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Seawater Plasma as the most Abundant Classical Plasma on Earth - Studies on Individual Activities and Pressures. [1]

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Abstract

In the third Chapter of Fortov's last book [1] in extension to a foregoing book [2] several new topics have been included, among them classical plasmas including seawater. We consider seawater as a classical nonideal plasma with nonideality parameters near to one. We give here a survey of this new field and present applications to the individual activities and partial pressures of seawater. First we consider the available exact results of statistical physics for charged hard spheres. In difference to most previous studies of charged spheres with equal diameters we use the more flexible model of nonadditive diameters, where the independent contact distances of pairs are the free parameters. For this model we develop fully analytical nonlinear extensions of the standard Debye - Hückel approximations of individual activities and then a new extrapolation to the theory to partial pressures. The osmotic pressures are related to the chemical potential of the solvent, the freezing and boiling points etc. Special emphasis is put on predicting the properties of seawater plasma. We calculate the individual activities and the individual osmotic coefficients of a six - component "ideal seawater" model and compare with other available results.

1 Introduction

Seawater as the most abundant classical plasma on Earth and his role as a most important factor for our climate is overwhelming. Counting on our planet the number of free charges, we come to the conclusion that most free charges are to be found in the oceans. Vladimir Fortov, who preferred in his life always a very broad and global view on the problems of science, arrived at such insights in the discussion on the SCCS - conference 2017 in Kiel. On the conference excursion to Lübeck he pointed out to the present author that he planned a Russian version

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[1] Dedicated to the memory of Vladimir Fortov, December, 2020

of the book and proposed to include not only additional material on plasmas at high pressures and extreme conditions but also some considerations on reservoir of seawater on earth as an important non - ideal plasma. Vladimir explained to this author on a beer mat that the non - ideality parameter for a seawater electrolyte with a Landau length of about $\ell \sim .7nm$ and a mean ionic distance of somehow more than $d_0 \sim 1nm$ is between $\Gamma \sim .1$ and $\Gamma \sim 1$, i.e. about the same order as the nonideality parameter in a high -temperature, high - pressure $Cs-$ plasma.

It may be more than a strange coincidence that the founder of the Rostock school of statistical physics, the late Hans Falkenhagen (1895 - 1971), decided half a century ago, a year before passing away, to give a summary on nonideality effects in electrolytes [3, 4, 5]. These summaries were in part written together with this author and in part with Wolf - Dietrich Kraeft. They are a comprehensive treatment of the nonideality effects in electrolytes including thermodynamic and transport properties. Hans Falkenhagen understood the term nonideality as the deviations from Planck's theory of ideal solutions, which begin with the limiting laws by Debye and Onsager and the subsequent hard sphere corrections.

In same recent papers [6, 7, 8] we provided already some more recent applications to the activity coefficients and other properties of seawater electrolytes which complete the older material given in several books [1, 5, 9, 10].

We develop here in more detail the view that seawater is a classical nonideal plasma and give results of very recent studies on individual activities [6, 7, 8]. Then we extend the methods to calculations of the partial pressures and the osmotic coefficients of seawater. As well known, the thermodynamic properties of the ocean play a deciding role for modeling the climate on earth [11, 12, 13, 14, 15]. We responded this way also to urgent requests of international institutions and to evident needs for extending and deepening the knowledge on the physico-chemical properties of the components of seawater and other complex natural and technological electrolytes [15]. In spite of the primary role of seawater electrolytes for our life and in particular for our climate, this medium is not well represented in recent books and survey articles on electrolytes. In most of those publications, including our own work, the subject seawater is not even mentioned, despite of its dominant role for solving our urgent climate problems. Vladimir Fortov understood very well that the reliability of recent predictions on the temperature development in the next century depends crucially on our knowledge about the thermodynamics and nonideality effects of seawater which is not well studied.

Most of the methods used here are relatively simple and have been in principle been developed already long ago, however, only rarely including applications to

very complex electrolytes. We follow the convince of Fortov and other experts, that more knowledge on individual activity and transport coefficients of complex systems is important and of high relevance for climate research because of the influence of seawater on the energy exchange on the surface of our planet [13, 15]. Seawater is a rather complex electrolyte, containing as a rule more than 20 species some of them only in tracer concentrations. In addition to univalent ions, such as Na^+,K^+,Cl^-, several double - charged ions Mg^{2+}, Ca^{2+} and SO_4^{2-} are of importance for seawater properties. Therefore, before proceeding to applications we have to develop a new look at the analytical theory of electrolytic systems including ions with higher charges, where the differences between the individual and the mean activities are large [16, 17]. Since seawater is a mixture of ions with one or two charges we devote special interest to the consequences of charge asymmetry and of higher charging for the individual ionic properties.
According to Lewis, activities of species i are defined by chemical potentials [12]

$$\mu_i = \mu_i^0 + k_B T \ln(a_i/a_0). \tag{1}$$

Here, μ_i^0 is a specified reference chemical potential, k_B is the Boltzmann constant, T is the absolute temperature, a_i is the activity of the ion i, and a_0 is a constant that renders unitless the argument of the logarithm. (Note that in the physico-chemical literature this constant is often omitted but silently assumed to be $1mol/l$). For the definition of activity coefficients we have several possibilities depending in particular on the choice of units for the concentrations/mass relations. In our statistical calculations we use the ion molarity (in moles of the ion per dm^3) as the basic primary quantity. For seawater we use also the chlorine molality (m_{Cl}, in moles of chlorine per mass of pure water), rather than the traditional oceanographic measures "chlorinity" (Cl, per mass of seawater) or the "absolute salinity" (S_A or S, the mass of dissolved sea salt per mass of seawater). Those quantities express certain mass ratios and are mutually related. For a standard ocean, the absolute salinity is $S_A = 35.16504$. Note hat the statistical theory mainly uses concentrations instead of mass relations.
The so-called rational activity coefficients, f_i^* and f_i, correspond to the standard theory of solutions by Max Planck and were developed in many works in different forms [5]

$$a_i = x_i f_i^*, \qquad a_0 = 1; \qquad a_i = n_i f_i, \qquad a_0 = 1cm^{-3}. \tag{2}$$

Here, $x_i = N_i/\sum N_k$ are the mole fractions of the species i in the solute. The coefficients f_i have a dimension of reciprocal densities. Alternatively, the so-called practical (or molal) activity coefficients γ_i are defined using molalities. A standard method for estimating rational individual activities is the so-called virial expansion of the thermodynamic functions [3, 5, 10]. Methods for practical calculations were developed by many authors [11, 16].

Beside the individual activities a_i, also the partial osmotic coefficients related to the partial osmotic pressures P_i,

$$g_i = P_i/P_i^{id}, \tag{3}$$

play an important role for the ionic properties of electrolytes. As there are well-known difficulties to measure individual ionic properties, arbitrary conventions are often employed for quantities defined by the single-ion activity coefficients and the pH scale [13].

In the statistical theory, we are able to determine single - ion activities only up to uncertain linear terms in the electrical charges e_i. These principally uncertain contributions always cancel in the mean activities. Uncertainties in the experimental estimation of individual activities are therefore related to the violation of electroneutrality of samples. Theoretically this effect is connected with contributions which are linear in the charges e_i [1, 2]. These contributions are in the statistical theory principally uncertain, however they cancel out in the average and to not appear in the mean activities. We assume that this is also the reason for uncertainties we observe in the experiments. Then the uncertainties in the estimation of individual activities are connected with the space charge of the samples. Corresponding to these theoretical results, individual activities are not unique since terms linear in the charges remain uncertain in experiments as well as in the theory. These possibly conditional terms cancel out in the average and do not influence the mean activities.

With respect to seawater, sww thw works on the Gibbs function of seawater at oceanic salinities up to $40 g/kg$ [15, 14]. Pitzer equations are semi - empirical formulas for individual ion properties including activity coefficients and pH of seawater [11]. We use here statistical methods following mostly the theoretical work of the school of Falkenhagen on the dependence of thermodynamic and transport data on individual ionic interactions, but so far without expensive applications to complex electrolytes. The basic methods have been described already in [6, 7] and are based on earlier work [3, 5, 16]. Our approach is consistent with all known exact results of the Friedman - Falkenhagen cluster expansions and provide reasonable results for mixtures including, 1 - 1- and 2-1- electrolytes and in particular to standard seawater. In the case of seawater we will find, that the model of non - additive radii provides a better description of the data [11] as the model of additive radii as used in most earlier work [16, 19]. For this reason we develop here the model of nonadditive radii with given contact distances. A description of conductance data based on the same model is in progress. As we mentioned for standard seawater very useful results have been obtained by Ulfsbo et al. [19] performing extensive MC calculations for a hard sphere model of seawater in the form of an electrolyte containing the major ions $Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}$, and the minor ions HCO_3^-, CO_3^{2-}. The results for mean salt-activity coefficients were compared with the Pitzer model, finding after fitting the radii in general good agreement over the temperature range 0 to $25^o C$ and salinity range $5 g/kg$ to $40 g/kg$. In the present paper we use analytical formulae and fit the contact distances R_{ij} to available data at $25^o C$.

We will explain here several statistical methods for the calculation of the partial osmotic coefficients [3, 5, 10].

