Short communication

# Revision of a theoretical expression for gas–liquid chromatographic retention

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## Abstract

In this communication, we revise some aspects of the [ideal gas/Van der Waals fluid] partition, derived in an earlier publication. The general character of the conclusions concerning the dependence of the partial molar free energy of solution, $\Delta G_s(n)$, on the chain length, $n$, of linear solute molecules is shown through the relationship with more general partition formulations. Simultaneously, the correction of an error in the expression of the retention time dependence on the phase ratio of the chromatographic column, $\beta$, is carried out. The misleading source of this error was redundant accounting in the solute translational contribution to $\Delta G_s(n)$. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

We recently published a discussion on the chain length dependence of gas–liquid chromatographic retention of *n*-alkanes [1]. The central objective of the report was to demonstrate that a non linear behavior for the partial molar free energy of solution, $\Delta G_s$, with the backbone carbon number, $n$, of solute chain molecules is expected theoretically. In chromatographic terms, this is translated into an expected non-linear behavior of ln $k$ with $n$, where $k$ is the retention factor. This aim was accomplished showing that, in diluted liquid solutions of linear flexible

molecules, such as the *n*-alkanes, the excluded volume effects introduce a non-linear contribution to $\Delta G_s(n)$. One aspect that needs to be clarified is the existent relationship between the employed formalism, the [ideal gas/Van der Waals fluid] partition, and more general approaches to the solvation process from the standpoint of statistical mechanics. The molecular formulation by Ben Naim [2,3] is probably the most cited theoretical background in statistical thermodynamics [4] and it is widely accepted as a general approach [5]. For this reason, a comparison of the outstanding remarks from both formalisms must be considered necessary for a clear comprehension on the general character of the conclusions concerning the expected non-linear behavior of $\Delta G_s(n)$.

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In Ref. [1], the application of the solute's chemical potential difference, between the liquid and gas solutions, led into an erroneous secondary implication. This involves an incorrect dependence of $\Delta G_s / RT$ with $\ln\beta$. The column phase ratio, $\beta$, is $^GV/^LV$, where $^GV$ and $^LV$ are the volumes of the gas and liquid phases, respectively. Hence, an additional dependence of the retention time, $t_R$, with $\beta$ was included. As will be shown by only applying statistical considerations, with no necessary reference to the standard states of solutions, this dependence on $\ln\beta$ should cancel out at the thermodynamic equilibrium.

Therefore, the objective of this communication is first to revise Ref. [1], providing the correction of a misleading error and, second, to show the general character of the conclusions concerning $\Delta G_s(n)$. The elements necessary for performing both tasks will be developed simultaneously by deriving again $\Delta G_s / RT$, now following only statistical concepts and avoiding any reference to the solutions' standard states. The latter are hypothetical entities necessary in the context of conventional thermodynamics for unequivocally defining solvation quantities in different concentration scales and under differing conditions [6–8]. Ben-Naim [2,3] showed that these are unnecessary for the statistical thermodynamic derivation of $\Delta G_s$, and also that several physical inconsistencies arise from their use.

## 2. The Van der Waals fluid formulation of the partition function

In the formalism of the Van der Waals (VW) fluid, described in Ref. [1], the constant $V$, $T$, $N$ canonical Gibbs ensemble is the statistical context (see e.g. Ref. [9]). The symbols denote the volume, temperature and number of particles defining the system, respectively. $N_2$ solute molecules are considered. The subscripts 1 and 2 respectively designate the solvent and solute. The solute–solvent interaction is represented by a continuum, a mean force field. This is quantified by a Boltzmann factor $\exp(-E_t / 2kT)$. $E_t$ is an effective average solute–solvent intermolecular potential energy of interaction. This approximation allows one to treat the solute molecules as independent particles moving in a mean field potential. Thus,

the canonical partition function, $Q$, can preserve the form for a system of independent, indistinguishable particles, $Q = q^N / N!$, $q$ being the molecular partition function.

