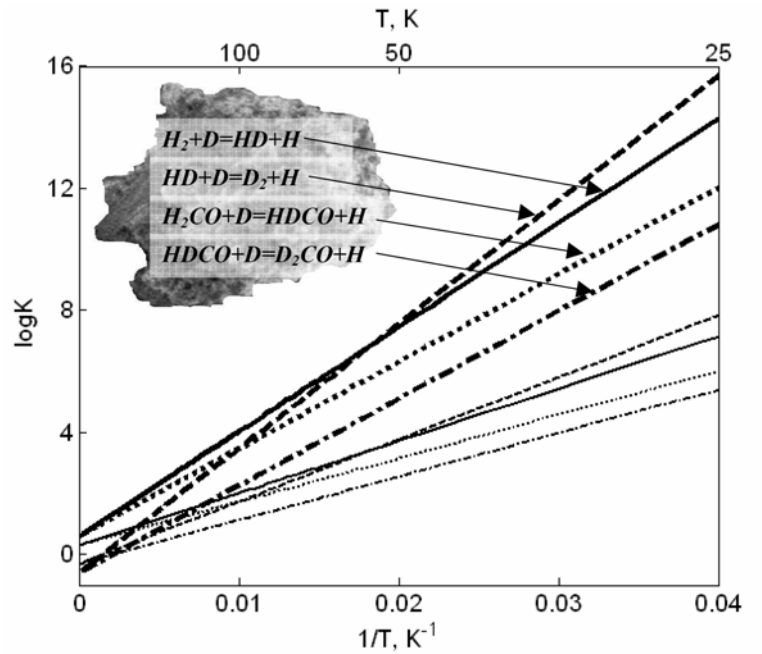

Fig.2. Equilibrium constants of H-D exchange reactions on the surface of an interstellar grain computed for the smallest reaction mixture (2 molecules, thick lines) compared to the TL values (thin lines).