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2 Interaction Potential Model and Methods of Statistical Thermodynamics

For the calculation of theoretical individual ionic activity coefficients we are using simple analytical expressions such as generalized Debye-Hückel-type approximations, virial expansions, and the analytical solutions for the mean spherical approximation for charged hard spheres (MSA). We start with the consideration of an arbitrary neutral ionic solution and specify then to selected components which are in particular relevant to seawater. Individual ionic activity coefficients will be be calculated for models of hard charged spheres with additive or nonadditive radii. In some earlier work [6, 7] we applied several methods based on statistical physics to calculate the individual activity coefficients for given models. In particular we developed several theoretical approaches for the model of charged hard spheres with non-additive contact distances R_{ij}. Let us repeat the main results. We follow the general concepts of the Mc Millan - Mayer theory theory of solutions [9] and start from approximations of the pair distribution, go then by the virial formula to the pressure, the osmotic coefficient, the electrical and the free energy. By Debye charging we obtain the Helmholtz free energy, and by partial differentiation the individual activity coefficients. We study an electrolyte with the electrolyte concentration n_0, the ion densities $n_i = \nu_i n_0$, the ion charges $e_i = z_i e$, and the ionic strength $I = n_0 \sum_i \nu_i z_i^2/2$. and concentrate on calculations of the excess properties [5, 10]. For the calculation of the excess thermodynamic functions we define first the potentials of average force between the ions. We split the interaction potential between the ions a and b, ψ_{ab}, of the average force into a Coulombic and a short-range part

$$\psi_{ab} = V_{ab}(r) + V'_{ab}(r); \quad V_{ab}(r) = z_a z_b k_B T(\ell/r); \quad \ell = (e^2/4\pi\varepsilon_0\varepsilon_r k_B T). \tag{4}$$

where $\varepsilon_r(T,p)$ is the relative dielectric constant of pure water and ℓ the Coulomb length (also called Landau length or double Bjerrum length), being functions of temperature and pressure. In the following we perform all calculations for the temperature $T = 298.15K$ (i.e. 25 degrees Celsius). and assume for the relative dielectric constant the value $\varepsilon_r = 78.36$. Then we get for the Coulomb length $\ell = 715.4pm$. By changing ℓ we may easily go to other conditions. For the short-range part, $V'_{ab}(r)$, different models are used [5, 10]. We consider here the model of charged hard spheres with given minimal contact distances, which are not necessarily additive:

$$V'_{ab}(r) = \infty \quad if \quad r < R_{ab}, \quad otherwise \quad V'_{ab}(r) = 0. \tag{5}$$

Here R_{ab} are the contact distances, forming a set of the smallest ion distances, one for each kind of ion pairs. This we consider as a kind of minimal model for the estimation of individual properties of ions in many-component complex electrolytic systems. The charges and contact distances are the basic parameter set of our system, relevant is that we will not assume additivity of the radii.
According to cluster theory [3, 5, 9, 10] we get in the lowest orders in the concentration up to $O(n_i^2)$, the following exact results (for the given potential model) which is correct up to quadratic order in the concentration [3, 5, 9, 10]

$$\ln f_i = -z_i^2 \ell\kappa \sum_j \zeta_j (1 - \kappa R_{ij} + \frac{5}{4}(\kappa R_{ij})^2 + O(\kappa^3)) - \frac{\pi}{3}\zeta_i \sum_j n_j \left[z_i z_j \ell\right]^3$$
$$\cdot [C + \ln(3\kappa R_{ij})] - \frac{\pi}{6}\sum_j n_j R_{ij}^3 \xi_{ij}^4 + \frac{\pi}{3}\sum_j n_j R_{ij}^3 + O(\xi_{ij}^5; n^{3/2}). \tag{6}$$

We introduced a specific factor ζ_i characterizing the individual properties of the components in unsymmetrical electrolytes. The factor ζ_i has the value $1/4$ for 1 - 1 electrolytes For unsymmetrical electrolytes the factors are different for the two components. In the case of 1 - 2 electrolytes, the single-charged ions correspond to $\zeta_1 = 1/18$ and the double-charged ions correspond to $\zeta_2 = 8/18 = 4/9$. For 1 - 3 electrolytes, the factors are $\zeta_1 = 1/56; \zeta_2 = 27/56$. The sum over the components is always equal to 1/2 for any mixture. These exact results of cluster theory, first derived by Friedman, set a strict standard for any new theory. Here we derive formulae which are fully consistent with cluster theory results. By differentiation of the free energy, we get for the activities first an expansion wtih respect to the parameter η_{ij} Then by using the technique of partial fraction representations we get the closed approximation

$$\ln f_i = \ln(\alpha_i) - z_i^2 \kappa \ell \sum_j \zeta_j \left[\frac{1}{(1+\eta_{ij})} + G_1(\xi_{ij}, \eta_{ij}, \zeta_i) + ... \right] \tag{7}$$

$$+ \frac{4\pi}{3} \sum_j n_j R_{ij}^3 + ...; \qquad \eta_{ij} = \kappa R_{ij}. \tag{8}$$

where the degree of ionization of species i is approximated by

$$\alpha_i = \frac{1}{1 + z_i^2 \kappa \ell \sum_i \zeta_i (\xi_{ij}^2/24) G_2(\eta_{ij})}. \tag{9}$$

At least up to the leading order $O(n_j)$ this approximation for the activities is in agreement with the exact expression derived from the cluster expansions for the free energy [3, 5, 9, 7]. It contains, however, in addition contributions of higher order in the parameter η, which strongly improve the convergence of the series. The first term leads us back to Debye's limiting law and to the DHE formula, the next order provides the extended limiting law of Poirier and Friedman and terms beyond.

The Euler functions $E_n(x)$ and $e_n(x)$ are well studied and tabulated [7, 6]. In the explicit expressions for the functions G_1, G_2 we use for numerical convenience mostly the modified Euler functions $e_n(x)$. For numerical calculations we have useful approximations

$$e_1(x) = x \exp(x) E_1(x) \simeq ax \ln\left(1 + \frac{1}{ax}\right), \qquad e_{n+1} = 1/(1+n/x) \quad n = 1, 2, ... \tag{10}$$

More precise approximations are given in [7, 6]. In the approximation for $e_1(x)$, the value $a = 1$ provides an upper bound and $a = 0.5$ a lower bound. For an approximation in the range $0 < x < 2$ we use the value $a \simeq 0.6147$ which has been obtained by fitting to the data in tables around $x = 1$ [7]. The approximation for $e_2(x), e_3(x), ...$ provides an upper bound. Numerical integrations of the integral representation of the G-function for several values $\eta < 3, |\xi < 10|$ have shown that these simplest approximations are reasonable for the cases we consider. Using these relations we find:

$$G_1(\xi,\eta,\zeta) = \frac{\xi}{18(1+\eta)^3}[e_1(3\eta) - \zeta(3\eta)\exp(-3\eta)], \tag{11}$$

$$G_2(\xi,\eta) = \sum_{m=4}^{\infty} \frac{\xi^{m-2}}{4m!(1+\eta)^m} e_{m-2}(m\eta). \tag{12}$$

Helpful for the convergence is, that the higher orders disappear more quickly with η, because the effective expansion parameter appears to be $e^2/(1+\eta)$.. The nonelectric terms are considered here only in linear approximation, at high densities we may use Carnahan-Starling-type approximations [10]. These corrections, however, may be essential only in the range of concentrations around $1 mol/kg$ and beyond. We note that the terms which are described by the functions G_1, G_2 tend to increase the difference between the activities of anions and cations. As a rule these terms increase up to a few tens of mol/dm^3 and then they decrease.
For the contribution of the ionic species i to the osmotic pressure we get by introducing the nonlinear Debye - Hückel distribution function into the virial formula

$$P_i = P_i^{id} + \frac{1}{3}u_i^{el} + \frac{2\pi}{3}n_i \sum_j n_j R_{ij}^3 \exp\left[\frac{\xi_{ij}}{(1+\kappa R_{ij})}\right] \tag{13}$$

Here the electrical energy density can be also expressed by Euler functions [6, **?**, **?**]. We define the weakly coupling, moderately coupling and strongly coupling parts of the osmotic pressure by

$$\beta P_i/(n_i k_B T) = g_i = 1 + g_i^{wc} + g_i^{mc} + g_i^{sc}. \tag{14}$$

Note that the strongly coupled contribution is negative and increases strongly with e^2. As a result the pressure my became negative what is here un - physical. Quite formally we may, in order to avoid negative values of g_i, transform the expression by replacing $1 + g_i^{sc}$ which can get negative values by the strictly positive expression $1/(1 - g_i^{sc})$. This way without changing the accuracy in the linear order in the density $O(n)$ we arrive at the mathematically more beautiful expression

$$\beta P_i/(nik_B T) = g_i = \frac{1}{1 - g_i^{sc}} + g_i^{wc} + g_i^{mc} \tag{15}$$

