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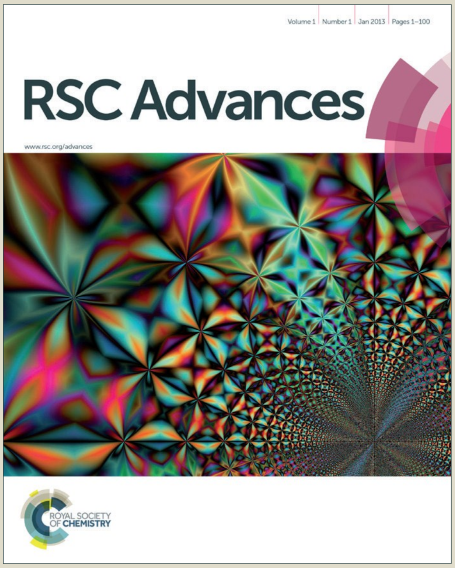

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Solvation Thermodynamics: Two formulations and some misunderstandings

by

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ABSTRACT

Conventional (Fowler-Guggenheim) and Ben-Naim's formulations of solvation thermodynamics are analyzed in parallel, emphasizing their differences and stressing their interconnections. The pivotal equations relating the thermodynamic functions in both theories are derived. Connections with Pierotti-Abraham's cavity-interaction partition model are also contemplated in detail. Evidence is presented that misinterpretations of some of the derived equations lead to wrong estimates of solvation thermodynamic quantities that have been detected in the output of some of the most popular quantum chemistry software packages (Gaussian 09).

Keywords*: solvation thermodynamics, free solvation energies, solvation enthalpies, solvation internal energies, conventional chemical potential, pseudochemical potential.*

1. Introduction.

Prediction of solvation free energies, ΔG^{sol}, is a subject of great interest in different fields like chemistry (thermodynamics[1] and kinetics[2]), biophysics and biochemistry[3], or drug design[4], among others. Particularly relevant and fruitful has been the use of solvation models in the study of systems of paramount importance in molecular biology by means of molecular simulations.[5]

In their classical text,[6] first published in 1939, Fowler and Guggenheim presented the theory of liquids and solutions of non-electrolytes. In particular, these authors derived the properties of ideal dilute solutions by regarding them as special class of regular solutions.

On the other hand, Ben-Naim published in 1978 a groundbreaking contribution,[7] where solvation thermodynamics was developed at the molecular level in a nonconventional manner by redefining the concept of solvation and by introducing an auxiliary quantity, the pseudochemical potential (PCP, μ^*), which in the case of a two-component solution represents the change in the Gibbs energy caused by the addition, at a fixed position, of one solute molecule to the solution while keeping T, P and the number of solvent molecules unchanged. The conventional definition of the chemical potential (CP, μ), did not include any restriction to the location of the additional solute molecule. Ben-Naim has emphasized that this apparently subtle difference allowed for a much more genuine definition of the solvation Gibbs energy and its derived thermodynamic quantities.

Indeed, Ben-Naim has shown[1,7] that classical statistical thermodynamics leads to a very powerful relationship between both chemical potentials CP and PCP, namely, $\mu = \mu^* + kT\log\{\rho\cdot\Lambda^3\}$ (see next sections), which is the pivotal expression of his novel formulation of solvation thermodynamics.

Ben-Naim has also stressed that while the conventional expressions for CP, like those found in the Fowler-Guggenheim text,[6] only apply to very dilute solutions of solutes, the above mentioned equation is valid for any kind of molecule in any fluid mixture, and for any concentration. It is this general character that has contributed greatly to the present popularity of Ben-Naim's formulation which is being widely used in the recent literature.

While both formulations lead to correct results, they must be handled and interpreted within their own context because, as shown in this paper, both the meaning and the numerical values of conventional (Fowler-Guggenheim's) and Ben-Naim's thermodynamic magnitudes are different from each other.

Unfortunately, as usually happens, the coexistence of different formulations brings along the possibility of some degree of confusion related to the fact that different magnitudes can receive the same denomination, thus causing misunderstandings and misinterpretations. Indeed, as will be shown in this article, it is not uncommon to find wrong values of solvation thermodynamic quantities in the outputs of some of the most popular quantum chemical software packages. We do believe that a substantial part of the existing confusion can be avoided by carrying out an elemental parallel analysis of the conventional (Fowler-Guggenheim) and Ben-Naim's formulations, making clear their differences and emphasizing their interconnections.

The lack in the literature of any in-depth study where the equations connecting both formulations are derived in a systematic manner, prompted us to tackle the present research. As will be shown in this paper, our analysis helps to prevent potential confusions arising from the simultaneous references in the literature to both formulations. In particular, we will focus on the solvation thermodynamic functions of a solute in solution as computed by means of continuum solvation medium models. We will present evidence that some packages of software, which are employed as a reference software in quantum calculations by a large number of researchers, do not employ the correct expression for computing neither the partial enthalpies ($\overline{H}_s^{sol}$) nor the partial entropies ($\overline{S}_s^{sol}$) of a solute in solution. Our aim is to highlight, with the help of a chosen specific example, the fact that a parallel analysis of the conventional and Ben-Naim's theories of solvation can be very helpful in computing and interpreting, in a proper manner, the solvation thermodynamic functions.

The article is organized as follows: We start in section 2 from Fowler-Guggenheim's formulas for the Helmholtz free energies of an ideal gas and an ideal dilute solution, and we derive mathematical expressions for the rest of thermodynamic functions. In section 3, we start from Ben-Naim's equation for the chemical potential of a molecule in gas-phase and in solution, and we obtain mathematical expressions to compute the thermodynamic functions in this alternative formulation. Appropriate formulas to compute conventional and Ben-Naim's solvation thermodynamic functions are deduced in section 4. Their relations to Ben-Naim's solvation ρ-process and x-process as well as to Pierotti-Abraham's solvation functions (widely employed in experimental studies for the prediction of thermodynamic solution parameters) are analyzed in some detail, thus allowing for a much deeper understanding about the meaning of solvation magnitudes in both formulations. The pivotal equations connecting the conventional and Ben-Naim's solvation thermodynamic functions are also obtained. Finally, in section 5 we present a numerical application of the equations derived in previous sections, showing how the analysis carried out throughout this paper, helps to uncover errors detected in the output of some of the most popular quantum chemistry software.

2. Thermodynamic functions in Fowler-Guggenheim's formulation.

Throughout this article, both molecular and molar units will be employed, as indicated. The notation used is the traditional one found in the literature. A slightly more elaborated notation is chosen for denoting the different standard states in order to stress their meaning.

2.1 Ideal gases.

The Helmholtz free energy of an ideal gas can be written as[6]

$$F^g = NE_0^g - NkT\log\left[\frac{(2\pi mkT)^{3/2}}{h^3}\frac{V^g}{N}\right] - NkT - NkT\log j^g(T) \qquad (1)$$

where N is the number of gas molecules of mass m occupying the volume V^g at temperature T, k is Boltzmann's constant, h Planck's constant, and $j^g(T)$ denotes the partition function for all the internal degrees of freedom of the solute in gas-phase. E_0^g represents the solute electronic energy. This term shifts the origin of energies to allow for a direct comparison with the quantum packages' outputs (see

Tables 2 and 3). It is not included in Fowler-Guggenheim’s original formulation. Superscripts “g” and “sol” indicate gas-phase and solution, respectively. The symbol “log” stands for natural logarithm.

From eq (1), one gets

$$\overline{F}^{g} = \left(\frac{\partial F^{g}}{\partial N}\right)_{P,T} = E_0^{g} - kT\log\left[\frac{(2\pi mkT)^{3/2}V^{g}}{h^{3}}\right] - kT + kT\log N - kT\log j^{g}(T) \qquad (2)$$

$$\mu^{g} = \left(\frac{\partial F^{g}}{\partial N}\right)_{V,T} = E_0^{g} - kT\log\left[\frac{(2\pi mkT)^{3/2}V^{g}}{h^{3}}\right] + kT\log N - kT\log j^{g}(T) \qquad (3)$$

On the other hand, from eq (3)

$$\overline{S}^{g} = -\left(\frac{\partial \mu^{g}}{\partial T}\right)_{P} = -k\log\{\rho^{g}\Lambda^{3}/j^{g}(T)\} + \frac{5}{2}k + E_{\mathrm{int}}^{g}/T \qquad (4)$$

where $\Lambda = h/(2\pi mkT)^{1/2}$, ρ^g = N/V^g is the number density and $kT(\partial\log j^{g}(T)/\partial T)_{P} = kT(\partial\log j^{g}(T)/\partial T) = E_{\mathrm{int}}^{g}/T$. In classical systems the momentum partition function Λ^3 is independent of the environment, whether it is a gas or a liquid phase.[1]

Eq (3) can be written as

$$\mu^{g} = E_0^{g} - kT\log kT + kT\log\{\Lambda^{3}/j^{g}(T)\} + kT\log P \qquad (5)$$

It should be recalled at this point that the adoption of a specific standard state represents the choice of a given value for the molar volume (or number density) appearing in the equations for the calculations of chemical potential and partial molecular (molar) entropies (their translational part). We can define the standard partial Gibbs free energy and entropy of solute as

$$\mu^{o,g} = E_0^{g} + kT\log\{\Lambda^{3}/[kT\cdot j^{g}(T)]\} \qquad (6)$$

and

$$\overline{S}^{o,g} = -k\log\{\Lambda^3/[kT\cdot j^g(T)]\} + \frac{5}{2}k + E^g_{\text{int}}/T \qquad (7)$$

where the standard state “o,g” corresponds to an hypothetical ideal gas at P = 1 bar (1 atm). Thus, using molar units and standard conditions (T = 298.15 K), we have RT/1 bar = V^g_m = 24.5 L·mol^{-1}.[8,9] Let us symbolize such an standard state by: {g-ideal, P = 1 bar; V_m = 24.5 L·mol^{-1}}. In some occasions (see section 5), a concentration scale standard state is considered. Under such circumstances eqs (6) and (7) become

$$\mu^{\oplus,g} = E^g_0 + kT\log\{\rho^{\oplus}\cdot\Lambda^3/j^g(T)\} \qquad (8)$$

$$\overline{S}^{\oplus,g} = -k\log\{\rho^{\oplus}\cdot\Lambda^3/j^g/T)\} + \frac{5}{2}k + E^g_{\text{int}}/T \qquad (9)$$

where $\rho^{\oplus,g}$ is the number density defining the standard state “$\oplus, g$”. For an ideal gas at P = 1 bar and 298.15 K we have $\rho^{\oplus,g} = 1bar/RT = 1/24.5mol\cdot L^{-1} = 0.041M$. Let us symbolize such an standard state by {g-ideal, $\rho^g = 0.041M$; V_m = 24.5 L·mol^{-1}} or in general {g-ideal, ρ^g; V_m}, when the value of ρ^g is different from 0.041M (P ≠ 1bar).

It should be noted that standard states “o,g” and “$\oplus, g$”are fully equivalent when $\rho^{\oplus,g} = \rho^g = 0.041M$ [i.e. $\mu^{\oplus,g} = \mu^{o,g}$ and $\overline{S}^{\oplus,g} = \overline{S}^{o,g}$; see eqs (6)-(9)].

