Nanoscale thermodynamic aspects of plasma catalysis

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ABSTRACT

Plasma catalysis continues to gain increasing scientific interest, both in established fields like toxic waste abatement and emerging fields like greenhouse gas conversion into value-added chemicals. Attention is typically focused on the obtained conversion process selectivity, rates and energy efficiency. Much less attention is usually paid to the underlying mechanistic aspects of the processes that occur. In this contribution, we critically examine a number of fundamentally important nanoscale thermodynamic aspects of plasma catalysis, which are very relevant to these processes but so far have been overlooked or insufficiently covered in the plasma catalysis literature.

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1. Introduction

The central idea in catalysis is to facilitate an alternative pathway for a chemical reaction to occur through the use of a catalyst. This alternative pathway is subject to a lower energy barrier, resulting in higher reaction rates. The catalyst will typically lower certain barriers more than others, and stabilize certain intermediates more than others, such that the catalyst also determines the selectivity towards the desired end products [1–3]. Provided that the reactants are supplied and the products are removed efficiently, the catalyst properties ultimately determine the dominant reaction pathways, as well as their selectivity, rates, products and energy efficiency [4–6].

Most of the catalyst materials are nanostructured [7]. This can be achieved by controlling their synthesis, as is the case for nanoparticles and nanoporous materials [3,8]. The catalysts also feature nanoscale roughness, which also plays a role in many catalytic processes [9,10]. Catalyst properties strongly depend on their structure and size [2,6,11]. To make a catalytic process as cost-effective as possible, the total catalyst surface area should be maximized. In this way the exposure of catalytically active sites is maximized while the used amount of catalytic material is reduced.

In heterogeneous catalysis, this is accomplished by dispersing the catalyst over a suitable (most often nanoporous) support and by deliberately allowing the catalyst to form nanofeatures, thereby dramatically increasing the surface area compared to an atomically smooth surface [12,13]. Clearly, taking into account the nanoscale nature of the catalyst is of prime importance.

At the microscopic level, the catalytic process may be divided in three steps:

1) arrival and binding (e.g., physi- or chemisorption) of the reactants to the catalyst surface;
2) physico-chemical surface processes such as physical diffusion and chemical reactions; and
3) desorption of the catalytic reaction products into the gas phase.

While catalytic processes are traditionally treated using physical and chemical kinetics approaches, thermodynamics play a crucial role in each of these steps. Thermodynamics is concerned with the description of systems in terms of the exchange of energy and matter with their surroundings, and determines to what extent the reaction can proceed. As the reaction approaches the equilibrium, as determined by the thermodynamic equilibrium constant for a given set of reaction conditions, the reaction rate will drop accordingly. Therefore, a complete description of the catalytic process requires considering thermodynamics next to the kinetics of the process.

Classical thermodynamics deal with macroscopic systems under equilibrium conditions where time is not a parameter. Plasma catalysis, however, is typically a far-from-equilibrium process, where large fluxes of energy and matter are continuously delivered to the catalyst [14–16]. The thermodynamic complexity of plasma nanocatalysis is further increased by the nanometer length scale of the

system. For instance, it is well known that both non-equilibrium and nanoscale effects play very important roles in plasma-based catalyzed growth of nanotubes [17–19]. In this case, fluxes of atomic, radical, molecular, excited, etc. species, as well as ions, electrons and photons impinge on the nano-catalyst, leading to out-of-equilibrium-growth of the (nanoscale) structure. Here we will focus on nanoscale thermodynamic aspects relevant to plasma catalysis.

2. Theoretical description of thermodynamics for nanoscale systems

Various approaches to describe the thermodynamics of nanosystems have been developed, including nanothermodynamics by Hill [20], Tsallis thermodynamics [21], nanoscale thermodynamics based on classical thermodynamics [22], and fluctuation theorems [23].

At the nanoscale, the classical macroscopic laws of thermodynamics no longer hold, and modifications or alternative descriptions are required. Consider for example an icosahedral Ni_{147} cluster, which has an apex-to-apex diameter of about 1.5 nm and a surface-to-volume ratio of around 5. As will be shown below, both the melting temperature and adsorption energy on its surface depend on the exact size and structure. Standard equilibrium thermodynamics are not very well suited to describe such a system, because of inherent fluctuations in structure and energy. In fact, due to these fluctuations, definition of static equilibrium becomes rather difficult, if not impossible. This is why structural characteristics in nanoscale systems vary dynamically, in contrast to the quasi-static equilibrium of macroscale objects.