This expression is however, not only a mathematically more beautiful, but is has also a deeper quasi - chemical meaning as we will show in a next section.
Similar to these approximations for the pressure we get also corresponding expressions for for the activities. We start as in our previous work from the same approximations of the pair distribution and obtain first the free energy; then by differentiation the individual activity coefficients [7, 6]. We checked that the results are consistent with the exact results obtained by the theory of cluster expansions for the activity coefficients at small concentrations (densities) [10, 3, **?**]. For an elegant representation of the thermodynamic functions we introduced the fractions k_i which were used already by Onsager in transport theory. These fractions are specific for the components of each electrolyte. We used earlier instead of k_i the letter $\zeta_i = k_i/2$, here we prefer Onsager's notation changing, however, Onsager's letter q_i to our notation k_i. For 1-1 electrolytes we get the value $1/2$ for both components, for 2-1 electrolytes the factors are different. For ions with $z_i = 2$ we get $k_i = 2/3$ and the ion component with $z_i = 1$ correspond to $k_i = 1/3$. Note that these differences are essential for the splitting between the individual osmotic coefficients and activities.
Our result for the osmotic coefficients in DHX approximation reads

$$g_i^{sc} = -\frac{1}{3}2\pi\sum_j n_i R_{ij}^3 \sum_{m=4}^{\infty} \xi_{ij}^m \Big(\frac{e_{m-2}((m-1)\eta)}{((m-1)!(1+\eta)^{m-1}(m-1)\eta} - \frac{1}{m!(1+\eta)^m} \Big) \tag{16}$$

where the Euler function is represented as $E_n(x) = xexp(x)e_n(x)$. In a different form we may write the partial osmotic coefficients and the activities as

$$g_i = 1 - \frac{1}{6} z_i^2 \kappa\ell \cdot \sum_j k_j \tilde{G}(\kappa R_{ij}, \xi_{ij}), \quad lnf_i^{el} = -\frac{1}{2} z_i^2 \kappa\ell \cdot \sum_j k_j G(\kappa R_{ij}, \xi_{ij}), \tag{17}$$

The G - functions refer to the activities and the functions with a tilde $\tilde{G}$ refer to the pressure and, by the way, also to internal energy. The G - functions are sums of terms representing the different orders in ξ_{ij}^k. However $\tilde{G}_k \neq G_k$:

$$G(x) = G_0(x) + G_1(x) + G_2(x); \qquad \tilde{G}(x) = \tilde{G}_0(x) + \tilde{G}_1 + \tilde{G}_2(x) \tag{18}$$

In simplest approximation we use here for the zeroth order G_0 the Debye - Hückel - approximation; more advanced is the Mean Spherical Approximation (MSA) and the related Henderson - Smith approximation (HSA) [6]. In DH - approximation we find

$$G_0(x) = \frac{1}{1+x}, \qquad \tilde{G}_0(x) = \frac{1}{1+x} - \frac{x}{2(1+x)^2}. \tag{19}$$

The more advanced nonlinear Debye - Hückel - approximations (DHX) take into account the first- and second-order terms $G_1(x), G_2(x), \tilde{G}_1(x), \tilde{G}_2(x)$ [6]. For a convenient representation we introduce the auxiliary functions

$$e_1(x) = x\exp(x)\cdot E_1(x); \quad e_2(x) = x(1-e_1(x)); \quad e_n(x) = \frac{x}{n-1}(1-e_{n-1}(x)). \tag{20}$$

Using these definitions and approximations we we find for the strong coupling part of the osmotic coefficients

$$\begin{aligned} g_i^{sc} &= -2\pi\sum_j n_j R_{ij}^3 \sum_{m=4} \frac{(\xi_{ij}/(1+\eta_{ij})^m)}{(m-3)m!}(1+\frac{m}{3}\eta) \qquad (21)\\ &= -2\pi\sum_j n_j R_{ij}^3 [K_{04} + \frac{\eta}{3}\tilde{K}_{04}](\xi_{ij}/(1+\eta_{ij})) \end{aligned}$$

where we introduced the Kirkwood functions [5]

$$K_{04}(x) = \sum_{m=4}^{\infty} \frac{x^m}{(m-3)m!}, \qquad \tilde{K}_{04}(x) = \sum_{m=4}^{\infty} \frac{x^m}{(m-3)(m-1)!} \tag{22}$$

which is well known in electrolyte theory [5]. Cutting the series in ξ behind the third term (sixth order in ξ) we find the different representation

$$G_1(\xi,\eta,\zeta) = \frac{\xi}{18(1+\eta)^3}[e_1(3\eta) - \zeta(3\eta)\exp(-3\eta)], \tag{23}$$

$$G_2(\xi,\eta) = \frac{\eta}{\xi^2}\Big[\frac{(\xi/(1+\eta))^4}{24(1+4\eta)} + \frac{(\xi/(1+\eta))^5}{96(2+5\eta)} + \frac{(\xi/(1+\eta))^6}{480(3+6\eta)} + ..\Big]. \tag{24}$$

$$\tilde{G}_1(\xi,\eta) = \frac{\xi}{18(1+\eta)^3} b[e_1(2\eta) - 3\eta\zeta\exp(-3\eta)], \tag{25}$$

$$\tilde{G}_2(\xi,\eta) = \frac{\eta(1+\eta/3)}{\xi^2}\Big[\frac{(\xi/(1+\eta))^4}{24(1+3\eta)} + \frac{(\xi/(1+\eta))^5}{120(2+4\eta)} + \frac{(\xi/(1+\eta))^6}{720(3+5\eta)} + ..\Big]. \tag{26}$$

We may convince ourselves that at zero density $\eta = 0$ the convergence is getting unsatisfactory for $|\xi| > 6$, however for larger η say $\eta = 1$ the convergence is improved and we may extend the calculations to $|\xi| \simeq 10$, covering solutions of interest for seawater. Further we note that both functions $G_2(\xi,\eta)$ and $\tilde{G}_2(\xi,\eta)$ are positive for positive arguments and they agree for small ξ and small η. For larger values of the arguments $\tilde{G}_2(\xi,\eta)$ is larger.

3 Association effects in semi- chemical description

The semi - chemical picture comes in, when the Pade approximation $(1+g_i^{sc}) \to 1/(1-g_i^{sc})$ is interpreted as introducing the degree of ionization of the ions i i.e. the relation between free ions and the total number of ions i by

$$\tilde{\alpha}_i = \frac{1}{1-g_i^{sc}} = \frac{1}{1+\frac{1}{2}z_i^2\kappa\ell\cdot\sum_j k_j\tilde{G}_2(\kappa R_{ij},\xi_{ij})}. \tag{27}$$

In principle we could stop here and proceed to calculations. The very fact, however, that in many electrolytes including also seawater the presence of multiple -charged ions leads to association effects, calls for some deeper discussion. Note that we have in principle the same situation in plasmas, where the presence of multiple - charged ions also leads to bound state effects, i.e. formation of atoms [2, **?**]. The theory of bound states in systems with Coulombic interactions has a long history which begins with Bjerrums work, which cannot be discussed here in detail. How can take into account at least weak association relevant for seawater? As well- known since Onsagers work, there is some freedom in the choice of methods and in the definition of the bound states. We follow here the line of semi - chemical methods. In the case of activity - based methods we have made profit from methods developed by Justice [**?**, 20]. Here we will use a semi - chemical method based on the pressure which also avoids explicit definitions of bound states. This method which is quite effective, can be giver a stronger foundation by methods based on the grand - canonical ensemble [2]. Here we prefer quite simple arguments based on chemical ideas. In order to explain the key ideas we start from an naive chemical description of a binary electrolyte consisting of the densities of n_+ free anions, n_- free cations and n_0 bound pairs, being in chemical equilibrium described by the mass action law (n - total number of free plus bound cations)

$$\frac{n_0}{n_+n_-} = nK(T); \qquad n = n_+ + n_0. \tag{28}$$

The pressure is then given by

$$\beta p = n_+ + n_- + n_0 + \beta p^{ex} \tag{29}$$

We introduce the definition of the degree of ionization $\alpha = n_+/n = n_-/n$ and the degree of association $\delta = 1-\alpha$ and the mass action law

$$\delta = 1-\alpha = \alpha^2 nK_2(T), \quad or \quad \frac{1-\alpha}{\alpha} = \alpha nK_2(T). \tag{30}$$

we find

$$\beta p = n_+(1+\alpha)n + \beta p^{ex} = 2n - \delta n + \beta p^{ex}. \tag{31}$$

Note that in a statistical formulation the mas action constant of pair formation is related to the bound state part of the second virial coefficient in the fugacity expansion $K_2(T) = 2b''_{+-}$. Near to full ionization $\alpha \simeq 1$ a zeroth approximation gives $\alpha^0 = 1 - nK(T)$. This approximation , however, is not appropriate since α^0 is even not positive definite. The result is much better, when we start from the second form of relation (30) which gives in the first iteration and in an improved version positive definite expressions [2, **?**]

$$\alpha^{(1)} = \frac{1}{1+a_2}; \qquad \alpha^{(2)} = \frac{1+nK_2(T)/2}{1+3nK_2(T)/2}; \qquad a_2 = nK_2(T) = 2nb''_{+-} \tag{32}$$

These relations suggest, to select a big negative term which follows the ideal pressure and identify it with he mass action constant. In our case of osmotic pressure we propose to identify the term proportional to $\tilde{G}_2$, which is strictly negative as the contribution of association association. In a next step we identify this with the degree of association $\delta = 1 - \alpha$ which is proportional to the mass action constant, This way we arrive in first approximation at the degree of ionization of species i

$$\alpha_i^1 = \frac{1}{1 + \frac{1}{2}z_i^2 \kappa\ell \cdot \sum_j k_j \tilde{G}(\kappa R_{ij}, \xi_{ij})} \tag{33}$$