It is straightforward to show that eqs (3) and (2) lead, respectively, to

$$\overline{H}^g = -T^2\left(\frac{\partial\mu^g/T}{\partial T}\right)_P = E^g_0 + kT^2\alpha^g_p + \frac{3}{2}kT + E^g_{\text{int}} = E^g_0 + \frac{5}{2}kT + E^g_{\text{int}} \qquad (10)$$

and

$$\overline{U}^g = \overline{H}^g - P\overline{V}^g = -T^2\left(\frac{\partial\overline{F}^g/T}{\partial T}\right)_P = E^g_0 + \frac{3}{2}kT + E^g_{\text{int}} \qquad (11)$$

where, for an ideal gas, the thermal expansion coefficient $\alpha_p^g = (\partial V^g / \partial T)_P / V^g = 1/T$.

2.2 Ideal dilute solutions.

According to Fowler and Guggenheim,[6] the Helmholtz free energy of an ideal dilute solution of a solute, “s”, in a solvent, “l”, (solute-solvent assembly) can be given by

$$F^{sol} = F_l(T, V^{sol} - N_s \overline{V}_s^{sol}, N_l) + N_s\left[E_{0,s}^{sol} - \chi_{ls} + kT\log\{\Lambda_s^3 / V^{sol}\} - kT + kT\log N_s - kT\log j_s^{sol}(T)\right] \quad (12)$$

where N_s solute molecules, having a constant potential energy $-\chi_{ls}$ (representing the solute-solvent interaction), move freely in a region of volume V^{sol}. The N_l solvent molecules are occupying the $V_l^{sol} = V^{sol} - N_s \overline{V}_s^{sol}$ volume available and make a contribution $F_l(T, V^{sol} - N_s \overline{V}_s^{sol}, N_l)$ to the total Helmholtz free energy. $j_s^{sol}(T)$ represents the contribution of the internal motions of the solute molecules and $E_{0,s}^{sol}$ the solute electronic energy, the latter not included in Fowler-Guggenheim’s original formulation.

From eq (12), one obtains for the solute CP

$$\mu_s^{sol} = \left(\frac{\partial F^{sol}}{\partial N_s}\right)_{T,V,Nl} = \left(\frac{\partial F_l}{\partial N_s}\right)_{T,V,Nl} + E_{0,s}^{sol} - \chi_{ls} + kT\log\{\Lambda_s^3 / V^{sol}\} + kT\log N_s - kT\log j_s^{sol}(T) \quad (13)$$

It is easy to show (see Appendix A) that $(\partial F_l / \partial N_s)_{T,V,Nl} \approx P\overline{V}_s^{sol}$, and then

$$\mu_s^{sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_s^{sol} + kT\log\{\Lambda_s^3 / V^{sol}\} + kT\log N_s - kT\log j_s^{sol}(T) \quad (14)$$

According to Pierotti,[8] $-\chi_{ls}$ is the molar potential energy of the solute in the solution relative to infinite separation, P the hydrostatic pressure, and

$-\chi_{ls} + P\overline{V}_s^{sol}$ represents the reversible work required to introduce one solute molecule into a solution of concentration N_s/V^{sol} (see in the next section its relation to Ben-Naim's W(s|l) coupling work of solute to the system).[1,7] As remarked by Fowler and Guggenheim,[6] $P\overline{V}_s^{sol}$ is usually negligible at ordinary pressures (see below) and it is not considered when calculating the derivative with respect to T. On the other hand, Fowler and Guggenheim also mention[6] that the term $-\chi_{ls}$ may depend on T, but in this work (see section 5), $-\chi_{ls}$ [or W(s|l); see eqs (29) and (30) in the next section] has been estimated through the Gaussian 09 (G09) package of programs,[10] by adopting the generalized Born approximation and the formalism of atomic surface tensions and the solvent-accesible surface areas as a model for the solvent (including cavity, dispersion and solvent reorganization energy contributions), where no dependence on T is considered (the T dependence inherent to the dielectric constant[6] is not taken into account). From the operational viewpoint, the above implies that the term $[\partial(-\chi_{ls} + P\overline{V}_s^{sol})/\partial T]_{P,Nl,Ns}$, which contributes to $\overline{H}_s^{sol}$ through $-T^2\left(\frac{\partial\mu_s^{sol}/T}{\partial T}\right)_{P,Nl,Ns}$ and to $\overline{S}_s^{sol}$ through $-\left(\frac{\partial\mu_s^{sol}}{\partial T}\right)_{P,Nl,Ns}$, becomes zero. It is straightforward to confirm that the terms $[\partial(-\chi_{ls} + P\overline{V}_s^{sol})/\partial T]_{P,Nl,Ns}$ appearing in the expressions for $\overline{H}_s^{sol}$ and $\overline{S}_s^{sol}$ when the T dependence of $-\chi_{ls}$ and $P\overline{V}_s^{sol}$ terms is taken into consideration, cancel each other out when the corresponding μ_s^{sol} magnitude is computed from $\overline{H}_s^{sol} - T\overline{S}_s^{sol}$. In other words, the expression found for μ_s^{sol} [i.e. eq (14)] does not depend on whether or not the T dependence of $-\chi_{ls} + P\overline{V}_s^{sol}$ has been assumed. As will be remarked in section 4, the assumption that $-\chi_{ls} + P\overline{V}_s^{sol}$ does not exhibit T dependence is not, in general, a very accurate approach.

Consequently, from eq (14) we find

$$\overline{S}_s^{sol} = -\left(\frac{\partial \mu_s^{sol}}{\partial T}\right)_{P,Ns,Nl} = -k\log \rho_s^{sol}\Lambda_s^3 / j_s^{sol}(T) + \frac{3}{2}k + kT\alpha_p^{sol} + E_{\mathrm{int},s}^{sol}/T \qquad (15)$$

where $\alpha_p^{sol} = (\partial V^{sol}/\partial T)_{P,Ns,Nl}/V^{sol} \approx (\partial V^l/\partial T)_P/V^l = \alpha_p^l$ is the thermal expansion coefficient of the solvent and $kT(\partial \log j_s^{sol}(T)/\partial T)_{P,Ns,Nl} = kT(\partial \log j_s^{sol}(T)/\partial T) = E_{\mathrm{int},s}^{sol}/T$.

On the other hand, eq (14) can be written as

$$\mu_s^{sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_s^{sol} + kT\log\{\Lambda_s^3/j_s^{sol}(T)\} + kT\log N_s/N_T - kT\log(V^{sol}/N_T) \qquad (16)$$

where $N_T = N_s + N_l$ is the total number of molecules in solution (solute plus solvent).

Now, for a ideal dilute solution where $N_l/N_T \to 1$ and $V^{sol} \to V_l$ $(V^{sol}/N_T \to V_l/N_l = V_{l,Nl})$ one gets

$$\mu_s^{sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_s^{sol} + kT\log\{\Lambda_s^3/[j_s^{sol}(T)\cdot V_{l,Nl}]\} + kT\log x_s \qquad (17)$$

where $V_{l,Nl}$ represents the pure solvent molecular volume (inverse of the pure solvent number density). We can now define the standard partial Gibbs free energy of the solute (conventional standard CP) as

$$\mu_s^{o,sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_s^{sol} + kT\log\{\Lambda_s^3/[j_s^{sol}(T)\cdot V_{l,Nl}]\} \qquad (18)$$

Similar arguments applied to eq (13) lead to the following equation for the standard partial entropy of the solute

$$\overline{S}_s^{o,sol} = -k\log\{\Lambda_s^3/[j_s^{sol}(T)\cdot V_{l,Nl}]\} + \frac{3}{2}k + kT\alpha_p^l + E_{\mathrm{int},s}^{sol}/T \qquad (19)$$

The standard state “o,sol” (mole fraction scale) corresponds to an hypothetical ideal solution (fulfilling Henry’s law) at T and P of the solution, where the solute mole fraction is the unity ($x_s = 1$). Thus, using molar units and standard conditions for $V_{l,Nl}$, we have $V_{l,m} = 0.018$ L·mol^{-1}.[8,9] Let us symbolize such an standard state by: {sol-Henry, $x_s \rightarrow 1$; $V_m = 0.018$ L·mol^{-1}}. Figure 1 collects, in a p_{solute}-x_{solute} graphic, the different standard states adopted for the solute throughout the present work.

In order to emphasize that eqs (14) and (15) correspond to a concentration scale standard state, they can be rewritten as

$$\mu_s^{\oplus,sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_s^{sol} + kT\log\{\rho_s^{\oplus,sol}\cdot\Lambda_s^3 / j_s^{sol}(T)\} \tag{20}$$

$$\overline{S}_s^{\oplus,sol} = -k\log\{\rho_s^{\oplus,sol}\cdot\Lambda_s^3 / j_s^{sol}(T)\} + \frac{3}{2}k + kT\alpha_p^l + E_{\text{int},s}^{sol} / T \tag{21}$$

where $\rho_s^{\oplus,sol}$ is the number density defining the standard state "$\oplus,sol$". It corresponds to an hypothetical ideal solution (fulfilling Henry's law) at T and P of the solution, where the solute concentration is $\rho_s^{\oplus,sol}$. Let us symbolize such an standard state: {sol-Henry, ρ_s^{sol}; V_m}, for a solution of concentration $\rho_s^{\oplus,sol} = \rho_s^{sol}$

As mentioned in section 2.1, we need to introduce this additional standard state here to analyze the G09 output in section 5.

On the other hand, from eq (14)

$$\overline{H}_s^{sol} = -T^2\left(\frac{\partial \mu_s^{sol}/T}{\partial T}\right)_{P,Ns,Nl} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_s^{sol} + \frac{3}{2}kT + kT^2\alpha_p^l + E_{\text{int},s}^{sol} \tag{22}$$

It is important to stress at this point that while $P\overline{V}_s^{sol}$ arises from the first term contribution (F_l) to the solution Helmholtz free energy (F^{sol}) in eq (12), $kT^2\alpha_p^l$ comes from the term $-N_s kT\log V^{sol}$. Both contributions are in most cases negligible (for instance, using molar units and standard conditions, in the case of solute water in water solution: $RT^2\alpha_p^{l,water} = 4.5{\cdot}10^{-2}\,kcal{\cdot}mol^{-1}$ and $P\overline{V}_{water}^{sol} = 4.4{\cdot}10^{-4}\,kcal{\cdot}mol^{-1}$), but according to Fowler and Guggenheim,[6] they should not be omitted until the final stage to avoid apparent inconsistencies.

On the other hand, from eq (22) we obtain

$$\overline{U}_s^{sol} = \overline{H}_s^{sol} - P\overline{V}_s^{sol} = E_{0,s}^{sol} - \chi_{ls} + \frac{3}{2}kT + kT^2\alpha_p^l + E_{\text{int},s}^{sol} \tag{23}$$

3. Thermodynamic functions in Ben-Naim's formulation.

Ben-Naim starts from the relation between the CP of a molecule s, μ_s^{φ}, in gas-phase (φ=g) or in solution (φ=sol), and the corresponding PCP, $\mu_s^{*,\varphi}$ [1,11]

$$\mu_s^{\varphi} = \mu_s^{*,\varphi} + kT\log\{\rho_s^{\varphi}\Lambda_s^3\} \tag{24}$$

Both μ_s and μ_s^* represent the change in Gibbs energy caused by the addition of one molecule s to the system keeping T, P, and the number of other type of molecules present in the system (if any) unchanged. While for μ_s^* the center of mass of the added molecule is placed at a fixed position, in the case of μ_s the new molecule is released to wander in the entire volume.

