# Theoretical prediction of thermodynamic equilibrium constants of chemical reactions in water

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## Abstract

In this work we characterize the thermodynamics of two simple chemical reactions in water. Applying the quasi-gaussian entropy theory to the molecular dynamics calculations, we model the equilibrium constant and its temperature dependence along the typical water isochore. Such a theoretical–computational approach could be useful to predict the optimal condition for chemical reactions in condensed phase at a very low computational cost.
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## 1. Introduction

Understanding and predicting the thermodynamics of chemical reactions in condensed phase at different conditions has always represented a 'holy grail' for chemists. The possibility of virtually handling the matter is in fact extremely appealing not only intrinsically but also for many applications ranging from organic synthesis to industrial processes. However a reliable modelling of liquid solutions has been for many years extremely challenging and only in the last decades has become computationally accessible [1]. In this respect many efforts have been done for the calculation of excess partial molar properties and in particular the excess chemical potential [2,3], which is the key parameter for addressing the whole chemical thermodynamics in liquid solution. In a number of recent publications [4,5], we have proposed a rigorous and relatively low-cost approach for evaluating the whole statistical mechanics and thermodynamics of highly diluted liquid solutions in the framework of The Quasi Gaussian Entropy Theory (QGE) [6]. The most appealing feature of this approach, whose computational procedure is essentially based on classical molecular dynamics (MD) simulations of a box of one solute molecule embedded in a meaningful number of solvent molecules, is the possibility of evaluating the excess chemical potential variation accompanying whatever chemical reaction at whatever temperature.

In this paper we have applied this method for studying the thermodynamics of two simple chemical reactions in water solution which are of a certain fundamental and practical interest. The first one is the so-called water–gas shift reaction.

$$CO_{(aq)} + H_2O_{(aq)} \rightarrow CO_{2(aq)} + H_{2(aq)} \qquad (1)$$
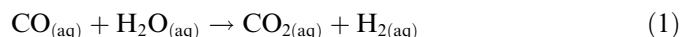
which, because of its importance, has been extensively studied by several investigators in particular at non-

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standard conditions (e.g. supercritical and near-supercritical conditions) [7,8].

The second one is the $S_N2$ hydrolysis of chloromethane which is a benchmark reaction both for synthetic organic chemistry and for mechanistic studies

$$CH_3Cl_{(aq)} + OH^-_{(aq)} \rightarrow CH_3OH_{(aq)} + Cl^-_{(aq)} \qquad (2)$$
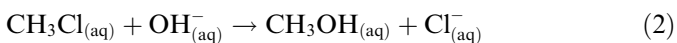
This paper is organized as follows. In the first part, we briefly describe the essential features of the theoretical approach. In the methodological section the technical details are provided and, finally, the results and the conclusions are illustrated.

## 2. Theoretical section

The large body of QGE theory for the evaluation of statistical mechanics and thermodynamics of highly diluted solutions is described elsewhere [4–6,9–17]. In this paper we only report the essential theoretical features utilized in the present investigation. Let us consider a solution containing $N$ highly diluted solute molecules and $N_s$ solvent molecules. As shown in previous papers [5,6], for highly diluted solutes their partial molar thermodynamics can be fully obtained by a solution containing a single solute molecule embedded in $n_s = N_s/N$ solvent molecules. The excess Helmholtz free energy of such a system, i.e. the free energy variation between the actual system and its reference condition where the total potential energy (the excess energy $\mathcal{U}'$) has been removed, [6] is

$$A'(T) = n_s a'_s + a' \qquad (3)$$

where $a'_s$ and $a'$ are the partial molecular excess free energies of the solvent and solute, respectively. The partial molecular excess free energy is obviously related to the excess chemical potential $\mu'$ according to the relations: [5]

$$a'_s = \mu'_s - p'v_s \qquad (4)$$
$$a' = \mu' - p'v \qquad (5)$$

where $p'$, $v$ and $v_s$ stand for the excess pressure and the partial molecular volume of the solute and of the solvent, respectively. The excess (Helmholtz) free energy of the system can be written as [5]