Without going into the details, we may be found in the cited books for the case of gas plasmas [1, 2, **?**] we will show now that this procedure may be extended also to the association of more than 2 charges. Applications to Hydrogen, Helium and Lithium plasmas have given more recently in [21]. Here we consider now first the classical association of two anions and one double charged cation. We think here about $MgCl_2$, where the cation Mg^{2+} binds the two ions Cl_-. This case is structurally equivalent to the binding of two electrons by a double - charged He^{2+} - ion. This way we may follow the procedure developed in plasma physics [2]. Defining the the two association constants a_2 for pairing of two charges and a_3 for a triple formation $+--$. Translating the method described above for pair formation to triple formation we get

$$P = P^{id}[\frac{1}{3} + \frac{2}{3}Z(a_2, a_3)] + P^{ex}; \tag{34}$$

$$Z(a_2, a_3) = 1 - a_2 - a_3 + 2a_2^2 + 3a_3^2 + a_2 a_3 + \ldots \simeq \frac{(1 + a_2/4 + a_3/2)}{(1 + 5a_2/4 + 3a_3/2)} \tag{35}$$

Here the meaning of the sum over states $Z(a_2,a_3)$ is the degree of full ionization, i.e. the number of free double - charged ions to the total number of those ions (counting free and bound ions). We see, that for the limit case $Z=0$ the relative osmotic pressure goes to $1/3$ in comparison to the case of full ionization $Z=1$. This way we may treat the case of weak association (nearly full ionization) in $MgCl_2$ - solutions, provided we are able to identify the association constant for electrostatic triple association. We explained here the procedure for the example $MgCl_2$. By exchanging $+$ and $-$ we are able to treat also triple association of salts like Na_2SO_4. An earlier semi - chemical picture for the activities [**?**] which leads to

$$\tilde{\alpha}_i \simeq \frac{1}{1+z_i^2\kappa\ell\sum_j \zeta_j G_2(\eta_{ij},\xi_{ij},\zeta_i)}. \tag{36}$$

The comparison shows, that the expressions derived from the osmotic pressure approach and those from the activity approach agree at small densities as far as κ is small. However the higher orders in κ (i.e. higher orders in density) may differ. In general, the differences stay, however, within the limits of the accuracy of the semi - chemical approach.

We cannot go here into a detailed theoretical foundation of the semi - chemical picture and mention only that it is connected with statistical ensemble descriptions between canonical and grand - canonical ensemble [1, 2]. The key idea of the approach to seawater is discussed already in [6]. In a forthcoming Research Gate preprint we will apply the osmotic pressure approach to conductivities. Note that the problem to calculate all other excess potentials has also been solved in some approximation. The excess chemical potential of the solute μ_0^{ex} may be calculated using the Gibbs-Duhem relation

$$\sum_{i=0,1,\ldots s} N_i d\mu_i^{ex} = 0. \tag{37}$$

In our foregoing work we studied in detail the methods for calculating the excess chemical potentials of the ions. In order to find the excess chemical potential of the solvent we consider the equilibrium between an electrolyte and a pure solvent separated by a semi-permeable membrane. The equilibrium condition for the solvent molecules is [5]

$$\mu_0'(p,T) = \mu_0''(p+P,p,S) \tag{38}$$

The difference of pressures is the osmotic pressure. For small osmotic pressure, and neglecting the (small) compressibility of the solvent and assuming a linear relation between chemical potential and osmotic pressure, we may expand and we get finally an expression for the excess chemical potential of the solvent in terms of the excess osmotic pressure

$$\mu_0^{ex}(p,T,S) = -v_0 P^{ex}(p,T,S) \tag{39}$$

where v_0 is the partial molar volume of the solvent. We may introduce here the excess osmotic pressure given above in order to find the complete excess Gibbs function [5].

In systems with double - charged ions we may reach Bjerrum parameters in the range of 6 -9 and even larger, in pairings with triple charged ions we may also reach this range. The Bjerrum parameter is the electrostatic energy between two ions at their contact distance, divided by the thermal energy, kT. As known from tabulated numerical values [3, 5], the virial functions change sign at $\xi \simeq 4$ and higher order effects in ξ start to grow in a very fast way beyond $\xi = +5$. Therefore we need then a different treatment higher order terms, which otherwise would create very large negative contributions to the activities. The simplest way to replace the pure physical description by a quasi - physical view is the method of Justice and Justice [20]. This approach is based on a generalization of the known exact compressibility equation to ionic solutions derived by Rasaiah and Friedman. We have shown, following these ideas of Justice and Justice [20], how the higher order terms $G_2(\eta,\xi)$ and the orders beyond may be treated effectively [7]. In this framework the diverging negative term of highest order proportional to G_2 is replaced by a positive logarithmic expression. Values for the fitted radii of the halide ions obtained by a simultaneous fit of data to MSA are given in in [16]. As we will show, the model of additive charges which well describes all halides but seems to be unable to describe complex mixtures with a high number of pair interactions like seawater. We conclude this section with some remarks about multiple charged ions giving rise to Bjerrum - pairing. Higher charged ions are of much interest for applications. There are several possibilities to take ion association into account [3, 5, 10, 20, 22]. We prefer here for several reasons a physical or say better a semi - chemical description. At first, this has the advantage for the treatment of highly complex systems like seawater, to be more simple. At second, and this is a serious point, we do not need to introduce and to define all the possible molecular complexes what leads for seawater with many possible pairings to an explosion of possibilities. Instead we need here only an account of the cluster integrals describing two - particle and three - particle interactions. The disadvantage is, that this physical or semi - chemical approach works only at small concentrations so far as the frequency of pair - and triple - formation is still low. This is an open problem to be treated.

4 Problems of fitting data and applications

We will show that for seawater the physical approach works for the region of lower salinities up to about $S \sim 35$, what means moderate salt concentrations, i.e. from small to standard salinities. The main reason is the improved convergence of cluster series as discussed before due to additional screening. In many imbeddings with additional screening like in seawater th η - parameter is of the order of one i.e. the effective interaction strength has a value by a facto two lower than in in a solution in pure water. This means that e.g. $MgSO_4$ which has in pure water an interaction strength of about $\xi_{+-} \sim 6-8$ comes down to the region $\alpha_{+-} \sim 3-4$. Exactly here are the reasons, why in seawater and in related solutions our simple analytical tools still work. Of course, at really high concentrations, a fully chemical approach may be more effective, in spite of the disadvantages and complications mentioned above. An alternative tool are of course MD or MD simulations [19]. In order to avoid any possible instabilities we follow a more simple approach which goes back to the work of Justice and Justice in the 70ths [20, 7] which is justified by the statistical compressibility approach. For introduction of this approach we consider electrolytes with ions carrying more than one charge as e.g. sulphuric acid containing the ions SO_4^{2-} and the halides of Mg^{2+} and Ca^{2+}. We we will concentrate on the treatment of electrolytes relevant for seawater which contain several double - charged ions as Mg^{2+}, SO_4^{2-}, and Ca^{2+} ions. Table 1 gives a few of the contact distances which we will use for calculations [6]. Note that we have after a new fitting some contact distances modified in comparison to the table given in [6]. We restrict here the study to the range, where association is still weak, say, less than $1/3$ of the ions are bound by electrostatic effects. Then in some cases the state may be described by more simple physical (or pseudo - chemical) methods as e.g. developed in the work of Justice [20]. This way we are able avoid the solution of highly nonlinear mass action laws for electrolytes which show at higher concentrations numerically unstable solutions or phase transitions which were not observed in seawater. The comparison with the results for the activities shows, the this is a lowest approximation, in the next order logarithmic corrections are to be expected. Anyhow together with our equations for the activities we have now in hand a set of formulae which should be able to describe a large class of thermodynamic and transport data. Our guiding rule for fitting the theory to data for real systems is to fit data sets simultaneously with a minimum of theoretical assumptions. The unknown parameters are in our case the contact distances R_{ij} i. e. we have to fit for solutions with 2,3,4, or 5 ion altogether 3,6,10, or 15 parameters, respectively. These numbers are strongly increasing with the number of ions. For the standard seawater model with 6 ions we need already an estimate of 21 unknown parameters which we have to fit simultaneously to all available experimental data. This hard task requires to include all available knowledge about the contact distances including information from other sources, such as ion mobilities and Born relations for the radii. Further we may include also some information about microscopic parameters from recent Monte-Carlo (MC) and Molecular-Dynamics (MD) computer simulations [19]. A microscopic method which provided important information about the effective radii are MD simulations which provide most direct information about the contact distances. In most complex systems like seawater the number of unknown parameters is at the limit of our possibilities. It has been shown in other work that the MC approach, which treats the ions as charged hard spheres with additive radii, i.e. a smaller number of parameters, a good description of real data is achieved [19]. It has been demonstrated that the model with additive radii is able of accommodating important effects by adjustment of effective ionic radii differing from the known crystallographic radii. Among the reasons explaining these deviations is hydration which increases the effective ionic radii. Another reason are strong cation-anion interactions where the effective anion radius (sulphate and carbonate in this case) is smaller than the crystallographic radius. The point we want to make here is, that for the description of complex systems like seawater the model of hard charged ions with given contact distances is much better suited for fitting data as the model of hard charged spheres with given additive radii. The reason is the larger number of parameters and therefore a larger flexibility. For example we have in the model of additive radii just 6 radii as free parameters for fitting seawater data, but already 21 free contact distances to fit for the ion model with contact distances. The possibility to adapt the 21 contact data to seawater data has been demonstrated in [6, 7] and the result is in part reflected in the data given in Tab. 1. However, in order to increase the precision of fitting parameters we should increase the data collection. The open problem is therefore, to include the big data collections about conductivity in our consideration. The idea how to adapt to data goes back to the methodological tools developed by the school of Hans Falkenhagen in Rostock, shortly after his passing away in 1971. In particular, at the 1977 Faraday discussion the method had been presented as a tool for finding individual properties such as individual activities and mobilities, as outlined the works [16]. Briefly, the idea is summarized in the following recipe:

1. Collect data containing information on individual properties, say, activity coefficients and conductivities, for a group of ”overlapping” data sets. What we mean with overlapping data sets are chains or loops of dissolved ionic pairs like $Br-K$, $K-Cl$, $Cl-Na$, $Na-Br$. In spite, the fact that data on one electrolyte are not sufficient to isolate the information on individual ions, the data for larger groups containing many chains and, if possible, even closed loops, may provide sufficient information to estimate the individual properties.
2. Derive closed statistical equations for the observed properties based on certain models for the interaction potentials. In simplest case, assume hard-sphere models with individual contact distances for ion pairs as shown above and proceed to more advanced models like step potentials for the average ion-ion interactions.
3. Fit the theory to the data for groups of ions containing chains and loops and complete the given information on contact distances of ions with data from microscopic simulations.