According to Ben-Naim[1]

$$\mu^{*,g} = E_0^g + W(s\,|\,g) - kT\log j^g(T) = E_0^g - kT\log j^g(T) \tag{25}$$

$$\mu_s^{*,sol} = E_{0,s}^{sol} + W(s\,|\,l) - kT\log j_s^{sol}(T) \tag{26}$$

where the contribution of the electronic energy of solute, $E_{0,s}^{\varphi}$, has been included.

W(s|x), Ben-Naim's coupling work, is the average Gibbs energy of interaction of s with its entire surroundings (other gas molecules, x = g, or solvent molecules, x = l). Of course, for an ideal gas, the coupling work, W(s|g), is zero. Note that in the gas phase, where only one type of molecules is present, the subscript "s" becomes unnecessary and has been eliminated, as we also did in the case of Fowler-Guggenheim's formulation (see section 2).

Equations (24), (25) and (26) lead to

$$\mu^g = E_0^g + kT\log\{\rho^g \Lambda^3 / j^g(T)\} \tag{27}$$

which, of course, matches eq (5) ($\rho^g = N_s/V^g = P/kT$), and

$$\mu_s^{sol} = E_{0,s}^{sol} + W(s\,|\,l) + kT\log\{\rho_s^{sol} \Lambda_s^3 / j_s^{sol}(T)\} \tag{28}$$

Comparison of eq (28) with eq (14) in Fowler-Guggenheim's formulation ($\rho_s^{sol} = N_s/V^{sol}$) allows one to conclude that

$$W(s\,|\,l) = -\chi_{ls} + P\overline{V}_s^{sol} \tag{29}$$

Thus, Ben-Naim's coupling work of the solute s to the system, corresponds to Fowler-Guggenheim's reversible work required to introduce one solute molecule into the solution (at one fixed position).[12,13] Indeed, Ben-Naim describes in detail how the solvation of any solute in any solvent can always be decomposed into two parts: creation of a suitable cavity ($P\overline{V}_s^{sol}$) and then turning on the other parts of the solute-solvent interaction ($-\chi_{ls}$).[12,13] As $P\overline{V}_s^{sol}$ is usually negligible (see section 2.2), we have

$$W(s\,|\,l) \approx -\chi_{ls} \tag{30}$$

Ben-Naim's definition of μ_s^* can be generalized to any partial molecular thermodynamic function, $\overline{X}_s^*$: it will represent the change in the particular function considered due to the addition of one molecule of solute at a fixed position in the system. Let us obtain explicit expressions for Ben-Naim's partial molecular entropies, enthalpies and internal energies.

Bearing in mind that $\overline{S}_s = -(\partial\mu_s / \partial T)_P$, one gets from eqs (25)-(28)

$$\overline{S}^{g} = \overline{S}^{*,g} - k\log\{\rho^{g}\Lambda^{3}\} + \frac{3}{2}k + kT\alpha_{p}^{g} \tag{31}$$

$$\overline{S}_{s}^{sol} = \overline{S}_{s}^{*,sol} - k\log\{\rho_{s}^{sol}\Lambda_{s}^{3}\} + \frac{3}{2}k + kT\alpha_{p}^{sol} \tag{32}$$

where, as already mentioned above, for an ideal gas, $\alpha_{p}^{g} = 1/T$, and for an ideal dilute solution, $\alpha_{p}^{sol} \approx \alpha_{p}^{l}$ (thermal expansion coefficient of the solvent). Combination of eqs (31) and (4), and eqs (32) and (15) leads to the following explicit expression for Ben-Naim's partial molecular entropies of the solute in gas-phase and in solution

$$\overline{S}_{s}^{*,\varphi} = k\log j_{s}^{\varphi}(T) + E_{\mathrm{int},s}^{\varphi}/T \qquad (\varphi = \mathrm{g, sol}) \tag{33}$$

The solute partial molecular enthalpies $\overline{H}^{g}$ and $\overline{H}_{s}^{sol}$ are obtained from $\overline{H}_{s}^{\varphi} = \mu_{s}^{\varphi} + T\overline{S}_{s}^{\varphi}$, using equations (24), (31) and (32)

$$\overline{H}^{g} = \mu^{*,g} + T\overline{S}^{*,g} + \frac{3}{2}kT + kT^{2}\alpha_{p}^{g} = \overline{H}^{*,g} + \frac{5}{2}kT \tag{34}$$

$$\overline{H}_{s}^{sol} = \mu_{s}^{*,sol} + T\overline{S}_{s}^{*,sol} + \frac{3}{2}kT + kT^{2}\alpha_{p}^{l} = \overline{H}_{s}^{*,sol} + \frac{3}{2}kT + kT^{2}\alpha_{p}^{l} \tag{35}$$

Although rather obvious, it is important to stress at this point that $kT^{2}\alpha_{p}^{g} \neq kT^{2}\alpha_{p}^{l}$. Indeed, in the case of water, for instance, using molar units and standard conditions, $RT^{2}\alpha_{p}^{g,water} = 0.59 kcal{\cdot}mol^{-1}$ and $RT^{2}\alpha_{p}^{l,water} = 4.5{\cdot}10^{-2} kcal{\cdot}mol^{-1}$. While the latter can be neglected without appreciable lost of accuracy for most of applications, the former becomes of the order of standard state corrections and should be taken into consideration.

A second important remark is that for an ideal gas, the term kT that must be added to $\overline{U}_{s}^{g}$ to get $\overline{H}_{s}^{g}$ (see eqs 10-11), arises from the contributing term $kT^{2}\alpha_{p}^{g}$. Since $kT = P\overline{V}^{g}$, one can write $\overline{H}^{g} = \overline{U}^{g} + P\overline{V}^{g}$. In other words, for an ideal gas $kT^{2}\alpha_{p}^{g} = P\overline{V}_{s}^{g}$. In sharp contrast, for the case of a solute in solution, the terms

$kT^2\alpha_p^l$ and $P\overline{V}_s^{sol}$ are different contributions to $\overline{H}_s^{sol}$ [see eq (22)], as stressed in the previous section.

The above points, although trivial, should be taken into account in order to avoid misunderstandings leading to some serious mistakes detected in the literature. In particular, we will show in section 5 that some rather popular packages of software (for instance, the G09 package of programs),[10] with a huge number of users, do contribute to create confusion in this regard.

It is easy to show that eqs (25) and (34) with $\overline{S}^{*,g} = -(\partial\mu^{*,g}/\partial T)_{P,Nl,Ns}$, within Ben-Naim's formulation, lead to eq (10) in Fowler-Guggenheim's formulation. Similarly, eqs (26), (29) and (35) with $\overline{S}_s^{*,sol} = -(\partial\mu_s^{*,sol}/\partial T)_{P,Nl,Ns}$, result in eq (22). Consistency between both formulations is thus, once again, confirmed.

Combination of eqs (34) and (10) on one hand, and eqs (35), (29) and (22) on the other hand, leads to explicit expressions for Ben-Naim's partial molecular enthalpies of the solute in gas-phase and in solution,

$$\overline{H}^{*,g} = E_0^g + E_{\text{int}}^g \tag{36}$$

$$\overline{H}_s^{*,sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_s^{sol} + E_{\text{int},s}^{sol} \tag{37}$$

In order to get the expressions for Ben-Naim's partial molecular internal energies, we start from Ben-Naim's expression for the partial molecular volume[1]

$$\overline{V}_s^{\varphi} = \overline{V}_s^{*,\varphi} + kT\beta_T^{\varphi} \qquad (\varphi = \text{g, sol}) \tag{38}$$

where $\beta_T^{\varphi} = (\partial V^{\varphi}/\partial P)_T / V^{\varphi}$ is the isothermal compressibility coefficient, that for an ideal gas reduces to 1/P and for a liquid phase becomes so small that can be safely neglected.[1]

Bearing in mind that $\overline{H}^{*,\varphi} = \overline{U}^{*,\varphi} + P\overline{V}^{*,\varphi}$ (φ = g, sol), equations (36)-(38) lead to

$$\overline{U}^{*,g} = E_0^g + E_{\text{int}}^g \tag{39}$$

$$\overline{U}_s^{*,sol} = E_{0,s}^{sol} - \chi_{ls} + E_{\text{int},s}^{sol} \tag{40}$$

4. Solvation thermodynamic functions.

In the previous section we have derived explicit expressions for Ben-Naim's solute partial molecular properties $\overline{X}_s^{*,\varphi}$. The relevance of such magnitudes lies in the fact that the solvation thermodynamic functions can be defined in a very convenient way in terms of Ben-Naim's $\overline{X}_s^{*,\varphi}$ (see below).

In Fowler-Guggenheim's formulation, the solvation Gibbs free energy is obtained from eqs (6) and (18)

$$\Delta G^{o,sol} = \mu_s^{o,sol} - \mu_s^{o,g} = E_{0,s}^{sol} - E_0^g - \chi_{ls} + P\overline{V}_s^{sol} + kT\log(V_m^g / V_{l,m}) \tag{41}$$

where we have used the fact that $kT/(1bar{\cdot}V_{l,Nl}) = RT/(1bar{\cdot}V_{l,m}) = V_m^g / V_{l,m}$. As stressed in section 2, according to the standard states employed in this formulation (see section 2),[8] V^g_m = RT/1bar is the molar volume of an ideal gas at P = 1 bar and T = 298.15 K (V^g_m = 24.5 L·mol^{-1}), and $V_{l,m}$ is the pure solvent molar volume ($V_{water,m}$ = 0.018 L·mol^{-1} for water solutions under standard conditions). As usual, we assume throughout this work that the thermal contributions from internal motions of the system (i.e. rotation and vibration) are very similar in gas-phase and in solution, thus cancelling each other out [$j^g(T) = j_s^{sol}(T)$ and $E^g_{int} = E^{sol}_{int,s}$]. Equation (41) is fully consistent with the works by Pierotti[8] and Abraham and Nasehzadeh[14] where solvation molar Gibbs free energies are computed as

$$\Delta G^{o,sol} = \overline{G}_{CAV} + \overline{G}_{INT} + RT\log(V_m^g / V_{l,m}) \tag{42}$$

with $\overline{G}_{CAV}$ and $\overline{G}_{INT}$ being the partial molar Gibbs energies associated with the creation of a cavity ($P\overline{V}_s^g$) and with the solute-solvent interactions when the solute is in the cavity ($-\chi_{ls}$), respectively. Solute electronic contribution $E_{0,s}^{sol}-E_0^g$ must be added to eq (42) to make it compatible with eq (41).

Equation (41) represents, within the conventional formulation of thermodynamics of solution, the energy involved in the transference of a solute between gas-phase in the standard state: (hypothetical gas ideal with P = 1 bar) whose chemical potential is $\mu_s^{o,g}$ [see eq (6)], and solution in the standard state: (hypothetical ideal dilute solution fulfilling Henry law with $x_{solute} \to 1$) whose chemical potential is $\mu_s^{o,sol}$ [see eq (18)].[14] It is the so-called "solvation x-process" in Ben-Naim's formulation. That is to say, $\Delta G(x-process)=\Delta G^{o,sol}$. In other words, Ben-Naim's x-process corresponds to Fowler-Guggenheim's solvation process.

