



Micha Polak* and Leonid Rubinovich

Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

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*Corresponding author: Micha Polak, Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, 84105, Israel, E-mail: mpolak@bgu.ac.il

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Research Article

Prediction of Enhanced Dimerization inside Dilute Alloy Nanoparticles

Abstract

According to a unique nano-confinement effect of entropic origin, predicted by us several years ago for the equilibrium state of chemical reactions, the equilibrium-constant and extent are greatly enhanced depending on the small number of molecules involved, and for many reactions also on the nano-space size. This work explored the validity of this effect in the case of elemental dimerization reactions within dilute alloy nanoparticles with separation tendency, $Pd - Ir$ cuboctahedra in particular. Employing a simple model for the system energetics, computations based on the exact canonical partition-function reveal nano-confinement induced Ir_2 dimer stabilization within Pd surface segregated nanoparticles, reflected e.g., by up to ~60% increased dimerization extent and by doubling of the $\ln K_D$ vs. $1/T$ slope, as compared to the macroscopic thermodynamic limit. The dual role of the configurational entropy, namely mixing of Ir/Ir_2 vs. Pd/Ir is elucidated. Study based on more elaborate energetic models is desirable as the next step of this research.

Introduction

As shown by us some years ago [1], the involvement of small numbers of molecules in a closed reaction space can considerably affect the chemical equilibrium. Thus, significant increase of the reaction extent was predicted for the case of exothermic reactions as compared to that of the corresponding macroscopic system (in the thermodynamic limit, TL). This nanoconfinement entropic effect on chemical equilibrium (NCECE) is universal in a sense that it stems only from the limited amount of molecules in a reaction mixture, resulting in a reduced number of mixed reactant-product microstates in the closed system [1,2]. The effect was predicted for the case of nucleotide dimerization within molecular cages [2] and verified for DNA hybridization [3] that was studied experimentally before [4]. The NCECE is relevant to several advanced routes for the synthesis of encapsulated organic molecules, metallic or inorganic nanoclusters, and other nanoscale structures and applications.

While the NCECE is expected mostly in molecular nanosystems, this effect that arises from fundamental mixing-entropy variations can in principle be manifested also in other reaction classes, e.g., in alloy systems. The present study focuses on the distinct case of constituent atom equilibrated dimerization within phase-separating alloy nanoparticles (NPs). Namely, the main question of this study concerns whether confined dimerization can exhibit significant NCECE effects. Being a first stage in phase separation (or the main

process in very dilute alloys) that can affect chemical and physical properties, dimerization inside NPs seems to be a sensible issue for theoretical-computational modeling. For this goal fcc-based $Pd - Ir$ NPs have been chosen, because of the strong Pd tendency to segregate at the alloy surface, making the Pd -rich core a natural confined space for Ir solute atoms entirely surrounded by 12 nearest-neighbor (NN) Pd atoms. Moreover, $Pd - Ir$ nanoparticles are efficient catalysts, e.g., promoting preferential oxidation of CO in the presence of excess H_2 in proton exchange membrane fuel cells [5-7]. Recently, chemical-order in "magic-number" $Pd - Ir$ NPs was studied by means of density functional theory (DFT) computations [8] and compared to those obtained by the Free-Energy Concentration Expansion Method (FCEM) [9], using derived coordination-dependent bond-energy variations (CBEV) [10] and by the Birmingham Cluster Genetic Algorithm with the Gupta potential [11].

In this work, Ir dimerization in cuboctahedron dilute cores of the magic-number size series [12] is studied (namely, 13, 55, 147, 309, 561 and 923 atom cores inside 55, 147, 309, 561, 923 and 1415 atom alloy NPs, respectively) in the framework of the NN interaction approximation. Energetic equivalence of all intra-core Ir atomic sites and of all Ir_2 dimer locations is assumed, since, as noted above, they are all surrounded by Pd only (Figure 1). This includes also the subsurface sites, namely possible CBEV effects are ignored in this study. Correspondingly, the energy of the $2Ir \leftrightarrow Ir_2$ intra-core dimerization "reaction" equals the doubled bulk Effective Pair

Interaction (EPI), $\Delta E = 2V = (w^{PdPd} + w^{PdIr} - 2w^{IrIr}) \approx -74$ meV, as derived from DFT-computed low-temperature formation enthalpy [13]. Formulas for the equilibrium dimerization extent, equilibrium constant and the NP entropy are derived below based on canonical statistical mechanics and applied in MATLAB computations. Then, the results are evaluated for possible NCECE manifestations by comparison to the corresponding values of a hypothetical macroscopic alloy with the same composition and dimerization energy.