For first applications we study the chlorides, which play the most relevant role for our life, and also for the properties of seawater. The IUPAC recommendations from 2002 propose to use the Bates - Guggenheim report [12] as a kind of standard for Cl^- ions. Bates and Guggenheim recommended by the name of the ”Commission in Electrochemical Data” [12] to use for normalization a standard for chlorine ions. We show in Fig. 1 a comparison with the Bates formula for the Cl^- ion. Further we show some recently measured points representing data for the activities of Cl^- (black) and H^+ ions (red) measured by Sakaida and Kakiuchi [**?**] We note that the estimate of Bates works only for $c < 0.1 mol/dm^3$, then deviations from the DHX theory appear. In comparing the Bates - Guggenheim formula with the approximations DHE and DHX, we see that the differences, are small for $c < 0.2 mol/dm^3$ but cannot be neglected for $c > 0.2 mol/dm^3$. In addition to the charges, the basic parameters of the simple statistical theory presented above on the basis of the cluster expansions for the model of hard charged spheres are the contact distances of the centers of the charged spheres. A significant improvement of the DHE is achieved by the nonlinear corrections given in DHX and the mean spherical approximation MSA. As we have seen the standard version of the MSA is valid only for the case of additive radii.

We may proceed to electrolytes including ions with higher charges using the Justice method as explained above. Summarizing: The main difference to our earlier methods developed for 1-1 electrolytes is:

(i) The very specific role played by the contribution stemming from G_1 expressing asymmetries between the ions.

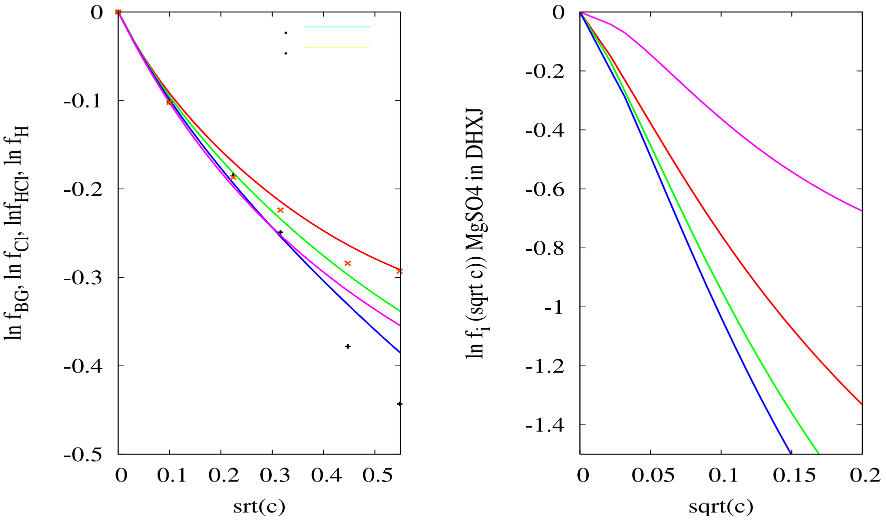

Figure 1: Left panel: The individual and the mean activity coefficients for HCl according to the extended Debye-Hückel approximation. Deviations of the individual activity coefficients from the mean depend mainly on anion-anion and cation-cation interactions. The lowest (at small c) curve (violet) demonstrates the Bates-Guggenheim recommendation for the Cl^- ion. The other curves were calculated with our theory for Cl^- ions (blue), the mean activity of HCl (green) and above the prediction for the hydronium ions H^+. The colored points represent data for the activities of Cl^- (black) and H^+ ions (red) measured 2011 by Sakaida and Kakiuchi [17]. In the right panel we show individual and the mean activity coefficients for $MgSO_4$ calculated with the DHX approximation in combination with the Justice method. From below, the curves belong to: SO_4^{2-}, Na_2SO_4, Na^+. The upper curve represents $\ln(\alpha)$,

(ii) The Justice - transformation moves a big contribution linear in density responsible for electrostatic association to the argument of a logarithmic contribution without changing the correctness linear in density order.
We note, that the present theory which avoids an explicit use of the MAL is correct only for higher degrees of ionization say $\alpha_i > 3/4$.
The application of the DHX approximation or the MSX approximation in combination with the Justice method to $MgSO_4$ - electrolytes works only for concentrations below $c = 0.1 mol/dm^3$ and leads at higher concentrations to problems which are already at the limit of the applicability of the Justice method. The reason is that the Bjerrum parameters reach already values of $b \simeq 8$. As a general tendency we note that the degree of ionization reaches e.g. for $MgSO_4$ a minimum at $c \simeq 0.1$ and increases then again [7, 22]. This minimum is not observed in our estimates for single electrolytes based on the Justice method. However we will show in next section that in mixtures with a dominance of 1 - 1 electrolytes like in seawater with dominating $NaCl$, the situation much improves, since we have an additional screening. The degree of ionization is in the Justice approximation for pair association given above. Since the G_2 function rapidly decreases with κ any increase of κ by additional 1 - 1 - host ions increases the degree of ionization. This is the essential point for a correct description of seawater given later. For higher accuracy requirements, and for higher concentrations, the Justice approximation may fail and we have to use a fully chemical approach using MAL and MSA as developed earlier based on the references [7, 22]. We refer to examples of a full chemical description, with applications to the osmotic and the activity coefficient for a 2-2 electrolyte with completely symmetrical radii $R_{+-} = R_{++} = R_{--} = a$, which were given in the works [3, 10, 22]. An extension has been developed by Yeh, Zhou and Stell and the relation between chemical and physical approaches has been discussed e.g. by Schröer and others [2]. The chemical approach using MAL and MSA is shown in [22] to be in good agreement with the results from the integral-equation method [6]. We prefer here the simpler fully physical approach based on the Justice method since this is much more simple and suffices for cases of weak association and for our purpose of seawater treatment for low and medium salinities as we will show in next section.
An application of our treatment of electrolytes $MgSO_4$ is shown in Fig. 1. In this case our approach yields correct results only for the smallest concentrations, say for $c < 0.05 mole/dm^3$. Nevertheless the expressions given here are candidates for applications to mixtures including higher charges ions and in particular to seawater solutions. For higher accuracy requirements, and for higher concentrations, the Justice approximation may fail and we have to use then possibly a fully chem-

ical approach using MAL and MSA as developed earlier based on the references [7, 22]. We refer to examples of a full chemical description, with applications to the osmotic and the activity coefficient for a 2-2 electrolyte with completely symmetrical radii $R_{+-} = R_{++} = R_{--} = a = 420pm$, which were given in the works [3, 10, 22]. Many investigators overlook that the treatment is much simplified by the presence of a high concentration of the 1 - 1 electrolyte $NaCl$. The reason is the influence of the prefactor f_{+-}^2 which appears in the mass action law in front of the mass action constant. According to our approach, this pre - factor is in lowest approximation in dependence of concentration given by

$$f_{+-}^2(c) \simeq \exp[-z^2 \ell \kappa G_0(\kappa R_{+-})] \tag{40}$$

This prefactor depends strongly on the screening parameter κ which is very different for ions in pure water and in seawater. Let us look at an example $MgSO_4$ in water and in standard seawater. In the case of standard seawater with $S \sim 35$ the concentration of $MgSO_4$ is about $c \sim 0.025 mol/dm^3$ and according to our estimates [6] the prefactor may reach a value as small as $f_{+-}^2 \simeq 0.02$. In a solution in pure water and about the same concentration of $MgSO_4$ of about $c \sim 0.025 mol/dm^3$ the κ is much smaller and we estimate a prefactor $f_{+-}^2 \simeq 0.14$. This large difference by a factor about 5 - 10, is the reason why we are allowed to apply the method of linearization of the mass action law (the method of Justice) in the case of seawater. Clearly, this method should not be applied in the case of pure water.
So far we discussed only individual activities and discussed the problems of fitting the free parameters of the theory to data. In a next section we will apply this procedure to the standard model of seawater with 6 ions and 21 free contact parameters but before we will discuss some other problems of applications to bound state formation in with Multiple charged ions.