Ben-Naim also defines what he denotes as the "solvation ρ-process", in which one molecule of solute is transferred from an ideal gas phase into an ideal solution (Henry's law) at fixed temperature and pressure and such that $\rho_s^{sol}=\rho^g$. Application of eqs (5) and (14) leads to

$$\Delta G(\rho-process)=(\mu_s^{sol}-\mu^g)_{\rho_s^l=\rho^g}=E_{0,s}^{sol}-E_0^g-\chi_{ls}+P\overline{V}_s^{sol}+kT\log\left(\frac{\rho_s^{sol}}{\rho^g}\right)_{\rho_s^{sol}=\rho^g}=$$

$$=E_{0,s}^{sol}-E_0^g-\chi_{ls}+P\overline{V}_s^{sol} \qquad (43)$$

Combination of eqs (25), (26), (29) and (43) leads to

$$\Delta G^{*,sol}=\mu_s^{*,sol}-\mu_s^{*,g}=\Delta G(\rho-process) \qquad (44)$$

where $\Delta G^{*,sol}$ represents Ben-Naim's solvation Gibbs free energy.

It is important to stress, as Ben-Naim does,[1] that while $\Delta G^{*,sol}$ and $\Delta G(\rho-process)$ are equal in magnitude, they correspond to two different processes. The process involved in the definition of $\Delta G^{*,sol}$ represents the change in Gibbs free energy when moving one solute molecule of solute from a fixed position in an ideal gas phase into a fixed position in an ideal dilute solution at constant temperature and pressure, which obviously differs from the ρ-process as defined above.

The claimed superiority of Ben-Naim's solvation magnitudes $\Delta X^{*,sol}$ when compared with their related Fowler-Guggenheim's $\Delta X^{o,sol}$ values have been summarized by that author as follows:[15] (a) while the conventional standard state free energy is not a bona fide measure of the average free energy of interaction of a solute with its surroundings, $\Delta G^{*,sol}$ is a direct measure of it. Indeed, it can be shown that $\Delta G^{*,sol} = -kT < \exp[-B_s / kT] >$,where B_s is the total interaction energy of a solute s at a fixed position, (b) while $\Delta G^{*,sol} = \mu_s^{*,sol} - \mu^{*,g}$ applies to solutions of any concentration, the conventional standard free energies $\Delta G^{o,sol} = \mu_s^{o,sol} - \mu^{o,g}$ are only valid for very dilute solutions, (c) while the magnitudes $\Delta X^{*,sol}$ pertain to the same process of solvation, when using the conventional standard magnitudes of solution, one usually applies different processes to different thermodynamic magnitudes, and (d) while the specification of a standard state is mandatory when using conventional standard free energies, no standard state definition is required in Ben-Naim's formulation.

Combination of eqs (41), (43) and (44) leads finally to the pivotal equation which establishes the relationship between solvation Gibbs free energies in Fowler-Guggenheim's and Ben-Naim's formulations[11]

$$\Delta G(\rho - process) = \Delta G^{*,sol} = \Delta G^{o,sol} - kT \log(V_m^g / V_{l,m}) \qquad (45)$$

On the other hand, eqs (43) and (44) lead to

$$\Delta G^{*,sol} = E_{0,s}^{sol} - E_0^g - \chi_{ls} + P\overline{V}_s^{sol} \qquad (46)$$

which is the explicit expression for Ben-Naim's Gibbs free energy of solution.

The solvation molecular enthalpy is obtained from eqs (10) and (22)

$$\Delta H^{o,sol} = \overline{H}_s^{sol} - \overline{H}^g = E_{0,s}^{sol} - E_0^g - \chi_{ls} + P\overline{V}_s^{sol} - kT + kT^2 \alpha_p^l \qquad (47)$$

Equation (47) is fully consistent with the results of Pierotti[8] and Abraham and Nasehzadeh[14] who compute the solvation molar enthalpies according to

$$\Delta H^{o,sol} = \overline{H}_{CAV} + \overline{H}_{INT} + \alpha_p^l RT^2 - RT \tag{48}$$

with $\overline{H}_{CAV}$ and $\overline{H}_{INT}$ being the partial molar enthalpies associated with the creation of a cavity and to the solute-solvent interactions when the solute is in the cavity, respectively. Solute electronic contribution $E_{0,s}^{sol} - E_0^g$ must be added to eq (48) to make it compatible with eq (47).

It should be recalled that Pierotti[8] and Abraham and Nasehzadeh[14] assume that $\overline{G}_{INT} = \overline{H}_{INT}$ but $\overline{G}_{CAV} = \overline{H}_{CAV} - T\overline{S}_{CAV}$ [with $\overline{S}_{CAV} = -(\partial P\overline{V}_s^{sol} / \partial T)_{P,Nl,Ns}$], thus implying that while -χ_{ls} (interaction term) is independent of T, $P\overline{V}_s^g$ (cavity term) is allowed to depend on T. As mentioned in section 2.2, in the present work, neither -χ_{ls} nor $P\overline{V}_s^g$ are considered to be T dependent and therefore, not only $\overline{G}_{INT} = \overline{H}_{INT} = -\chi_{ls}$ but also $\overline{G}_{CAV} = \overline{H}_{CAV} = P\overline{V}_s^{sol}$ [see eq (42)]. In this regard, it is easy to show from eqs (7) and (19) that

$$T\Delta S^{o,sol} = T\overline{S}_s^{o,sol} - T\overline{S}_s^{o,g} = -kT + kT^2\alpha_p^l - kT\log(V_m^g / V_{l,m}) \tag{49}$$

and also from eqs (7), (19) and (33) we find

$$T\Delta S^{o,sol} = T\Delta\overline{S}^{*,sol} - kT + kT^2\alpha_p^l - kT\log(V_m^g / V_{l,m}) \tag{50}$$

which represents the pivotal equation connecting the solvation entropies in Fowler-Guggenheim's and Ben-Naim's formulations.

From eqs (41), (47) and (49) it is seen that, as expected, $\Delta G^{o,sol} = \Delta H^{o,sol} - T\Delta S^{o,sol}$. Of course, eq (47) could also be derived from this latter equation, using $\Delta S^{o,sol} = -(\partial \Delta G^{o,sol} / \partial T)_{P,Nl,Ns}$ together with eq (41), and assuming that $-\chi_{ls} + P\overline{V}_s^{sol}$ is independent of T ($E_{0,s}^{sol} - E_0^g$, involving the electronic energies of the molecule in solution and gas-phase, does not depend on T).

It is clear either from eq (33) or from (49)-(50) that $\Delta S^{*,sol} = 0$. Of course, this is again a direct consequence of the simplification adopted in this work that W(s|l) (or equivalently $-\chi_{ls} + P\overline{V}_s^g$) is independent of T. As stressed in section 2.2, such a restriction has been imposed for consistency with G09,[10] for we will analyze the thermodynamic solvation G09 output in the last section of this article. However, we must insist that it is a rather crude approximation. Indeed, in the case of water solute in water solution at 298.15 K, $\Delta G^{*,sol} = -6.324$ kcal·mol^{-1}, $\Delta H^{*,sol} = -9.974$ kcal·mol^{-1}, and $\Delta S^{*,sol} = -12.24$ cal·K^{-1}·mol^{-1}.[11]

It is easy to show[1] that, unlike solvation Gibbs free energies, solvation enthalpies for Ben-Naim's ρ- and x-processes are identical to each other. Bearing in mind that Fowler-Guggenheim's solvation enthalpy, $\Delta H^{o,sol}$, does correspond to the change in enthalpy of Ben-Naim's x-process (i.e. the change in enthalpy involved in the x-process is $\overline{H}_s^{sol} - \overline{H}^g$), we can finally write

$$\Delta H^{o,sol} = \Delta H(\rho - process) = \Delta H(x - process) \qquad (51)$$

From eqs (34) and (35) we obtain

$$\Delta H^{o,sol} = \overline{H}_s^{sol} - \overline{H}^g = \overline{H}_s^{*,sol} - \overline{H}^{*,g} - kT + kT^2\alpha_p^l = \Delta H^{*,sol} - kT + kT^2\alpha_p^l \qquad (52)$$

which represents the pivotal equation connecting the solvation enthalpies in Fowler-Guggenheim's and Ben-Naim's formulations.[11]

On the other hand, comparison of eqs (47) and (52) leads to

$$\Delta H^{*,sol} = E_{0,s}^{sol} - E_0^g - \chi_{ls} + P\overline{V}_s^{sol} \qquad (53)$$

which is the explicit expression for Ben-Naim's enthalpy of solution.

It is important to emphasize that unlike solvation Gibbs free energy [see eq (45)], Ben-Naim's solvation enthalpy, $\Delta H^{*,sol}$, differs from the change in enthalpy for the ρ-process, $\Delta H(\rho - process)$. Equations (47) and (53) imply that, likewise for Gibbs energies, when computing solvation enthalpies, two different estimates can be done, namely, Fowler-Guggenheim's $\Delta H^{o,sol}$, or Ben-Naim's $\Delta H^{*,sol}$. Thus, while authors like Wilhelm et al. [16,17] or Abraham et al.[14] report $\Delta H^{o,sol}$ (as well as $\Delta G^{o,sol}$) values, Ben-Naim[1,10] reports $\Delta H^{*,sol}$ (as well as $\Delta G^{*,sol}$) values. In this context, it is interesting to note that in Cabani et al's compilation,[9] one finds Fowler-Guggenheim's $\Delta H^{o,sol}$ enthalpies and Ben-Naim's $\Delta G^{*,sol}$ Gibbs free energies.

Regarding solvation internal energies, eqs (11) and (23) lead to

$$\Delta U^{o,sol} = \overline{U}_s^{sol} - \overline{U}^{g} = E_{0,s}^{sol} - E_0^{g} - \chi_{ls} + kT^2 \alpha_p^l \tag{54}$$

and from eqs (39) and (40) we get

$$\Delta U^{*,sol} = \overline{U}_s^{*,sol} - \overline{U}^{*,g} = E_{0,s}^{sol} - E_0^{g} - \chi_{ls} \tag{55}$$

Combination of eqs (54) and (55) gives

$$\Delta U^{*,sol} = \Delta U^{o,sol} - kT^2 \alpha_p^l \tag{56}$$

which represents the pivotal relationship between solvation internal energies in Fowler-Guggenheim's and Ben-Naim's formulations.