For the generalized VW fluid, in the infinite diluted regime, the way to establish the average potential energy of a solute molecule is by computing the average distribution of solvent molecules around the 'central' solute. By 'central' is meant that the origin of a spherical coordinate system is located at the center of mass of the solute molecule, which is exclusively surrounded by solvent. The average distribution of solvent molecules around the solute is described by the radial distribution function $g(r)$. This function somehow describes the organization pattern or 'structure' of the liquid phase solution. The average is obtained assuming that the potential energy is pair-wise additive:

$$E_t = \frac{N}{V} \int_{r_{21}^*}^{\infty} U_{21}(r)\, g(r)\, 4\pi r^2\, \mathrm{d}r \tag{1}$$

$U_{21}(r)$ is the two-body, solute–solvent, attractive term of the VW potential function, $r_{21}^*$ is the VW radius.

The partition function of the VW fluid is:

$$Q = \frac{1}{N!} \left( \frac{V_f}{\Lambda^3} \right)^N \left[ \exp(-E_t / 2kT) \right]^N q_{r,v}^N \tag{2}$$

$V_f$ is the free volume of the system, i.e., that part of the system that is not affected by excluded volume effects. This is the difference between the total volume of the system, $V$, and the excluded volume $U_e$, viz. $V_f = V - U_e$. The cube of de Broglie's thermal wavelength $\Lambda = h / \sqrt{2\pi mkT}$ is the partition function for the momentum of translation, $m$ being the mass of the molecule. The internal partition function, $q_{r,v}$, accounts for contributions due to internal degrees of freedom (rotational and vibrational), allowed by the molecular structure. In the canonical ensemble, the reduced chemical potential of the solute, $\mu_2 / kT$, is related to the partition function, $Q$, by:

$$-\frac{^L\mu_2}{kT} = \left( \frac{\partial \ln Q}{\partial N_2} \right)_{V,T,N_1}$$

$$= \ln\left( \frac{^L V_f}{\Lambda_2^{3L} N_2} \right) - \frac{E_t}{2kT} + \ln {}^L q_{r,v_2} \tag{3}$$

The second equality corresponds to the application of Eq. (2). The left superscript, L, on the symbols indicates that we are applying the VW fluid partition function to the liquid phase solution. The first term of the sum is the translational contribution in a system of $^{L}N_2$ free rigid particles, only taking into account the three translational degrees of freedom of hypothetical rigid spheres. The second term accounts for the interaction of the rigid particle with its environment (a continuum, a mean field representing the solvent). The last term takes into consideration the internal degrees freedom of the solute. For our particular case of linear flexible molecules, there are $3n - 5$ internal degrees of freedom.

An equivalent expression to Eq. (3) can be written for the solute's chemical potential in an ideal gas solution, eliminating the interaction term and assuming that the entire volume of the gas phase, $^{G}V$, is accessible for the molecules.

At the thermodynamic equilibrium, the chemical potential of the solute in the ideal gas solution equals that in the liquid: $^{G}\mu_2 = {}^{L}\mu_2$. Then, by applying Eq. (3), and that corresponding to the ideal gas solution, derives:

$$\ln\left(\frac{^{L}\rho_2}{^{G}\rho_2}\right)_{eq} \equiv \ln K \equiv -\frac{\Delta G_s}{RT}$$

$$= -\frac{E_t}{2kT} + \ln\frac{^{L}q_{r,v_2}}{^{G}q_{r,v_2}} + \ln(1 - u_e) \quad (4)$$

The number density of solute molecules is $\rho_2 = N_2/V$. The ratio of number densities in both phases is equal to the ratio of molar concentrations, which is, in turn, equal to the distribution coefficient as it is currently defined in thermodynamics of the continuum: $K \equiv {}^{L}c_2/{}^{G}c_2$. The free volume of the liquid solution, $^{L}V_f$, from Eq. (3) was substituted into Eq. (4) by $^{L}V_f = {}^{L}V(1 - u_e)$, where $u_e$ is the excluded volume fraction of the liquid solution $(u_e = U_e/{}^{L}V)$. Then, the free volume fraction of the solution is $(1 - u_e)$.