Higher charged ions are of much interest for applications. There are several possibilities to take ion association into account [3, 5, 10, 20, 22]. We prefer here for several reasons fully physical or semi - chemical descriptions. At first, this has some advantages for the treatment of complex systems like seawater. At second, and this is the main advantage, we do not need to introduce and to define all the possible molecular complexes what leads for seawater to an explosion of possibilities. Instead we need here only an account of the cluster integrals describing two - particle and three - particle interactions. The disadvantage is, that this physical approach works only at small concentrations so far as the frequency of pair - and triple - formation is still low. We will show that for seawater the physical approach still works at least for the region of lower salinities, what means moderate salt concentrations. At really high concentrations, a fully chemical approach seems to be more effective, in spite of other disadvantages. As we demonstrated in foregoing works [6, 7] the mass action law (MAL) approach leads sometimes to mathematical difficulties as e.g. non - uniqueness of the solutions and instabilities of numerical procedures. In order to avoid these difficulties here we follow a more simple approach which goes back to the work of Justice and Justice in the 70thies which is nothing else than a simplified version of the standard chemical approach based on mass action laws [7] which is justified by the statistical compressibility approach. For introduction of this approach we consider here first only electrolytes with ions carrying more than one charge as e.g. sulphuric acid containing the ions SO_4^{2-} and the halides of Mg^{2+} and Ca^{2+}. In order to have an example relevant for recently developed technologies we mention the double - and triple charged ions of vanadium in the new vanadium - redox - flow batteries considered as a possible solutions of our problems with energy storage. Here we will concentrate on the treatment of electrolytes relevant for seawater which contain several double - charged ions as Mg^{2+}, SO_4^{2-}, and Ca^{2+} ions. Table 1 gives a few of the contact distances which we will use for calculations [6]. We restrict here the study to the range, where association is still weak, say, less than $1/3$ of the ions are bound by electrostatic effects. Then in many cases the state may be described by more simple physical (or pseudo - chemical) methods as e.g. developed in the work of Justice [20]. This way we are able avoid the solution of highly nonlinear mass action laws for electrolytes which show sometimes numerically unstable solutions or even phase transitions which were not observed in seawater.

Note that we have after a new fitting adapted some contact distances in comparison to the table given in [6]. In the combination of double - charged ions with Cl^- ions we reach Bjerrum parameters in the range of 4 - 6 and even larger, in pairings with triple charged ions we may reach the range of 6 - 8. The Bjerrum parameter is the electrostatic energy between two ions at their contact distance, divided by the thermal energy, kT. As known from tabulated numerical values [3, 5], the function overall interaction function$K_0(\xi)$ changes sign at $\xi \simeq 4$ and higher order interaction function $K_4(\xi)$ starts to grow in a very fast way beyond $\xi = +5$. The latter function which describes the Coulombic association is quickly reaching high values of $K_4(\xi) > 10^2$. This shows that we need a different treatment of that term, which otherwise would create very large negative contributions to the activities. We have shown in our RG-Preprints parts I and II, following the ideas of Justice and Justice [20], how the higher order terms $G_2(\eta, \xi)$ and the higher orders beyond, which increase so strongly with interaction strength ξ_{ij} may be taken into account. The main aspect of a chemical approach is that associates

Table 1: Table of contact distances for several ion pairs including alkaline earth metal ions, sulphate ions and adapted ”ideal seawater” ions used here.

$A-B$ ion pair	R_{AB}	R_{AA}	R_{BB}
$Na-Cl$	350	400	360
$K-Cl$	310	280	360
$Mg-Cl_2$	350	440	360
$Ca-Cl_2$	250	400	360
Na_2-SO_4	250	400	380
K_2-SO_4	360	280	380
$Mg-SO_4$	300	440	380
$Ca-SO_4$	320	440	380
$Na-K$	300	400	280
$Na-Mg$	520	400	380
$Na-Ca$	500	400	440
$K-Mg$	280	280	380
$K-Ca$	290	280	440
$Mg-Ca$	330	440	440
$Cl-SO_4$	300	360	380

are considered in the chemical view as extra particles. This means e.g. that the association of one anion and one cation at a degree α reduces the effective density of anions to αn_1 and of cations to αn_2. The simplest way to replace a physical description by a chemical view is the method of Justice and Justice [20]. This approach is based on a generalization of the known exact compressibility equation to ionic solutions derived by Rasaiah and Friedman [9]. Let us briefly repeat the main idea of this approach. In simplest case of some symmetry between anions and cations the the exact compressibility equation of Friedman and Rasaiah expresses the mean activities by the correlation function G and reads

$$\frac{d\ln f_{+-}}{dc} = -\frac{G}{1+cG}; \qquad G = \tilde{G}_{+-} + \tilde{G}_{++} \qquad \tilde{G}_{ij} = \int d\mathbf{r}(F_{ij}(r) - 1). \quad (41)$$

where c denotes the concentration and G_{ij} the ionic correlation function. We note the remarkable fact that in an exact formula for the activities the correlation integrals appear in an alternative form as $1+G$ in the denominator. Neglecting the weak dependence of G on the concentration, Justice and Justice perform the integration and rewrite this formula by some manipulations separating the short and the long range contributions

$$\ln f_{+-} \simeq \ln\frac{1}{1+cG} \simeq \ln\frac{1}{1+n_0 K(T,a)} - \frac{\beta z^2 e^2 \kappa}{D_0(1+\kappa a)} + \frac{8\pi}{3} n_0 a^3 \qquad (42)$$

Here, the first term is written in the form $\ln\alpha$ and α is interpreted as the degree of dissociation and $K(T,a)$ is a kind of Bjerrum mass-action constant, depending on temperature and contact distance. This interpretation as a degree of dissociation corresponds to a quasi - chemical view. A strong argument in favor of this approach is that in the exact compressibility equation for ionic solutions by Friedman and Rasaiah [9, **?**] a similar structure with a denominator appears. We note that in particular the large bound-state contributions stemming from the $+-$ correlations appear in the denominator. While the compressibility approach is in principle in no way more correct than the virial approach, it seems, however, to be more appropriate for weakly associating electrolytes. This gives us the right to proceed to a mixed semi - chemical approach like Justice. In a fully chemical description, the degree of dissociation follows from a minimization of the free energy and is determined by a mass-action constant and a mass-action law. In a more physical view, the first term expresses the fact that the density is reduced due to the association by a factor $\ln(\alpha)$ and formally, the term corresponds to a summation of contributions which increase with the Bjerrum parameter and are of higher order in the concentration. Within the formalism developed by Justice and Justice [20], a big (negative) contribution which in the virial approach is linear in concentration and reduces the log of the activity $-n_0 K(T,a)$ is in the compressibility approach interpreted as a mass-action term. Notice the formal analogy of this approach to a first-order solution of the MAL which we write in simplest case

$$\frac{1-\alpha}{\alpha^2} = n_0 K(T,a); \qquad \alpha \simeq \alpha_J = \frac{1}{(1+n_0 K(T,a))}. \tag{43}$$

The solution is correct in first linear order. This way we may say that the Justice approximation corresponds to a quasi - chemical approach of expressing the log of activities of associating electrolytes. We transfer now the idea of the Justice-Justice method to our basic DHX - equations by interpreting the large positive term depending on either $K_4(\xi)$ or $G_2(\xi)$ as a kind of mass-action constant. This way taking into account all contributions from the function $K_4(\xi)$ and treating this term in the spirit of the opposite charge approximation we find in the framework of the Justice - Justice approach for the degree of free ions of kind i

$$\alpha_i^1 = 1/(1 + z_i^2 \kappa \ell \sum_j [\zeta_i G_2(\xi_{ij}, \kappa R_{ij})]. \tag{44}$$

Using these estimates for the degrees of ionization which take into account only effects of order e^8 we get now along the Justice - Justice route for the activities the following approximation which we call DHX including Justice effects:

$$\ln f_i = \ln \alpha_i^{(1)} - \frac{e_i^2 \kappa}{D_0 k_B T} \sum_j \zeta_j \left[\frac{1}{1+\eta_{ij}} + G_1(\xi_{ij}, \eta_{ij}, \zeta_i) \right] + \frac{8\pi}{3} \sum_j n_j R_{ij}^3. \tag{45}$$

The MSX - approximation has the same shape, it follows by the change $\eta \to \eta'$. By assuming this view we have transformed a big negative term appearing in the virial expansion to the positive argument of a logarithmic function. From the mathematical point of view this does not worsen the accuracy but gives more meaningful physico - chemical results. This is so - to - say, our key idea which provides very efficient expressions. The dangerous terms leading to negative activities are ”screened” and we found by using the Justice ideas a simple and useful semi - chemical description. Note that at present this estimate for electrostatic association contains only the second order in the interaction parameters ξ_{ij} i.e. e^8, we omitted so far the higher order contributions. This may lead to increasing errors for $\xi_{ij} > 6$. However this approach may be sufficiently accurate for 2 - 1-