Before ending this brief parallel analysis on Fowler-Guggenheim's and Ben-Naim's formulations of solvation thermodynamics, we would like to mention that Jorgensen's group[18] computed solvation enthalpies by using the expression (in molar units)

$$\Delta H^{o} = \Delta E^{o} + P\Delta V^{o} - RT \tag{57}$$

where[18] ΔE^{o} is the energy change on transferring the solute from the gas-phase to solution [$\Delta U^{o,sol}$ in our notation: see eq (54)], ΔV^{o} is the partial molar volume of the solute ($\overline{V}_s^{sol}$ in our notation). Eqs (47) and (54) lead to

$$\Delta H^{o,sol} = \Delta U^{o,sol} + P\overline{V}_s^{sol} - RT = \Delta U^{o,sol} + P(\overline{V}_s^{sol} - \overline{V}^{g}) = \Delta U^{o,sol} + P\Delta V^{o,sol} \tag{58}$$

with the solvation volume $\Delta V^{o,sol} = \overline{V}_s^{sol} - \overline{V}^{g}$. Eq (58) is equivalent to eq (57) (note that PΔV^o in Jorgensen's notation is $P\overline{V}_s^{sol}$), thus showing that the equations derived in this work are consistent with Jorgensen's formula.

In the next section, we will show that a certain confusion has been detected in the literature regarding the correct application of the equations derived in this article. In particular, we will present evidence that the G09 package of programs,[10] which is employed as a reference software in quantum calculations by a large number of researchers, does not employ the correct expression for computing neither the partial enthalpies ($\overline{H}_s^{sol}$) nor the partial entropies ($\overline{S}_s^{sol}$) of a solute in solution.

5. Practical application.

Table 1 gathers the most important equations derived in the previous sections. Tables 2 and 3 collect the computed values of the thermodynamic magnitudes considered in the present work for the particular case of water solute in water solution, which has been chosen as a representative system where we focus our analysis.

Calculations were carried out by means of the G09 package of programs.[10] The equations implemented in G09 for computing thermochemical data have been described in detail in a technical report available at the official Gaussian Website.[19] Tables 2 and 3 compile the values appearing in the G09 output file together with the results obtained from the application of the equations derived in this work (see Table 1). Since the conclusions of the present work do not depend at all on the level of theory employed in the calculations, we have chosen a rather standard low-level (see Table 2 for details) to avoid diverting attention of the reader from the nuclear point analyzed in this work, namely, the correct use of solvation thermodynamic formulas in practical cases.

The values in Table 2 corresponding to the gas-phase magnitudes (row 2) in columns 1-6 have been taken from the G09 output and match those computed from the equations derived in this work and collected in Table 1. However, in the case of solution calculations (row 4), we detected discrepancies between the $\overline{H}_s^{sol}$,

$T\overline{S}_s^{o,sol}$ and $\mu_s^{o,sol}$ values in the G09 output (columns 4-6, row 5; values in parentheses) and the ones computed with the formulae in Table 1 (columns 4-6, row 4). Thermodynamic magnitudes corresponding to Ben-Naim's formulation ($\overline{X}^{*,\varphi}$ with φ = g, sol; columns 7-10) have been computed using formulas in Table 1 and the appropriate data from the G09 output (Ben-Naim's magnitudes are not provided explicitly in the G09 output). Let us analyze the origin of such discrepancies.

The expression employed in G09 to compute the translational component of the partial molar entropy of the solute in both gas-phase and solution calculations is[19]

$$\overline{S}_{s,trans}^{\varphi}(G09) = R\{-\log(\Lambda_s^3 / V_m^{\varphi}) + \frac{5}{2}\} \qquad (\varphi = \mathrm{g, sol}) \qquad (59)$$

with V^{φ}_m = 24.5 L·mol^{-1}. That is to say, G09 uses the same value for V^{φ}_m in gas-phase and solution calculations. It is straightforward to show that it is equivalent to state that G09 employs concentration scale standard states for gas-phase and solution with identical concentrations, namely, $\rho^g = \rho_s^{sol} = 1bar/RT = 1/24.5 mol{\cdot}L^{-1} = 0.041M$, in molar units [i.e. {g-ideal, $\rho^g = 0.041M$; V_m = 24.5 L·mol^{-1}} standard state for gas-phase and {sol-Henry, $\rho_s^{sol} = 0.041M$; V_m = 24.5 L·mol^{-1}} standard state for solution]. After adding the contributions from the internal degrees of freedom, the resulting equation for the partial molar entropy, $\overline{S}_s^{\oplus,\varphi}$, agrees with eqs (7) and (9), namely, the ones derived in this work for the gas-phase calculations. Then, the G09 value for $T\overline{S}_s^{\oplus,sol}$ is computed in molar units as

$$T\overline{S}_s^{\oplus,sol}(G09) = -RT\log\{\Lambda_s^3 / [RT{\cdot}j_s^{sol}(T)]\} + \frac{5}{2}RT + E_{\mathrm{int},s}^{sol} \qquad (60)$$

As a consequence, the G09 values for $T\overline{S}^{\oplus,g}$ (0.021436 hartree) and $T\overline{S}_s^{\oplus,sol}$ (0.021441 hartree) are virtually identical (the negligible discrepancy observed, less than 2·10^{-3} kcal·mol^{-1}, arises from the difference in the contributions from the internal degrees of freedom after geometry optimizations in each phase). It should be noted that the difference between the two mentioned entropy contributions as computed with eqs (19) (the equation derived in this work: $T\overline{S}_s^{o,sol}$) and (60) [the equation employed by G09: $T\overline{S}_s^{\oplus,sol}$), respectively, is (molar units), $RT + RT\log(RT/V_{l,m})$. The first term is associated with the error involved in the G09 incorrect use of the gas-phase equations (59) and (60) for calculations in solution. The proper equation to be used in solution calculations is eq (19) that involves (molar units) $\frac{3}{2}RT + RT^2\alpha_p^l$ (with $RT^2\alpha_p^l \approx 0$) instead of $\frac{5}{2}RT$. The second term arises from the use of different standard states and consequently different values for the volume in eqs (19) [standard state: {sol-Henry, $x_s \rightarrow 1$; $V_m = 0.018$ L·mol^{-1}}] and (60) [concentration scale standard state: {sol-Henry, $\rho_s^{sol} = 0.041M$; $V_m = 24.5$ L·mol^{-1}}].

Thus we can conclude that the $T\overline{S}_s^{\oplus,sol}(G09)$ value overestimates by RT the correct magnitude. When properly computed with eq (19), which is referred to the {sol-Henry, $x_s \rightarrow 1$; $V_m = 0.018$ L·mol^{-1}} standard state, $T\overline{S}_s^{o,sol}$ becomes 0.013689 (see Table 2). If the {sol-Henry, $\rho_s^{sol} = 0.041M$; $V_m = 24.5$ L·mol^{-1}} standard state is chosen for the solution calculations (as G09 does), the correct $T\overline{S}_s^{\oplus,sol}(G09)$ value [as computed with eq (21)] would be: 0.021441 – RT = 0.020497 hartree. It must be emphasized that while the overestimation by RT is a mistake, the choice of any of the two mentioned standard states is free. Consequently, both values (0.013689 and 0.020497 hartree) are correct, provided the appropriate standard state is specified.

It is notheworthy that the $T\Delta S^{\oplus,sol}(G09)$ solvation magnitude is computed as [see eqs (60) and (7)]

$$
\begin{aligned}
T\Delta S^{\oplus,sol}(G09) &= T\overline{S}_s^{\oplus,sol}(G09) - T\overline{S}^{\oplus,g}(G09) = \\
&= -RT\log\{\Lambda_s^3/[RT\cdot j_s^{sol}(T)]\} + \frac{5}{2}RT + E_{\mathrm{int},s}^{sol} - \\
&\quad -[-RT\log\{\Lambda^3/[RT\cdot j^g(T)]\} + \frac{5}{2}RT + E_{\mathrm{int}}^g] = 0 \qquad (61)
\end{aligned}
$$

which agrees with $T\Delta S^{*,sol} = 0$ [see eqs (49)-(50)]. Consequently, the G09 output provides gas-phase and solution partial molar entropies that, although do not correspond to $\overline{S}^{*,\varphi}$ (φ = g, sol) Ben-Naim's magnitudes (i.e. the values in column 9, rows 2 and 4, in Table 2 do not match the G09 output: column 5, rows 2 and 5), their difference, by a lucky fluke, leads to Ben-Naim's solvation entropies (i.e. $T\Delta S^{\oplus,sol}(G09) = T\Delta S^{*,sol}$; see Table 3).

Regarding partial molar enthalpies, results collected in Table 2 show that G09 computes $\overline{H}_s^{sol}$ as

$$\overline{H}_s^{sol}(G09) = E_{0,s}^{sol} - \chi_{ls} + \frac{5}{2}RT + E_{\text{int},s}^{sol} \qquad (62)$$

However, according to the equations derived in this work, $\overline{H}_s^{sol}$ should be computed from eq (22) that, after neglecting the $kT^2\alpha_p^l + P\overline{V}_s^{sol}$ contribution (see section 2), differs from eq (62) in (molar units) RT (0.000944 hartree; see column 4, rows 4 and 5, in Table 2). That is, G09 overestimates $\overline{H}_s^{sol}$ in this amount. The mistake arises from the wrong tacit assumption in G09 that (molar units) $kT^2\alpha_p^l + P\overline{V}_s^{sol} = RT$. As mentioned, in sections 2 and 3, $RT^2\alpha_p^{l,water} = 4.5{\cdot}10^{-2}\,kcal{\cdot}mol^{-1}, P\overline{V}_{water}^{sol} = 4.4{\cdot}10^{-4}\,kcal{\cdot}mol^{-1}$ and RT = 0.59 kcal·mol^{-1}, and hence $kT^2\alpha_p^l + P\overline{V}_s^{sol}$ cannot be identified with RT.

Thus, the G09 solvation enthalpy is computed as

$$\begin{aligned}\Delta H_s^{sol}(G09) = \overline{H}_s^{sol}(G09) - \overline{H}^{g}(G09) = E_{0,s}^{sol} - \chi_{ls} + \frac{5}{2}RT + E_{\text{int},s}^{sol} - \\ -[E_0^g + \frac{5}{2}RT + E_{\text{int}}^g] = E_{0,s}^{sol} - E_0^g - \chi_{ls} \qquad (63)\end{aligned}$$

which agrees with $\Delta H^{*,sol}$, once the $P\overline{V}_s^{sol}$ term (4.4·10^{-4} kcal·mol^{-1}) is neglected [see eq (53)]. Therefore, like in the case of entropy, the G09 output provides partial molar enthalpies for gas-phase and solution calculations such that, although they are not $\overline{H}^{*,\varphi}$ (φ = g, sol) Ben-Naim's partial molar enthalpies (i.e.

the values in column 8, rows 2 and 4 in Table 2 do not match the G09 output: column 4, rows 2 and 5), their difference leads to Ben-Naim's solvation enthalpies (i.e. $\Delta H^{sol}(G09) = \Delta H^{*,sol}$; see Table 3).

Let us now comment on G09 chemical potentials. The $\mu_s^{\oplus,sol}(G09)$ value provided by G09 is "correct", but it is again a fluke. Indeed, $\mu_s^{\oplus,sol}(G09)$ is computed as $\overline{H}_s^{sol}(G09) - T\overline{S}_s^{\oplus,sol}(G09)$. According to the previous paragraphs, the RT incorrect contributions to $\overline{H}_s^{sol}(G09)$ and $T\overline{S}_s^{sol}(G09)$ values, will cancel each other out, thus leading to a correct $\mu_s^{\oplus,sol}(G09)$ value in the G09 output (-76.423076 hartree) that, according to what has been mentioned above, will correspond to the {sol-Henry, $\rho_s^{sol} = 0.041M$; V_m = 24.5 L·mol^{-1}} concentration scale standard state. The value $\mu_s^{o,sol}$ = -76.416267 hartree (see Table 2) computed from eq (18), neglecting the $P\overline{V}_s^{sol}$ term, is indeed also a correct value for the solute (water) chemical potential in solution (water), but this time, it corresponds to the {sol-Henry, $x_s \rightarrow 1$; V_m = 0.018 L·mol^{-1}} standard state.