In the employed lattice-gas model [14] microstates correspond to different arrangements of two *Ir* solute atoms on n available atomic sites, and to the locations of a single Ir_2 dimer at n' available NN bonds in the NP core (see examples in Fig.1b). Concentrations of *Ir* atoms and dimers are related to the nanoconfined (NC) reaction extent, ξ_D^{NC} ($\xi_D^{NC} = 0$ for pure reactants, $\xi_D^{NC} = 1$ for pure products),

$$\begin{aligned} c_a &= c_a^{\max} (1 - \xi_D^{NC}), \\ c_d &= c_d^{\max} \xi_D^{NC} \end{aligned} \quad (1)$$

where $c_a^{\max} = 2/n$ and $c_d^{\max} = 1/n'$.

Since the lattice-gas chemical-potential [14] depends on a "reduced concentration", $\frac{c}{1-c}$, the dimerization equilibrium constant is given by,

$$K_D = \frac{c_d / (1 - c_d)}{[c_a / (1 - c_a)]^2} \quad (2)$$

In order to calculate the above, the number of ways to arrange just two *Ir* atoms is given by the binomial coefficient, $\binom{n}{2} = \frac{n(n-1)}{2}$. Since n' arrangements corresponds to dimer locations, it has to be subtracted in the canonical partition function,

$$Q = \frac{n(n-1)}{2} - n' + n' \exp(-\Delta E/kT) \quad (3)$$

Thus, in addition to the energetics the dimerization is controlled by the overall numbers of intra-core atomic sites and NN bonds (straightforwardly computed by MATLAB). Starting from Q , the equilibrium properties of the system can be obtained, such as the reaction extent, namely, the probability of dimer formation,

$$\xi_D^{NC} = n' \exp(-\Delta E/kT) / Q \quad (4)$$

Then, the corresponding concentrations are obtained by eq.1 in order to compute the equilibrium constant (via eq.2).

For obtaining the reference TL equilibrium constant, the reaction entropy should be found (in addition to the known reaction energy)

$$K_D^{TL} = \exp[-(\Delta E - T\Delta S) / kT] \quad (5)$$

Thus, in the case of very large NPs and very high temperatures the reaction extent obtained by eqs.3-4,

$\xi_D^{\infty} \approx 2n'/n^2$, is substituted in eq.1 giving the concentrations, $c_a^{\infty} = 2/n$, $c_d^{\infty} = 2/n^2$. Then, according to eq.2 the high temperature limit, $K_D^{\infty} = 1/2$, and eq.5 gives $\Delta S = -k \ln 2$. The K_D^{TL} of the corresponding hypothetical macroscopic alloy computed for any T (by eq.5) together with eqs.1-2 yields,

$$\frac{c_d^{\max} \xi_D^{TL} / (1 - c_d^{\max} \xi_D^{TL})}{\{c_a^{\max} (1 - \xi_D^{TL}) / [1 - c_a^{\max} (1 - \xi_D^{TL})]\}^2} = \exp[-(\Delta E - T\Delta S) / kT] \quad (6)$$

This equation has to be solved numerically in order to find the TL reaction extent, ξ_D^{TL} .