In Ref. [1], it was shown that the third term, and last, of Eq. (4) is the one that introduces the non-linear behavior in $\Delta G_s(n)$. The reason is that, in solutions of chain molecules, the excluded volume fraction is not an additive function of the excluded volume of the monomers comprising the molecule, due to the connectivity of the chain. According to

Flory's theory for diluted solutions of chain-molecules, the dependence of the excluded volume fraction on $n$ is [1,10]:

$$u_e(n) = \frac{v_{m_2}}{v_{m_1}}(2\Phi - c\Phi^2 + ...)\,n^2 \quad (5)$$

The volumes of the monomers, or structural units, comprising the solute and solvent are $v_{m_2}$ and $v_{m_1}$, respectively. The dimensionless function $\Phi$ is the product $\Phi = \psi_1\,[1 - (\Theta/T)](v_{m_2}/v_{m_1})$, where $\psi_1$ is a function of the partial molar entropy of dilution at infinite dilution, and $\Theta$ is the temperature at which the theta state of the solution is attained [10]. The constant, $c$, has an order of $10^1$ for $n$-alkanes [1].

The volume pervaded by a chain molecule may be considered to be proportional to $<r^2>^{3/2}$, which is the cube of the root-mean-square end-to-end molecular distance, $r$ [11]. Monte Carlo calculations show that the volume of short polymethylene chains also grows approximately with $n^2$ [12].

## 3. Formulation by Ben Naim

Following basic statistical–mechanical considerations, Ben-Naim derived a very general expression for the chemical potential of the solute in an environment that can range from extremely diluted solutions to pure solute [2,3]:

$$\mu_2 = \mu_2^* + kT \ln \rho_2 \Lambda_2^3 \quad (6)$$

The 'pseudochemical potential', $\mu_2^*$, contains all of the relevant information concerning the interaction of the solute molecule with its medium, i.e., of the solvation. In the context of the $(p, T, N)$ ensemble, is defined as the Gibbs free energy difference for the process of adding only one solute molecule at a fixed position vector $\mathbf{R}_o$, in a system of $N_2$ solute molecules; preserving constant $p$, $T$ and the number of solvent molecules $N_1$:

$$\mu_2^* = G(p, T, N_2 + 1, N_1, \mathbf{R}_o) - G(p, T, N_2, N_1) \quad (7)$$

The second term of Eq. (6), $kT \ln(\rho\Lambda^3)$, was referred to as 'the liberation free energy' contribution to $\mu_2$. This denomination was preferred by Ben Naim to the traditional 'translational contribution' [see Eq. (3)],

due to the fact that, in certain systems, there is no proper translation, although a similar term may arise.

Eq. (6) can be derived in the canonical ensemble $(V, T, N)$, the grandcanonical $(V, T, \mu)$ or the $(p, T, N)$ ensemble [3]. The unique condition is the applicability of classical statistical mechanics ($\rho \Lambda^3 \ll 1$). In the $(p, T, N)$ ensemble, Eq. (6) is valid if $\rho_2 = N_2 / \langle V \rangle$, where $\langle V \rangle$ is the average volume of the system; while in the $(V, T, \mu)$ ensemble, it is valid if $\rho_2 = \langle N_2 \rangle / V$, where $\langle N_2 \rangle$ is the average number of particles in the system.