It has been stressed in section 4 that Ben-Naim's solvation Gibbs free energy $\Delta G^{*,sol}$ is identical in magnitude (although conceptually different!) to the ΔG(ρ-process) value. As noted there, this latter, is the energy involved in the transference of a solute from the gas-phase {g-ideal, ρ^g; V_m} standard state to the solution {sol-Henry, ρ_s^{sol}; V_m} standard state under the condition that number densities in both phases are identical ($\rho^g = \rho_s^{sol}$). This is exactly the situation considered in G09 where the number densities employed in both phases are 0.041M (molar units). Thus, according to what has been established in section 4, ΔG(ρ-process) coincides in magnitude with $\Delta G^{*,sol}$, Ben-Naim's solvation Gibbs free energy. Consequently, the solvation Gibbs free energy computed in G09, $\Delta G^{\oplus,sol}(G09) = \mu_s^{\oplus,sol}(G09) - \mu^{\oplus,g}(G09)$ = -76.423076 + 76.416029 = -0.007047 hartree = -4.4 kcal·mol^{-1}, coincides with Ben-Naim's solvation Gibbs free energy $\Delta G^{*,sol} = \mu_s^{*,sol} - \mu^{*,g}$ = -76.408996 + 76.401950 = -0.007046 hartree. We have used the fact, mentioned in section 2.1, that since in G09, ρ^g = 0.041M, then $\mu^{\oplus,g}(G09) = \mu^{o,g}$. Thus, likewise for entropies and enthalpies, the G09 output provides chemical potentials for gas-phase and solution calculations such that, although they are not $\mu^{*,\varphi}$ (φ = g, sol) Ben-Naim's pseudochemical potentials[1] (i.e. the values in column 10, rows 2 and 4 in Table 2 do not match the G09 output: column 6, rows 2 and 5), their difference leads to Ben-Naim's solvation Gibbs free energies (i.e. $\Delta G^{\oplus,sol}(G09) = \Delta G^{*,sol}$; see Table 3).

It is very instructive and conceptually clarifying to emphasize that the $\Delta G^{o,sol}$ solvation Gibss free energy computed within Fowler-Guggenheim's formalism (transference of a solute from the gas-phase {g-ideal, P = 1 bar; V_m = 24.5 L·mol^{-1}} standard state to the solution {sol-Henry, $x_s \rightarrow 1$; V_m = 0.018 L·mol^{-1}} standard state (see Table 3), i.e. (see Table 2) $\Delta G^{o,sol} = \mu_s^{o,sol} - \mu^{o,g}$ = -76.416267 + 76.416029 = -0.000238 hartree = -0.1 kcal·mol^{-1}, differs , in 4.3 kcal·mol^{-1} from the corresponding value in Ben-Naim's formulation, i.e. (see Table 2) $\Delta G^{*,sol} = \mu_s^{*,sol} - \mu^{*,g}$ = -76.408996 + 76.401950 = -0.007046 hartree = -4.4 kcal·mol^{-1}. These 4.3 kcal·mol^{-1}, that according to the previous paragraph correspond to the difference $\Delta G^{o,sol} - \Delta G(\rho - process)$, must be ascribed to the difference in Gibbs free energy between the two following transferences: (a) $\Delta G^{o,sol}$: {g-ideal, P = 1 bar; V_m = 24.5 L·mol^{-1}} → {sol-Henry, $x_s \rightarrow 1$; V_m = 0.018 L·mol^{-1}} and (b) $\Delta G(\rho - process)$: {g-ideal, ρ^g; V_m} → {sol-Henry, ρ_s^{sol}; V_m}, with $\rho^g = \rho_s^{sol}$. Indeed, Cabani et al. mention in their compilation[9] that the above difference (4.3 kcal·mol^{-1}) holds for the particular case where both number densities (gas-phase and solution) become 1M in the ρ-process (as stressed above, in the case of G09, both number densities are also identical, but this time their respective values are 0.041M).

Before ending, we think it is important to remark that G09 does not compute any Ben-Naim's thermodynamic quantity $\overline{X}^*$ (the values in the columns 7-10 in Table 2 have been computed by us from data in the G09 output, but they are not found explicitly in it). Furthermore, as concluded in this article, G09 provides wrong values for the partial molar enthalpies and entropies of a solute in solution. It is hoped that the present contribution can be helpful in order to reorganize the solvation thermodynamics section of the Gaussian packages of programs as well as of any other software where the solvation code may call for corrections. Despite the apparent present superiority of Ben-Naim's formulation over the conventional approach, we do suggest that an optimum output should provide detailed information regarding the two formulations considered in this article.

6. Conclusion

A parallel derivation of conventional (Fowler-Guggenheim) and Ben-Naim's formulations of solvation thermodynamics, emphasizing their differences and stressing their interconnections, is presented. Explicit equations for conventional ($\Delta X^{o,sol} = \overline{X}_s^{sol} - \overline{X}^{g}$) and Ben-Naim's ($\Delta X^{*,sol} = \overline{X}_s^{*,sol} - \overline{X}^{*,g}$) solvation magnitudes, with X being internal energies, enthalpies, entropies, and Gibbs free energies, have been obtained. Pivotal equations connecting both formulations have also been inferred.

Both theoretical frameworks were used to compute the solvation thermodynamic magnitudes for a standard system: water solute in water solution. Comparison with the Gaussian 09 output shows that this software does not estimate properly neither the partial molar entropies nor the partial molar enthalpies of a solute in solution.

The present article intends to be of help to researchers who need to apply solvation models in order to tackle the study of chemical, biophysical or biochemical systems which they may be interested in, as well as to software developers who implement the solvation thermodynamic equations in the available codes.

Acknowledgments

Profs. J. Fernández-Rico, J.M. García de la Vega, A. Largo, J.M. Lluch and E. Ortí were kept abreast of the present research at different stages of its development. I wish to thank their stimulating comments. The author is indebted to Ms. María Viña García-Bericua for her help with the artwork.

Appendix

The first term contribution to the Helmholtz free energy of solution (F^{sol}) in eq (12)[6] is

$$F_l = F_l(T, V^{sol} - N_s \overline{V}_s^{sol}, N_l) = F_l[T, V_l^{sol}(V^{sol}, N_s, \overline{V}_s^{sol}), N_l] \tag{A1}$$

where $V_l^{sol} (= N_l \overline{V}_l^{sol})$ is the volume available for the N_l solvent molecules

$$V_l^{sol} = V^{sol} - N_s \overline{V}_s^{sol} \tag{A2}$$

Let us use in the following V, V_l and $\overline{V}_s$, instead of V^{sol}, V_l^{sol} and $\overline{V}_s^{sol}$, for the sake of simplicity.

From (A1) and (A2) we get

$$dF_l = \left(\frac{\partial F_l}{\partial T}\right)_{Vl,Nl} dT + \left(\frac{\partial F_l}{\partial V_l}\right)_{T,Nl} \left[\left(\frac{\partial V_l}{\partial V}\right)_{Ns,\overline{V}_s} dV + \left(\frac{\partial V_l}{\partial N_s}\right)_{V,\overline{V}_s} dN_s + \left(\frac{\partial V_l}{\partial \overline{V}_s}\right)_{V,N_s} d\overline{V}_s\right] + \left(\frac{\partial F_l}{\partial N_l}\right)_{T,Vl} dN_l \tag{A3}$$

and

$$\left(\frac{\partial F_l}{\partial N_s}\right)_{T,V,Nl} = \left(\frac{\partial F_l}{\partial T}\right)_{Vl,Nl} \left(\frac{\partial T}{\partial N_s}\right)_{T,V,Nl} + \left(\frac{\partial F_l}{\partial V_l}\right)_{T,Nl} \left(\frac{\partial V_l}{\partial V}\right)_{Ns,\overline{V}s} \left(\frac{\partial V}{\partial N_s}\right)_{T,V,Nl} +$$

$$+ \left(\frac{\partial F_l}{\partial V_l}\right)_{T,Nl} \left(\frac{\partial V_l}{\partial N_s}\right)_{V,\overline{V}s} \left(\frac{\partial N_s}{\partial N_s}\right)_{T,V,Nl} + \left(\frac{\partial F_l}{\partial V_l}\right)_{T,Nl} \left(\frac{\partial V_l}{\partial \overline{V}_s}\right)_{V,Ns} \left(\frac{\partial \overline{V}_s}{\partial N_s}\right)_{T,V,Nl} +$$

$$+ \left(\frac{\partial F_l}{\partial N_l}\right)_{T,Vl} \left(\frac{\partial N_l}{\partial N_s}\right)_{T,V,Nl} \tag{A4}$$

But

$$\left(\frac{\partial T}{\partial N_s}\right)_{T,V,Nl}=0\,;\;\left(\frac{\partial V}{\partial N_s}\right)_{T,V,Nl}=0\,;\;\left(\frac{\partial N_s}{\partial N_s}\right)_{T,V,Nl}=1\,;\;\left(\frac{\partial V_l}{\partial \overline{V}_s}\right)_{V,Ns}=-N_s \qquad \text{(A5)}$$

On the other hand, for an ideal dilute solution $N_s \to 0$ and $V_l \to V$. Then,

$$\lim_{N_s\to 0}\left(\frac{\partial F_l}{\partial V_l}\right)_{T,Nl}\left(\frac{\partial V_l}{\partial \overline{V}_s}\right)_{V,Ns}\left(\frac{\partial \overline{V}_s}{\partial N_s}\right)_{T,V,Nl}=\lim_{N_s\to 0}\left[-N_s\left(\frac{\partial F_l}{\partial V_l}\right)_{T,Nl}\left(\frac{\partial \overline{V}_s}{\partial N_s}\right)_{T,V,Nl}\right]=$$

$$=\lim_{N_{s\to 0}}\left[-N_s P\left(\frac{\partial \overline{V}_s}{\partial N_s}\right)_{T,V,Nl}\right]=0 \qquad \text{(A6)}$$

where, in order to write the last equality of (A6), we have taken into account that $-(\partial F_l/\partial V_l)_{T,Nl}\approx-(\partial F_l/\partial V)_{T,Nl}$ is the pressure at which the pure solvent has the volume $V-N_s\overline{V}_s$. As stressed by Fowler and Guggenheim,[6] such a pressure will be quite close to the pressure P on the actual solute-solvent assembly.

Consequently, bearing in mind that according to (A2), $(\partial V_l/\partial N_s)_{V,\overline{V}_s}=-\overline{V}_s$, (A4) leads to

$$\left(\frac{\partial F_l}{\partial N_s}\right)_{T,V,Nl}=\left(\frac{\partial F_l}{\partial V_l}\right)_{T,Nl}(-\overline{V}_s)\approx P\overline{V}_s \qquad \text{(A7)}$$

in agreement with Fowler and Guggenheim [see eq (823,3 in p. 373 of Ref. 6].