To conclude the statistical-mechanical derivation, the NP configurational entropy per site is given according to the Shannon formula [15] by,

$$\frac{S}{kn} = -\left(\frac{n-1}{2} - \frac{n'}{n}\right) \frac{1}{Q} \ln \frac{1}{Q} - \frac{n' \exp(-\Delta E/kT)}{n} \frac{1}{Q} \ln \frac{\exp(-\Delta E/kT)}{Q} \quad (7)$$

According to the computations, the dimerization extent under nanoconfinement is significantly enhanced compared to the TL value based on the same c_a^{\max} and c_d^{\max} (Figure 2a), and can be expressed by its relative increase, $\delta\xi = (\xi_D^{NC} / \xi_D^{TL} - 1)100\%$ that reaches about 60% for core size $n=13$ (Figure 2b). This phenomenon is due to the NCECE that gradually weakens with increased NP size ("nanospace size effect" [2]), until for the 923-atom NP core the two extent curves almost coincide (Figure 2a). As shown in Figure 2c, the equilibrium constant is enhanced too and most of the $\log K_D$ vs. $1/T$ slopes are twice larger than the TL slope. Consequently, the logarithm ratios converge to 2 at the low temperature limit (Figure 2d). This slope doubling is characteristic e.g., of exothermic addition and dimerization reactions ($A + B = C$,

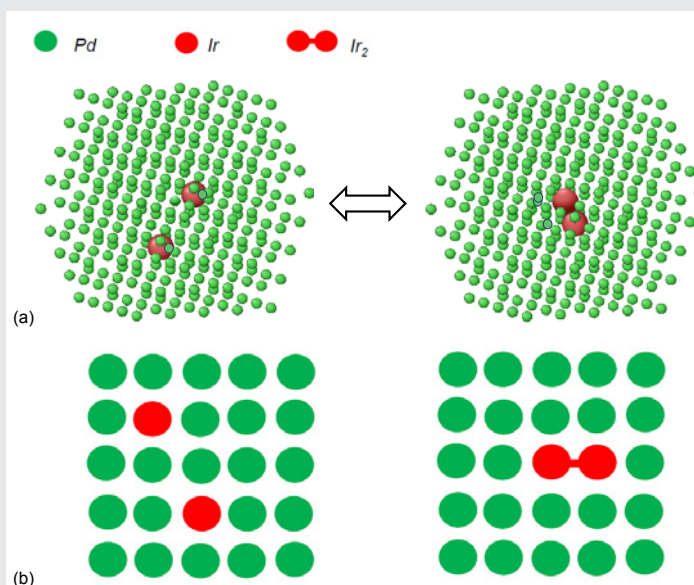


Figure 1: (a) Illustration of $2Ir \rightleftharpoons Ir_2$ equilibrated dimerization inside the 309-atom core of Pd surface-segregated 561-atom cuboctahedral nanoparticle. (b) 2D schematics of two representative configurations ("microstates"), corresponding to distributions of *Ir* atoms on atomic sites (left) and of Ir_2 dimers as nearest-neighbor bonds.

$2A=A_2$) in nanoconfined systems, and relates directly to the sum of the reactant stoichiometric coefficients [1]. Regarding the significant role of configurational entropy, it originates from two mixing contributions: (i) iridium (atomic, dimerized) with palladium atoms, and (ii) iridium atoms with dimers. The dissociation backward endothermic reaction, $Ir_2 \rightarrow 2Ir$, is promoted by temperature increase and by the NP-size dependent alloy dilution, (Figure 2a), in accordance with the Le Chatelier's principle. Thus, as can be further seen in Figure 3a, the entropy per site increases with temperature and the region of its most intensive rise (maximum slope) shifts to lower temperatures. Furthermore, the entire entropy plot shifts downwards with increasing NP size due to the dilution. All the above phenomena are reflected also in the TL curves towards which the NP curves approach with growing size. The NCECE stems primarily from deficiency of type (ii) mixing in NPs reflected in lowering of the entropy under nanoconfinement, S^{NC} , compared to the S^{TL} plot (Figure 3a). Since it is completely absent in the 2-atoms/1-dimer case under consideration, the corresponding relative decrease in entropy, $\delta S \equiv (S^{NC}/S^{TL} - 1)100\%$ (Figure 3b), is associated mainly with this lack of type (ii) mixing contribution in the NP. The gradual shrinking of δS with increasing NP size is attributed to the growing relative contribution of the nanospace-related mixing entropy, type (i). The δS minima, associated with the above-mentioned most intensive dissociation regions, follow their shift to lower temperatures with NP size increase. Furthermore, the minimum values obey distinct, nearly linear dependence on their temperatures (Figure 3c).