For an interacting solute molecule with internal degrees of freedom, the pseudochemical potential may be decomposed as:

$$\mu_2^* = W(2/1) - kT \ln q_{r,v_2} \tag{8}$$

In this equation, it is assumed that the internal degrees of freedom are independent of the interaction. $W(2/1)$ is the 'coupling work' of the solute into a fixed position $\mathbf{R}_o$ in the system. The system to which the solute is coupled, in our context of infinite dilution regime, would be composed solely of solvent molecules. The coupling work is the average energy of interaction of the solute with its entire surroundings and, for a rigid particle, is:

$$\frac{W(2/1)}{kT} = -\ln \langle \exp(-E_{21}/kT) \rangle \tag{9}$$

$E_{21}$ is the binding potential energy of the solute to the system at one specific configuration of molecules. The indicated average is the ensemble average over all possible configurations of molecules around the central solute. Strictly speaking, when the internal degrees of freedom of the molecule are affected by the interaction, both terms from the right-hand side of Eq. (8) cannot be determined separately. In this case, the pseudochemical potential has to be computed as $(^L\mu_2^* - {}^G\mu_2^*/kT) = -\ln \langle \langle \exp[-E_2(P)/kT] \rangle \rangle$. The first average is performed for all configurations of $N_1$ particles around the solute, at a specific conformation, $P$, of the latter. The second average is performed over all conformations of the solute, pondered by their statistical weights through the distribution function of conformations $y(P)$.

At the thermodynamic equilibrium, ${}^G\mu_2 = {}^L\mu_2$. Hence, by applying Eqs. (6) and (8), we have:

$$\frac{\Delta G_s^*}{kT} \equiv \frac{{}^L\mu_2^* - {}^G\mu_2^*}{kT} = -\ln \left( \frac{{}^L\rho_2}{{}^G\rho_2} \right)_{eq}$$

$$= \frac{W(2/1)}{kT} - \ln \frac{{}^Lq_{r,v_2}}{{}^Gq_{r,v_2}} \tag{10}$$

In the molar concentration scale, at infinite dilution, the definition of the (reduced) standard molar free energy of solution $\Delta G_s / RT$ is coincident in magnitude with the molecularly relevant solvation quantity $\Delta G_s^* / kT$ defined by Ben Naim [3].

Currently, the coupling work, $W(2/1)$, is, in turn, decomposed as follows [5]:

$$W(2/1) = W_{cav} + W_{elec} + W_{dispersion}, \text{ etc.} \tag{11}$$

The first term of the sum is the work of formation of the solute cavity. The cavity at the fixed position $\mathbf{R}_0$ is the volume of the system where the solute is placed, i.e., that domain that is excluded to all other particles; what in the context of the VW fluid is named the molecular 'excluded volume'. $W_{cav}$ takes into account that part of the intermolecular potential $(2/1)$ corresponding to a hard core, while the rest of the contributions concerning $W(2/1)$ are referred to as the 'soft' part of the solute–solvent interaction potential.

The scaled particle theory (SPT) provides a theoretical context for computing the free energy of cavity formation for hard spheres [3,5]. In the particular case of cavities of radius $r$ presenting a small value with respect to the radius of the solvent particle[1], the work of cavity formation has an exact expression [3]:

$$\frac{W_{cav}}{kT} = -\ln \left( 1 - \frac{N v_{cav}}{{}^L V} \right) \tag{12}$$

The probability of finding the volume $v_{cav} = 4\pi r^3 / 3$ occupied is $\rho v_{cav}$, where $\rho = N / {}^L V$ is the number density of particles that are potentially capable of occupying the cavity. Then, the probability of finding the volume $v_{cav}$ empty is $P_o(r) = (1 - \rho v_{cav})$. The relationship between the probability $P_o(r)$ and the reduced work of cavity formation is $W_{cav}/kT = -\ln$

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[1]It should be remarked that this condition is generally applicable to the gas–liquid chromatographic system. The solute molecule is always much smaller than the solvent.

$P_o(r)$. It should be noted that $Nv_{cav}$ plays the same role as the excluded volume of the system, $U_e$, does in the VW fluid. Eq. (12) provides a positive contribution to $W(2/1)$ (or in turn to $\Delta G_s$). The reason is that energy is always needed to build up an empty cavity in a fluid.