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Table 1. Thermodynamic functions for a solute in gas-phase, ($\overline{X}^{g}, \overline{X}^{*,g}$), in solution, ($\overline{X}_{s}^{sol}, \overline{X}_{s}^{*,sol}$), and solvation thermodynamic functions ($\Delta X^{o,sol}, \Delta X^{*,sol}$).Contribution $-\chi_{ls} + P\overline{V}_{s}^{sol}$ has been assumed to be independent of T (see the text for more details). Molar units are employed.

Solute in gas-phase	
$\overline{U}^{g} = E_{0}^{g} + \frac{3}{2}RT + E_{\text{int}}^{g}$	$\overline{U}^{*,g} = E_{0}^{g} + E_{\text{int}}^{g}$
$\overline{H}^{g} = E_{0}^{g} + \frac{5}{2}RT + E_{\text{int}}^{g}$	$\overline{H}^{*,g} = E_{0}^{g} + E_{\text{int}}^{g}$
$T\overline{S}^{o,g} = -RT\log\Lambda^{3}/[RT\cdot j^{g}(T)] + \frac{5}{2}RT + E_{\text{int}}^{g}$	$T\overline{S}^{*,g} = RT\log j^{g}(T) + E_{\text{int}}^{g}$
$\overline{G}^{o,g} = \mu^{o,g} = E_{0}^{g} + RT\log\Lambda^{3}/\left[RT\cdot j^{g}(T)\right]$	$\overline{G}^{*,g} = \mu^{*,g} = E_{0}^{g} - RT\log j^{g}(T)$
Solute in ideal dilute solution	
$\overline{U}_{s}^{sol} = E_{0,s}^{sol} - \chi_{ls} + \frac{3}{2}RT + RT^{2}\alpha_{p}^{l} + E_{\text{int},s}^{sol}$	$\overline{U}_{s}^{*,sol} = E_{0,s}^{sol} - \chi_{ls} + E_{\text{int},s}^{sol}$
$\overline{H}_{s}^{sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_{s}^{sol} + \frac{3}{2}kT + kT^{2}\alpha_{p}^{l} + E_{\text{int},s}^{sol}$	$\overline{H}_{s}^{*,sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_{s}^{sol} + E_{\text{int},s}^{sol}$
$T\overline{S}_{s}^{o,sol} = -RT\log\Lambda_{s}^{3}/[j_{s}^{sol}(T)\cdot V_{l,m}] + \frac{3}{2}RT + RT^{2}\alpha_{p}^{l} + E_{\text{int},s}^{sol}$	$T\overline{S}_{s}^{*,sol} = RT\log j_{s}^{sol}(T) + E_{\text{int},s}^{sol}$
$\overline{G}_{s}^{o,sol} = \mu_{s}^{o,sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_{s}^{sol} + RT\log\Lambda_{s}^{3}/[j_{s}^{sol}(T)\cdot V_{l,m}]$	$\overline{G}_{s}^{*,sol} = \mu_{s}^{*,sol} = E_{0,s}^{sol} - \chi_{ls} + P\overline{V}_{s}^{sol} - RT\log j_{s}^{sol}(T)$
Solvation functions	
$\Delta U^{o,sol} = E_{0,s}^{sol} - E_{0}^{g} - \chi_{ls} + RT^{2}\alpha_{p}^{l}$	$\Delta U^{*,sol} = E_{0,s}^{sol} - E_{0}^{g} - \chi_{ls}$
$\Delta H^{o,sol} = E_{0,s}^{sol} - E_{0}^{g} - \chi_{ls} + P\overline{V}_{s}^{sol} - RT + RT^{2}\alpha_{p}^{l}$	$\Delta H^{\cdot *,sol} = E_{0,s}^{sol} - E_{0}^{g} - \chi_{ls} + P\overline{V}_{s}^{sol}$
$T\Delta S^{o,sol} = -RT + RT^{2}\alpha_{p}^{l} - RT\log[RT/V_{l,m}]$	$T\Delta S^{*,sol} = 0$
$\Delta G^{o,sol} = E_{0,s}^{sol} - E_{0}^{g} - \chi_{ls} + P\overline{V}_{s}^{sol} + RT\log[RT/V_{l,m}]$	$\Delta G^{\cdot *,sol} = E_{0,s}^{sol} - E_{0}^{g} - \chi_{ls} + P\overline{V}_{s}^{sol}$

Table 2.[a] Solute electronic energies (Schrödinger equation) (E_o), energy contributions of the internal molecular degrees of freedom (E_{int}), molar potential energy of the solute in the solution ($-\chi_{ls}$), partial molar internal energies ($\overline{U}$), partial molar enthalpies ($\overline{H}$) and partial molar Gibbs free energies ($\overline{G}=\mu$) for water in gas phase (g) and water in solution (sol). All numbers in hartree (T=298.15 K).

E_o^g	E_{int}^g	$\overline{U}^g$	$\overline{H}^g$	$T\overline{S}^{o,g}$	$\overline{G}^{o,g}=\mu^{o,g}$	$\overline{U}^{*,g}$	$\overline{H}^{*,g}$	$T\overline{S}^{*,g}$	$\overline{G}^{*,g}=\mu^{*,g}$
-76.419737	0.022784	-76.395537	-76.394593	0.021436	-76.416029	-76.396953	-76.396953	0.004997	-76.401950
$E_{o,s}^{sol}-\chi_{ls}$ [b]	$E_{\text{int},s}^{sol}$	$\overline{U}_s^{sol}$	$\overline{H}_s^{sol}$	$T\overline{S}_s^{o,sol}$	$\overline{G}_s^{o,sol}=\mu_s^{o,sol}$	$\overline{U}_s^{*,sol}$	$\overline{H}_s^{*,sol}$	$T\overline{S}_s^{*,sol}$	$\overline{G}_s^{*,sol}=\mu_s^{*,sol}$
-76.426730	0.022736	-76.402578	-76.402578[c]	0.013689[d]	-76.416267[e]	-76.403994	-76.403994	0.005002	-76.408996
			(-76.401634)[f]	(0.021441)[g]	(-76.423076)[h]				

[a] The Gaussian 09 (G09) calculations leading to the output energies collected in this table were obtained by running the G09 route cards: *#b3lyp/6-31G(d,p) opt(calchffc) freq* and *#b3lyp/6-31G(d,p) opt(calchffc) scrf=(solvent=water) freq* for the gas-phase and solution calculations, respectively. When single values appear in the table, they correspond to the magnitude as computed with the formulae in Table 1. Values in parentheses, are the ones in the G09 output that differ from the values computed with formulas in Table 1.

[b] Assuming $P\overline{V}_s^{sol}\approx 0$.

[c] Computed from $\overline{H}_s^{sol}=E_{0,s}^{sol}-\chi_{ls}+\frac{3}{2}kT+E_{\text{int},s}^{sol}$, as proposed in this work (see eq 22 with $P\overline{V}_s^{sol}\approx 0$ and $RT^2\alpha_p^l\approx 0$).

[d] Computed from $T\overline{S}_s^{o,sol}=-RT\log\{\Lambda_s^3/[j_s^{sol}(T)\cdot V_{l,m}]\}+\frac{3}{2}RT+E_{\text{int},s}^{sol}$,with $V_{l,m}$ = 0.018 L·mol^{-1}, as proposed in this work [see eq (19) with $RT^2\alpha_p^l\approx 0$].

[e] Computed from $\mu_s^{o,sol}=E_{0,s}^{sol}-\chi_{ls}+RT\log\{\Lambda_s^3/[j_s^{sol}(T)\cdot V_{l,m}]\}$, with $V_{l,m}$ = 0.018 L·mol^{-1}, as proposed in this work [see eq (18) with $P\overline{V}_s^{sol}\approx 0$].

[f] Computed from $\overline{H}_s^{sol}(G09)=E_{0,s}^{sol}-\chi_{ls}+\frac{5}{2}RT+E_{\text{int},s}^{sol}$, as proposed in Gaussian 09 package of programs [see eq (62)].

[g] Computed from $T\overline{S}_s^{\oplus,sol}(G09)=-RT\log\{\Lambda_s^3/[RT\cdot j_s^{sol}(T)]\}+\frac{5}{2}RT+E_{\text{int},s}^{sol}=-RT\log\{\Lambda_s^3/[j_s^{sol}(T)\cdot V_m^g]\}+\frac{5}{2}RT+E_{\text{int},s}^{sol}$, with V^g_m = 24.5 L·mol^{-1}, as proposed in Gaussian 09 package of programs [see eq (60)].

[h] Computed from $\mu_s^{\oplus,sol}(G09)=\overline{H}_s^{sol}(G09)-T\overline{S}_s^{\oplus,sol}(G09)=E_{0,s}^{sol}-\chi_{ls}+RT\log\{\Lambda_s^3/[j_s^{sol}(T)\cdot V_m^g]\}$, with V^g_m = 24.5 L·mol^{-1}, as proposed in Gaussian 09 package of programs.

Table 3. Solvation thermodynamic functions for water solute in water solution, as computed by means of the conventional (Fowler-Guggenheim) and Ben-Naim's formulations together with the corresponding values as estimated from the Gaussian 09 outputs for gas-phase and solution runs. The approximations $P\overline{V}_s^{sol} \approx 0$ and $RT^2\alpha_p^l \approx 0$ have been adopted in all cases. All numbers in kcal·mol^{-1}.

	ΔU^{sol}	ΔH^{sol}	$T\Delta S^{sol}$	ΔG^{sol}	$\Delta G^{sol}(\exp.)$ [d]	Gas-phase standard state[e]	Solute in solution standard state[f]
Fowler-Guggenheim[a]	-4.4	-5.0	-4.9	-0.1	-2.05	{g-ideal; V_m = 24.5 L·mol^{-1}}	{sol-Henry; V_m = 0.018 L·mol^{-1}}
Ben-Naim[b]	-4.4	-4.4	0.0	-4.4	-6.32	–[g]	–[g]
Gaussian 09[c]	-4.4	-4.4	0.0	-4.4		{g-ideal; $\rho^g = 0.041M$ }[h]	{sol-Henry; $\rho_s^{sol} = 0.041M$ }[h]

[a] As computed from $\Delta X^{o,sol} = \overline{X}_s^{sol} - \overline{X}^g$ (X = U, H, S^o, G^o), using the values collected in Table 2.

[b] As computed from $\Delta X^{*,sol} = \overline{X}_s^{*,sol} - \overline{X}^{*,g}$ (X = U, H, S, G), using the values collected in Table 2.

[c] As computed from $\Delta X^{o,sol} = \overline{X}_s^{sol}(G09) - \overline{X}^g(G09)$ (X = U, H, S$^{\oplus}$, G$^{\oplus}$) with $\overline{X}_s^{sol}(G09)$ and $\overline{X}^g(G09)$ taken from the Gaussian 09 outputs for the gas-phase and solution calculations, respectively.

[d] From Ref 20.