$$A'(T) = kT \ln\langle e^{\beta\mathcal{U}'}\rangle - kT \ln\epsilon \qquad (6)$$

where $k \ln\epsilon$ is the confinement term taking into account the presence of effectively or virtually unaccessible phase space regions [5,6], which can be evaluated as indicated at the end of this section. The first term in Eq. (6), according to QGE theory, can be calculated assuming a 'quasi-Gaussian' distribution of the excess energy $\mathcal{U}'$. In particular, it has been shown [5,6,9,10,12–16] that one of the simplest 'quasi-Gaussian' distribution, i.e. the Gamma distribution, provides a simple and accurate model for treating fluid-state thermodynamics.

Hence, for Gamma state thermodynamics [5] we have

$$n_s a'_s + a' = U'_0 - T_0 C'_{V0} \Lambda(T) - kT \ln\epsilon \qquad (7)$$
$$\Lambda(T) = \frac{1}{\delta_0} + \frac{T}{T_0\delta_0^2} \ln\{1 - \delta(T)\} \qquad (8)$$
$$\delta(T) = \frac{T_0\delta_0}{T(1-\delta_0) + T_0\delta_0} \qquad (9)$$

where $U'_0 = U'(T_0)$ and $C'_{V0} = C'_V(T_0)$ represent the excess internal energy and heat capacity of the system of $n_s$ solvent molecules and one solute molecule at the reference temperature $T_0$ and $\delta_0$ is a dimensionless intensive property [6] independent of the temperature, that in the case of high dilution, can be directly determined by the solvent.

Subtracting the solvent partial excess free energy from Eq. (7) it immediately follows the solute excess chemical potential [5]

$$\mu' = u'_0 - c'_{V0}T_0\Lambda(T) - kT \ln\bar\epsilon + p'v \qquad (10)$$

where $u'_0$ and $c'_{V0}$ are the solute partial molecular excess internal energy and heat capacity evaluated at the reference temperature $T_0$, and $-kT \ln\bar\epsilon$ represents the partial solute molecular excess free energy due to the confinement.

It is therefore clear that according to this model it is possible to derive the whole statistical mechanics and thermodynamics of a highly dilute solution by using MD simulations of a single solute embedded in $n_s$ solvent molecules.

The parametrization of the model, Eq. (10), may be obtained considering the confined excess chemical potential $\mu^*$ and Helmholtz free energy $A^*$ via

$$\mu^* = \mu' + kT \left(\frac{\partial \ln\epsilon}{\partial n}\right)_{V,n_s} = \left(\frac{\partial A^*}{\partial n}\right)_{V,T,n_s} = \Delta A^* \qquad (11)$$
$$A^* = A' + kT \ln\epsilon \qquad (12)$$

where $\Delta A^*$ is the difference between the confined excess Helmholtz free energies of the solute–solvent system and of the pure solvent one, at fixed volume, and $n$ is the solute molecular number which can be used as a continuous variable given the macroscopic nature of the thermodynamic system considered.

From Eqs. (7), (10) and (11) we then have

$$\mu^* = u'_0 - c'_{V0}T_0\Lambda(T) + p^*v \qquad (13)$$
$$p^* = p' - \xi T \qquad (14)$$
$$\xi = k \left(\frac{\partial \ln\epsilon}{\partial V}\right)_{n,n_s} \qquad (15)$$

where $\Lambda(T)$, $p^*$, $p'$, $\xi$, being intensive properties, are given by the Gamma state obtained by the pure solvent simulations [5].

Therefore by fitting $\Delta A^*$ as provided by MD simulation with Eq. (13), we can evaluate $u'_0$, $c'_{V0}$ and the partial molecular volume $v$.

The confinement term, $kT \ln\epsilon$ may be associated with hard body excluded volume. In our previous studies [4,5] we have shown that its calculation can be relatively straightforward in the case of simple spherical solutes by