and 3 - 1 electrolytes. For 2 - 2- electrolytes and other higher valency ionic solutions we find interaction parameters $|\xi_{ij}| \geq 8$ and we may reach the limits of the Justice approach. In this region the higher order contributions to virial function K_4 steeply increase and cannot be approximated by the term e^8 of the Taylor series only. However we should take into account that the higher orders are subject to stronger screening effects and decrease quickly with increasing eta - values. In the range of large ξ - values we may work for strong interactions with asymptotic approximations for $|\xi_{ij}| \gg 6$ [3, 5, 7]. Note that the procedure of moving terms to the denominator is not unique. The procedure corresponds technically to summing up infinite series of terms in the cluster expansion. A deeper foundation of such a procedure may be developed on the basis of replacing density by fugacity expansions [2]. An important term for electrolytes with higher charges is the electrical contribution G_1 which is taking into account the charge asymmetry between the ions. This term is definitely responsible for a very specific asymmetry between the individual activities in 2-1 electrolytes. Note that the factors describing the asymmetry are e.g for magnesium chloride $\zeta_{Cl} = 1/6$ and $\zeta_{Mg} = 1/3$. We will show that the new form which is based on a transformation which did not change the accuracy allows us to include the description of 2-1 electrolytes without the heavy machinery of mass-action laws. Summarizing: The main difference to our earlier methods developed for 1-1 electrolytes is:
(i) The very specific role played by the contribution stemming from G_1 expressing asymmetries between the ions.
(ii) The Justice - transformation of a big contribution linear in density responsible for electrostatic association to the argument of a logarithmic contribution without changing the correctness linear in density order.
We note, that the present theory which avoids an explicit use of the MAL works only for higher degrees of ionization say $\alpha_i > 2/3$. On the other hand our expressions are candidates for applications to mixtures including higher charges ions and in particular to seawater solutions. We make profit of the fact that association ions appear in seawater only in very small concentrations. The application of the DHX approximation in combination with the Justice method to $MgSO_4$ - electrolytes in water works only for concentrations below $c = 0.05$ but leads at higher concentrations to problems which are already at the limit of the applicability of the Justice method. The reason is that the Bjerrum parameters reach already values of $b \simeq 8$, so some results need critical analysis and improvement. As a general tendency we note that the degree of ionization reaches for $MgSO_4$ a minimum at $c \simeq 0.1$ and increases the again [7, 22]. This minimum is not observed in our simple estimates based on the Justice method (see Fig. 2). Note that the degree of ionization is in

the Justice approximation for pure pair association given by

$$\alpha_i = \frac{1}{(1+\delta_i^{(2)})}, \quad \delta_i^{(2)} = 4\pi \sum_j n_j R_{ij}^3 \frac{\tilde{\xi}_{ij}}{(1+\eta_{ij})}[1 - e_1(4\eta_{ij})]). \tag{46}$$

We remember that the term in the denominator includes the higher order binding contributions to the second virial coefficient. For higher accuracy requirements, and for higher concentrations, the Justice approximation fails and we have to use a fully chemical approach using MAL and MSA as developed earlier based on the references [7, 22]. We refer to examples of a full chemical description, with applications to the osmotic and the activity coefficient for a 2-2 electrolyte with completely symmetrical radii $R_{+-} = R_{++} = R_{--} = a$, which were given in the works [3, 10, 22]. The chemical approach using MAL and MSA is shown in [22] to be in good agreement with the results from the integral-equation method [1, 10]. We prefer here the simpler fully physical approach based on the Justice method since this is much more simple and suffices for cases of weak association and for our purpose of seawater treatment for low and medium salinities.
We begin with the study of simple $Mg^{2+} - SO_4^{2-}$ and $Na_2 - SO_4$ electrolytes. The application of the DHX approximation to this electrolytes including the Justice treatment for pair association. The result is demonstrated in Fig. 2.

We discuss now the application of our treatment to the electrolyte Na_2SO_4. We note that in deawater the main partners for rhe association of SO_4^{2-} ions are the ions Na^+ and K^+. The concentrations of the double - charged ions in seawater are relatively low, around $0.05 mol/kg$ for Mg^{2+} and $0.01 mol/kg$ for Ca^{2+} ions and around around $0.05 mol/kg$ for SO_4^{2-}. This means, the most important partners of the ions Mg^{2+} and Ca^{2+} ions are the Chlor - ions and the most frequent partners of SO_4^{2-} ions are the Na^+ and K^+ ions. For all these combinations a new aspect cames into play, the triple association. In order to include this specific effect we will study in a next work triple association by including in lowest approximation the third virial coefficient.

5 Applications to "ideal seawater"

The basic standard solution of a simple seawater model (IAPSO Standard) contains the six most relevant seawater ions 1 - Na^+, 2 - K^+, 3 - Mg^{2+}, 4 - Ca^{2+}, 5 - Cl^-, 6 - SO_4^{2-} and about 24 less frequent ions [18]. About the concentrations we follow the relations corresponding to the paper [18] with some modifications for

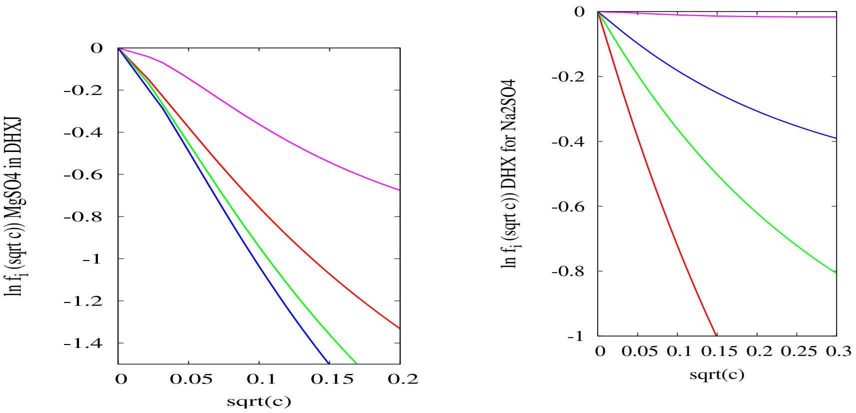

Figure 2: The individual and the mean activity coefficients for $MgSO_4$ calculated with the DHX approximation are shown in the left panel. From below, the curves belong to: Mg^{2+}, $MgSO_4$, SO_4^{2-}. The upper curve with a different shape represents $\ln(\alpha)$, i.e. the decrease of the activity due to association - pairing effects. In the right panel we show the mean activity coefficients for Na_2SO_4 calculated in DHX approximation in combination with Justice method. From below, the curves belong to: SO_4^{2-}, Na_2SO_4, Na^+, $\ln(\alpha)$. Note that the splitting between the mean and the individual activities is here rather large.

numerical reasons. For the composition we are assuming the mol fractions:

$$\nu_1 = .4182, \nu_2 = .0091, \nu_3 = .0476, \nu_4 = .0093, \nu_5 = .4906, \nu_6 = .0252.$$

We call this model here ”ideal seawater” since for modelling it may play a similar role as e.g. the model of Boltzmann’s ”ideal gas” or Planck’s ”ideal solution”. Some of the remaining ions such as H^+, OH^- and $HCO3^-$ may be considered as tracers. We study here the individual and mean ion activities as well as the osmotic coefficients for the ”ideal seawater” i.e. for our adapted version of the IAPSO standard model of seawater with solute concentrations ranging from typical Baltic-Sea salinities $S \sim 5$ to Atlantic salinity $S \sim 35 - 40$. Note that the main partners of the SO_4^{2-} ions in seawater are the magnesium ions Mg^{2+} and the Ca^{2+} ions which are in seawater not as frequent as the Na^+ and Cl^- ions but still in concentrations around $0.05 mol/kg$ for Mg^{2+} and $0.01 mol/kg$ for Ca^{2+} ions. In order to to demonstrate the predictions of the present methods for a standard sea water model with 6 components we give here without details a few figures

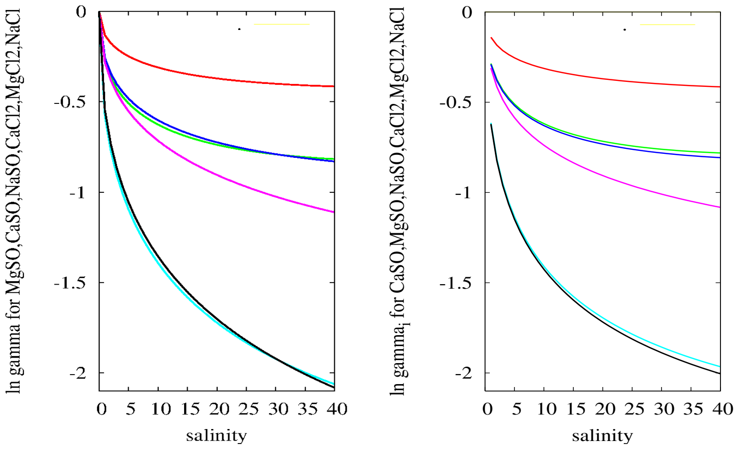

Figure 3: The mean activity coefficients of six most relevant components of standard seawater [18]. Left panel: The curves calculated here describe (looking at the smallest concentrations from above): $NaCl$, $MgCl_2$, $CaCl_2$, Na_2SO_4, $MgSO_4$, $CaSO_4$ as a function of salinity (solved gram salt per kilogram seawater), running between less than $5 g/kg$ (Baltic Sea) and about $40 g/kg$ (Atlantic Ocean). Right panel: Corresponding curves calculated by Pitzer methods or Monte Carlo simulations reported in [19].

giving the mean and the individual activities and the degrees of association od the ions. Our curves for the mean activities of the 6 main components are well compatible with the result of Monte Carlo calculations for the mean activities of seawater obtained by Ulfsbo et al. [19] and also with result obtained by the Pitzer approach [6, 11, 19] see Fig. 3. The agreement is so far only qualitative or semi - quantitative, respectivly, deviations up to 10 percent for some ions are observed. The reasons for the differences in particular for salts with double - charged ions have still to be explored in detail. In addition we present also some new result for for the degrees of association Fig.4, which are comparable with results for a parametrization given in [23]. Further we provide new results for the individual activities Fig. 5

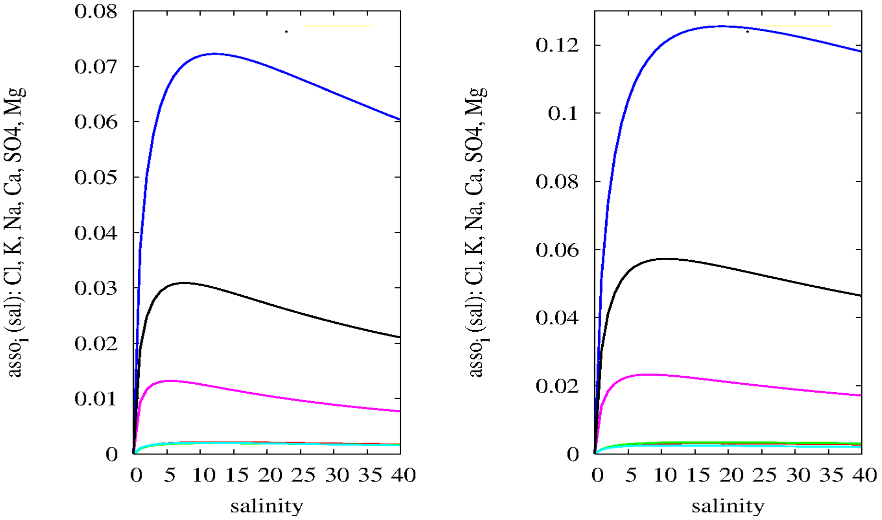

Figure 4: The degree of association $(1-\alpha_i)$ for the ions of seawater calculated in activity (left) and pressure - based approaches (right) on the basis of the DHX - approximation. The ions corresponding to the curves are (counted from below): $Cl^-, K^+, Na^+, Ca^{2+}, SO_4^{2-}, Mg^{2+}$.