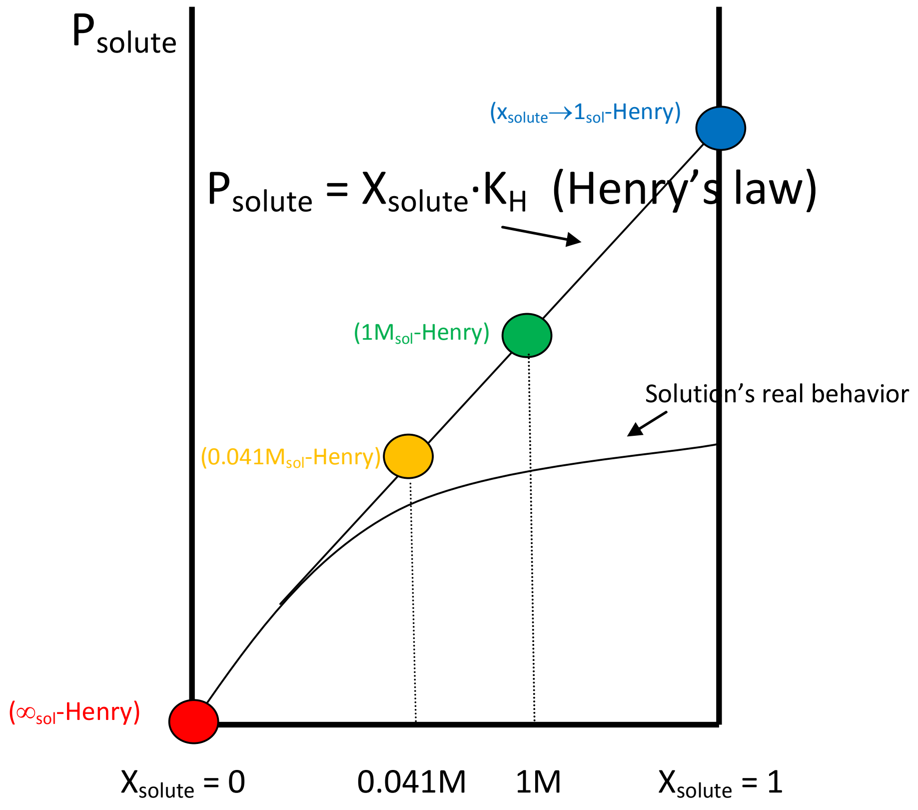
[e] The adopted gas-phase standard state corresponds to an ideal gas at standard conditions (P = 1 bar, T = 298.15 K), occupying the molar volume V_m.

[f] The adopted standard state for the solute in solution corresponds to an hypothetic ideal solution (fulfilling Henry's law) at P and T of the solution (we assume in this work standard conditions), where: (i) the solute mole fraction tends to unity ($x_s \rightarrow 1$) or (ii) RT/1bar = 24.5 L·mol^{-1} substitutes $V_{l,m}$ in eq (19) (i.e. concentration scale is employed to define the standard state, with $\rho_s^{\oplus,sol} = \rho_s^{sol} = 0.041M$; see eq (21) and the text for details).

[g] Ben-Naim's solvation magnitudes, $\Delta X^{*,sol}$, do not involve the definition of any standard state. The values in the table were computed from data in columns 7-10 in Table 2.

[h] G09 uses the same value of V^{φ}_m [see eq (59)] for the calculations in both phases (24.5 L·mol^{-1}). As discussed in the text, it means using concentration scale standard states with identical concentration for gas-phase and solution ($\rho^{\oplus} = \rho^g = \rho_s^{sol} = 0.041M$, in molar units).

Figure 1. The red point represents an ideally dilute solution fulfilling Henry's law. The orange: {sol-Henry, $\rho_s^{sol} = 0.041M$; $V_m = 24.5$ L·mol^{-1}}, green: {sol-Henry, $\rho_s^{sol} = 1M$; $V_m = 1$ L·mol^{-1}}and blue: {sol-Henry, $x_s \rightarrow 1$; $V_m = 0.018$ L·mol^{-1}} points represent fictitious states of the solute in which each solute molecule experiences the same intermolecular forces it experiences in the ideally dilute solution, where it is surrounded by solvent molecules. They are the hypothetical states arising from an extrapolation of the properties of solute in the very dilute solution to the limit of 0.041M, 1M and $x_{solute} = 1$ concentrations, corresponding to the different standard states mentioned throughout the present work. The orange point corresponds to the standard state adopted by the Gaussian 09 software in solvation calculations.



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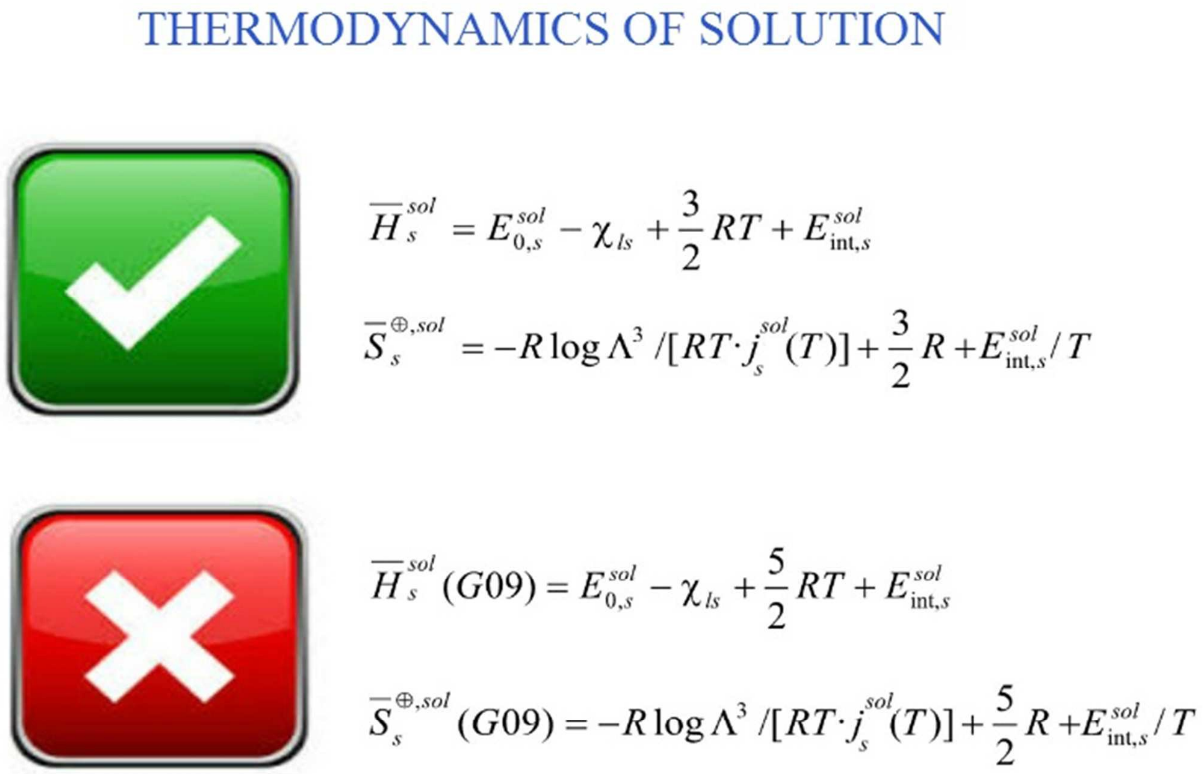
Solvation Thermodynamics: Two formulations and some misunderstandings

José Ángel Sordo



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$$\overline{H}_s^{sol} = E_{0,s}^{sol} - \chi_{ls} + \frac{3}{2}RT + E_{\mathrm{int},s}^{sol}$$

$$\overline{S}_s^{\oplus,sol} = -R\log\Lambda^3/[RT\cdot j_s^{sol}(T)] + \frac{3}{2}R + E_{\mathrm{int},s}^{sol}/T$$

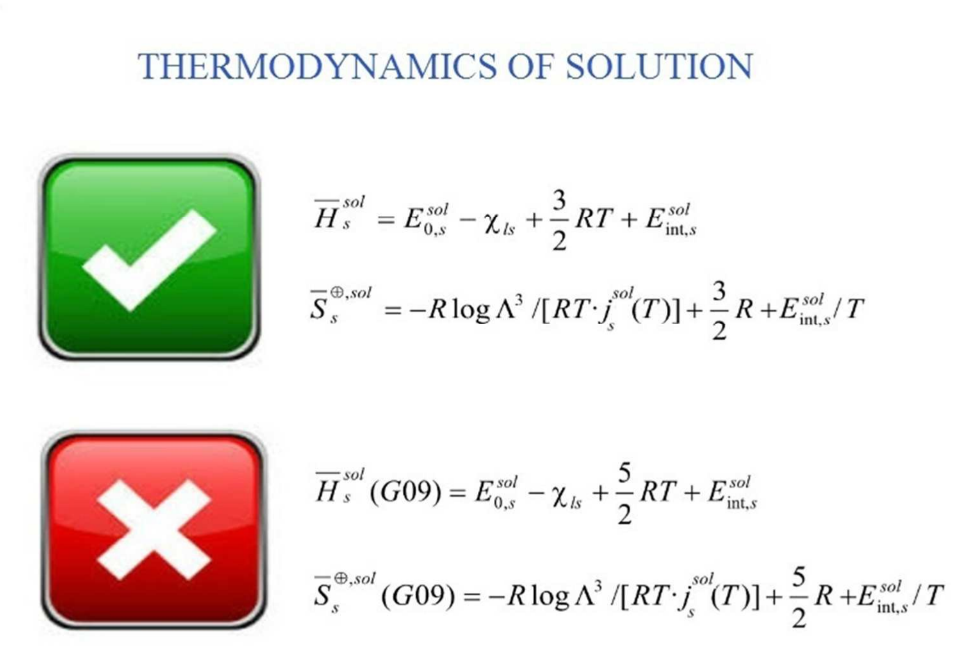
✗

$$\overline{H}_s^{sol}(G09) = E_{0,s}^{sol} - \chi_{ls} + \frac{5}{2}RT + E_{\mathrm{int},s}^{sol}$$

$$\overline{S}_s^{\oplus,sol}(G09) = -R\log\Lambda^3/[RT\cdot j_s^{sol}(T)] + \frac{5}{2}R + E_{\mathrm{int},s}^{sol}/T$$

<u>One sentence text highlighting the novelty of the work</u>:

The relations between conventional and Ben-Naim's formulations of solvation thermodynamics are derived and analyzed in detail.



$$\overline{H}_s^{sol} = E_{0,s}^{sol} - \chi_{ls} + \frac{3}{2}RT + E_{\mathrm{int},s}^{sol}$$

$$\overline{S}_s^{\oplus,sol} = -R\log\Lambda^3/[RT\cdot j_s^{sol}(T)] + \frac{3}{2}R + E_{\mathrm{int},s}^{sol}/T$$

$$\overline{H}_s^{sol}(G09) = E_{0,s}^{sol} - \chi_{ls} + \frac{5}{2}RT + E_{\mathrm{int},s}^{sol}$$

$$\overline{S}_s^{\oplus,sol}(G09) = -R\log\Lambda^3/[RT\cdot j_s^{sol}(T)] + \frac{5}{2}R + E_{\mathrm{int},s}^{sol}/T$$

211x158mm (96 x 96 DPI)

One sentence text

The relations between conventional and Ben-Naim's formulations of solvation thermodynamics are derived and analyzed in detail.