Finally, we can rewrite Eq. (10) in the same form as Eq. (4), using the nomenclature applied for the VW fluid:

$$-\frac{\Delta G_s}{RT} = -\frac{W(2/1)_{soft}}{kT} + \ln\frac{^L q_{r,v_2}}{^G q_{r,v_2}} + \ln(1 - u_e)$$

(13)

$W(2/1)_{soft}$ accounts for all contributions to the coupling work $W(2/1)$, with the exception of the work of cavity formation, which is indicated separately as the last term of the sum in accordance with the SPT limit case for low solute/solvent ratios of molecular radii.

## 4. Discussion

The [ideal gas/VW fluid] derivation of the chemical potential is limited to the canonical ensemble, requiring the formulation of some molecular hypotheses. Ben Naim's expression for the solute chemical potential can be derived from other ensembles without making specific molecular assumptions; hence it's generality. It should be noted that the hypotheses later needed for deriving Eq. (13) also have a very general character. From the comparison of Eq. (4) and Eq. (13), we see that both present basically the same features. However, the form to compute the interactions is different, as follows from the comparison of Eqs. (1) and (9). In the VW theory, the computation of the average potential energy of the solute molecule concerns the two-body attractive potential $U_{21}$.

From the general point of view of statistical thermodynamics, the ratio of numeral densities ($^L\rho_2/^G\rho_2 = K$) at equilibrium is the parameter defining the solvation process. As seen through Eq. (4) or Eq. (10), this is directly related to the relevant molecular thermodynamic quantities of solvation. In other words, the distribution coefficient $K$ unequivocally quantifies solvation without the necessity of defining

standard states for the solutions. This fact, which was discussed thoroughly in the ambit of chemical physics [2–4], has consequences of importance for gas–liquid chromatography. These will be treated in a forthcoming paper.

The volume ratio $\beta = {}^G V/{}^L V$, which belongs to the translational contribution to the solute's chemical potential, at the thermodynamic equilibrium, is contained in $K$ [Eqs. (4) and (13)], so it is eliminated from the right-hand side of these equations. We must conclude that the dependence of $\Delta G_s$ on $\beta$ cannot be sustained in the theoretical context of Ref. [1], and the incorrect Eq. (12) from that reference has to be replaced by Eq. (4) from the present report.

The application of Eq. (4) or Eq. (13) to the chromatographic retention of $n$-alkanes, which are long enough to admit intramolecular interactions ($n \geq 5$), renders:

$$t_R(n) = t_M + \exp[A + B(n - 2) + \ln(1 - Cn^2)] \quad (14)$$

Now, the only difference with Ref. [1] resides in the physical meaning of the first parameter in the exponential: $A = \ln(t_M/\beta) - \Delta G^+/RT$, where $t_M$ is the gas hold-up time. $-\Delta G^+/RT$ is the extrapolation of the sum $[-E_t/2kT + \ln(^L q_{r,v}/^G q_{r,v})]$, for $n$-alkanes admitting intramolecular interactions ($n \geq 5$) to $n = 2$. Therefore, we must assume that the conclusion derived in Section 7.1 of Ref. [1] is incorrect. The few experimental data from Fig. 3 in Ref. [1] should be reinterpreted with the aid of additional experimental information, a task that we shall face in a forthcoming paper.

## 5. Conclusions

A more general statistical treatment of the free energy of solution leads to the same conclusions obtained formerly with the simple [ideal gas/VW fluid] formulation. There is a non-linear contribution to $\Delta G_s(n)$ of linear flexible molecules arising from the fact that the pervaded volume by the solute molecule is not an additive property of the number of structural units comprising it. This is the consequence of chain connectivity, i.e. of the preservation of bond length and angles. In more general terms, the work of cavity formation does not present a linear

increase by incrementing the length of the chain solute. A direct consequence from this theoretical fact is that, in gas–liquid chromatography, we should expect a deviation from linearity in the plots of ln $k$ vs. $n$.

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