To summarize, a theoretical-computational study is introduced concerning elemental dimerization within cuboctahedral $Pd - Ir$ nanoparticles as a model system. Considering two solute Ir atoms confined under segregated Pd surface layer as lattice gas, statistical-mechanical computations reveal for the first time that "nanoconfinement entropic effect on chemi-

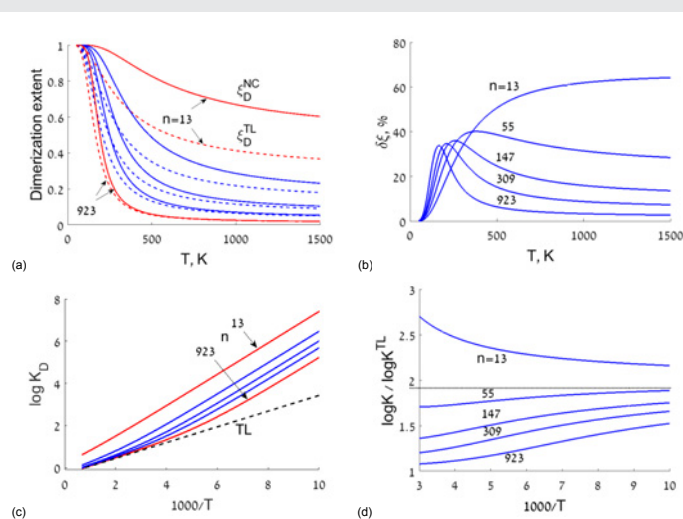


Figure 2: The temperature dependence of the dimerization extent (a), its relative increase, δS (b), the equilibrium "constants" (c), and the NC/TL ratios (d), computed for two Ir solute atoms in cores of cuboctahedral $Pd - Ir$ NPs containing 13, 55, 147, 309 and 923 atoms (size magic-numbers). The macroscopic TL values are given for comparison (dashed lines in (a) and (c)).

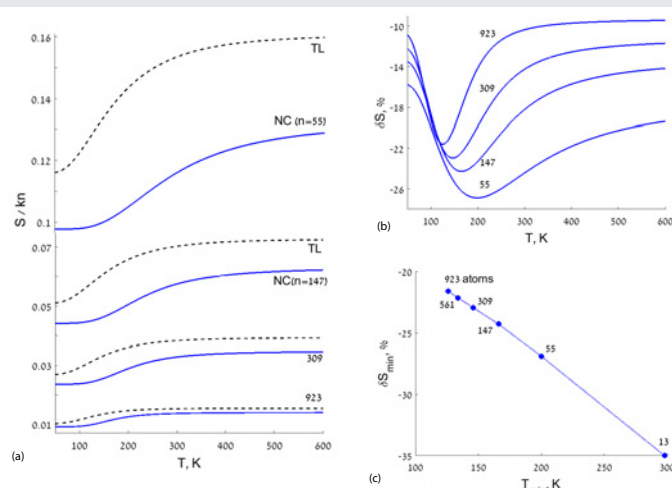


Figure 3: The dependence on temperature computed for different size NPs: (a) the configurational entropy per site (the numbers of core sites are indicated); (b) the corresponding relative decrease in entropy δS ; (c) the magnitude of the δS minimum.

cal equilibrium" (NCECE) induces significant enhancement of equilibrium solute dimerization, compared to the bulk alloy with the same composition. Being a kind of first stage of phase separation, the enhanced dimerization indicates strengthening of this tendency, unlike the known phenomena of diminished phase separation temperatures in nondilute alloy NPs. The predicted NCECE-induced dimerization enhancement can be relevant to alloy NP catalytic properties due to possible ligand effects such as bandwidth changes via hybridization of d-states of surface atoms with subsurface atoms [16]. Moreover, coordination-dependent bond-energy variations (CBEV) can make certain sites in the subsurface layer energetically preferable for solute atoms and dimers, thereby further affecting the alloy particle catalytic properties. Hence, a next step of the $Pd - Ir$ dimerization research, which is based on this energetic model, is desirable.

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