At the nanoscale, modifications or alternative descriptions of classical macroscale thermodynamics are often required. Some authors argue that no such modifications are needed and including a classical size-dependence (as in classical nucleation theory) is sufficient to describe and address the behaviour of nanoscopic systems [24]. Nonetheless, it is obvious that nano-catalysts exhibit modified properties relative to their macroscopic analogues, due to their large surface-to-volume ratio. Hence, standard equilibrium size-independent thermodynamics are not very well suited to describe such systems, because of (1) the finite nature of nanoscale structures, and (2) inherent fluctuations in structure and energy.

Below, we will examine the most important relations between the thermodynamic factors and catalytic effects in nanoscale systems, in particular affected by the plasma.

2.1. The Gibbs–Duhem equation at the nanoscale

The first conceptual framework for thermodynamics of nanoscale objects, referred to as "nanothermodynamics" [20,25], was established by Hill. We first consider traditional thermodynamics and then introduce the nanoscale effects [20], keeping the above in consideration. For a macroscopic one-component system the internal energy U may be expressed as a function of its three natural extensive variables:

$$U(S, V, N) = TS - PV + \mu N, \tag{1}$$

where S is the conventional entropy (an extensive state function), V is the volume and N is the number of particles. The other variables appearing in this equation are the temperature T, the pressure P and the chemical potential μ. Since the internal energy U is a state function, the total derivative

$$dU = SdT + TdS - PdV - VdP + \mu dN + Nd\mu \tag{2}$$

can be written as the sum of partial derivatives

$$
\begin{aligned}
dU &= \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,N} dN \\
&= TdS - PdV + \mu dN
\end{aligned}
\tag{3}
$$

Eq. (3) expresses conservation of energy, i.e., the first law of thermodynamics. Combining Eqs. (2) and (3) yields

$$SdT - VdP + Nd\mu = 0, \tag{4}$$

which is the well-known Gibbs–Duhem equation for macroscale systems. This equation states that changes in the intensive quantities T, P and μ are not independent.

Therefore, at the nanoscale, the internal energy (or any of the other thermodynamic potentials) in principle depends on the exact number of particles N the structure contains and how they are arranged [20]. As a result, fundamental thermodynamic equations like the Gibbs–Duhem equation are no longer valid. Indeed, in nanoscale systems, the detailed geometry and structure of the system must be taken into account, as well as the fact that surfaces, edges and corners are present and system rotation and translation may occur. According to Hill, the internal energy is now complemented by the so-called subdivision potential ε, which takes these factors into account at the ensemble level

$$U = TS - PV + \mu N + \varepsilon, \tag{5}$$

leading to

$$SdT - VdP + Nd\mu + d\varepsilon = 0, \tag{6}$$

which represents the nanoscale version of the Gibbs–Duhem equation. In a macroscopic system, the factors contributing to ε become negligible, and Eq. (5) reduces to Eq. (1). Eq. (6) in effect means that the intensive quantities T, P and μ may now be varied independently, or stated differently, that ε is a function of three independent variables T, P, and μ. Nanoscale systems thus have one more degree of freedom compared to macroscale systems.

2.2. Second law of thermodynamics and extensivity in nano-catalysis

An alternative view on thermodynamics at the nanoscale stems from the second law of thermodynamics. Indeed, the second law of thermodynamics may be violated in nanoscale systems for very short periods of time, due to fluctuations [26,27]. The Boltzmann definition of entropy is:

$$S = k_B \ln \Omega, \tag{7}$$

where S is the entropy of the system, k_B is the Boltzmann factor (which can be regarded as the thermodynamic unit of measurement of entropy), and Ω is the number of distinct ways of arranging the constituent particles consistent with the overall macroscale properties of the system. The Boltzmann entropy has two fundamental properties: (1) non-decrease, which means that when no heat enters or leaves the system the entropy cannot decrease, and (2) additivity, which means that that the entropy of two systems taken together is the sum of the separate entropies. In nanosystems, however, it is impossible to completely satisfy both properties.

Nonextensive thermodynamics is based on a new statistics introduced by Tsallis [21]. Tsallis statistics can be regarded as a modification of generalized Boltzmann–Gibbs statistical mechanics by relaxation of extensive properties to include non-extensive features. This can be seen as follows. In Tsallis thermodynamics, the Tsallis entropy is defined as [21,28]:

$$S = \frac{1 - \sum_{j}^{\Omega} p_j^q}{q - 1} \quad (q \in \mathbb{R}), \tag{8}$$