6 Conclusions

In the present survey of calculations for 1-1, 1-2 and 2-2 electrolytes, including seawater, we summarized several fully analytical statistical methods for calculat-

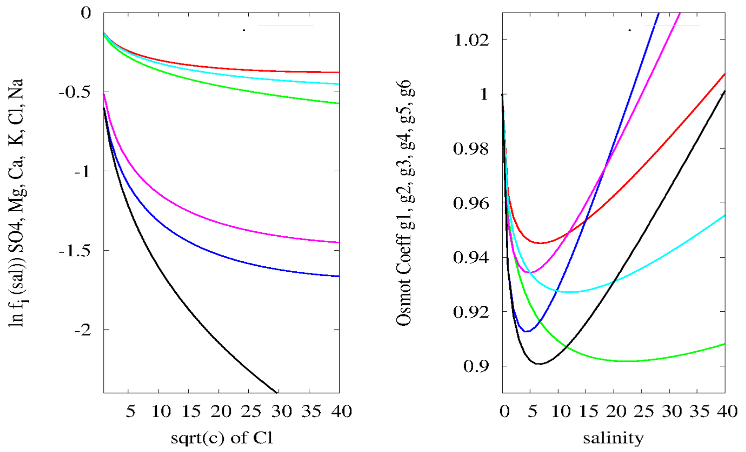

Figure 5: Left panel: The individual activity coefficients of the six most important ions in standard seawater- Right panel: Individual osmotic coefficients of the six relevant ions. We are sorting from below counting the values at salinity 5. The lowest curve represents the ion SO_4^{2-}, then follow the curves for Mg^{2+}, K^+, Ca^{2+}, Cl^-, Na^+.

ing activity coefficients and osmotic coefficients in combination with the Justice method for treating weak association.

Summarizing our findings: Based on results of statistical physics, we recommend in addition to standard methods for calculating individual activities such as the Bates - Guggenheim and the semi = empirical Pitzer equations, new statistical tools for the calculation of individual and mean activities of ions from lower concentrations up to moderate salinity. The methods are based on the model of hard spheres with non - additive radii are nonlinear Debye - Hückel method (DHX) supplemented by an application of the Justice - procedure to include weak association (electrostatic pairing effects). The Justice idea is to use elements of the compressibility equation schema in order to include higher order terms including association effects. The Justice method has been compared here with a semi - chemical description developed here on the basis of fugacity expansion for the pressure in [**?**, 2]. A comparison shows that the method based on fugacities and pressures seems to provide better results for seawater. We do not claim that the statistical formulae developed here with the aim of applications to seawater are in much better agreement with experiment as the semi- empirical methods used in practice nowadays. However we claim, that

(i) our results are physically quite transparent with respect to the model assumptions since we use only hard - charged sphere models and as parameters the charges and the non - additive contact distances,
(ii) the formulae obtained are relatively simple extensions of the tools of Debye - Hückel for the activities and osmotic coefficients and they are proven to be consistent up to the order $n^{3/2}$ with the exact results of Friedman's cluster theory,
(iii) the proposed formulae are fully analytical and results can be easily obtained on any home computer providing tables, and drawn by programs like gnuplot.
We use the methods of extended Debye - Hückel theories for a first, elementary estimate, (and later MSA in Henderson - Smith form for more precise calculations up to moderate concentrations) being exact up to order $O(c^{3/2})$ in the concentration. Justice's method is used for including weak association by treating higher order contributions from the second virial coefficient. We have shown that the semi - chemical methods by Justice, which are related to activities and the compressibility formalism, are useful for the treatment of weak association effects in seawater mixtures including 1 -1, 2-1 and 2 -2 electrolytes. The description of the association effects is even improved here by using a pressure description based on the fugacity formalism [1, 2, 21]. In the present semi - chemical (or semi - physical) picture no explicit definition of pairs or triples is needed, we have only to take care that the relevant contributions from the virial expansions with respect to the density or fugacity. which describe such association effects are included and correctly treated.
The input parameters we need in our theory are beside dielectric constants the contact distances of the ions, i.e. 3 distances for binary electrolytes, but 20 contact distances for 6 - component standard seawater. We derive these parameters by adaptation to the available data (method SOFD) and use in addition also microscopic information from Monte Carlo and Molecular Dynamics. In forthcoming work we will show that the present model describes also the transport properties like conductivities.
A comparison of our results for the mean activities of the 6 major salts in seawater $NaCl$, $MgCl_2$, $CaCl_2$, Na_2SO_4, $MgSO_4$, $CaSO_4$ as a function of salinity shows reasonable agreement with Monte Carlo and Pitzer data provided in the paper [19]. In addition to this we provide the individual activities of the 6 major ions.

Summarizing: The present approach, which is so far not fully explored, provides for seawater reasonable agreement with results from semi - empirical sets of formulae like the approach of the Pitzer group and the results of computer - time consuming Monte Carlo calculations. For standard seawater we need about 20 adapted contact distances, which may depend on temperature and pressure. So far all results are given only for 25 degrees Celsius, an extension to other temperatures makes no problems. Just to give an impression about the number of parameters needed in other approaches: In the popular MIAMI Ionic Interaction Models which are semi - empirically and based on so - called Pitzer equations one needs at each temperature nearly 100 parameters, most of them empirically found and being as a rule without precise microscopic interpretation. Our aim is not to replace these elaborated and practically very useful apparatus working with the Pitzer - like equations, but instead to complement this rather complicated apparatus by more transparent models with a parameter set which is still large (around 20) but anyhow having a clear physical meaning as contact distances.

Finally we would like to express our convince that objects like seawater, which are the key for our any reliable climate forecast, need much more attention from statistical physicists. We should not leave this highly relevant field entirely to experts in the art of fitting a relatively small set of reliable data and making far reaching predictions about the future of our planet by help of big computers on this spare basis.

We should better follow the good tradition founded by Vladimir Fortov, to make many reliable experiments, check all data again, again and again and develop on this basis appropriate theories, if possible in several versions to be compared and checked on the basis of the experimental material.

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References

[1] V.E. Fortov, V.S. Filinov, A.S. Larkin, W. Ebeling, Statistical Physics of Dense Gases and Nonideal Plasmas (in Russ.), Moscow 2020, to appear.

[2] W. Ebeling, V. Fortov, V. Filinov, Quantum statistics of dense plasmas and dilute gases, Springer Heidelberg 2017.

[3] H. Falkenhagen, W. Ebeling, in S. Petrucci (Ed.), Ionic Interactions vol. I, Chapter 1, Academic Press, New York 1971

[4] H. Falkenhagen, W. Ebeling, W. D. Kraeft, in S. Petrucci (Ed.), Ionic Interactions vol. I, Chapter 2, Academic Press, New York 1971

[5] H. Falkenhagen, Theorie der Elektrolyte, Hirzel Leipzig 1971

[6] W. Ebeling, R. Feistel, M.F. Camoes, On statistical calculations of individual ionic activity coefficients, Trends in Physical Chemistry, to appear (2020)

[7] W. Ebeling, R. Feistel, H. Krienke, On statistical calculations of individual ionic activity coefficients of electrolytes and seawater. Parts I. and IV , Research Gate April 2019, DOI: 10.13140/RG.2.2.18591.20640 2019)

[8] W. Ebeling, R. Feistel, On statistical calculations of individual ionic activity coefficients of electrolytes and seawater. Parts II - III, Research Gate 2020

[9] H.L. Friedman, Ionic Solution theory, Interscience New York 1962

[10] J.M.G. Barthel, H. Krienke, W. Kunz, Physical Chemistry of electrolyte Solutions, Modern Aspects, Steinkopf - Springer 1998.

[11] K. S. Pitzer, Actvity Coefficients in Electrolyte Solutions, CRC Press, Boca Raton (1991), p. 75-154

[12] R. G. Bates, E. A. Guggenheim, Report on the Standardization of pH and related terminology, Commission on Electrochemical Data (1960)

[13] G.M Marion, F.J. Millero, F. Camoes, P. Spitzer, R. Feistel, C.-T. Chen, pH of Seawater, Mar. Chem., **126** (2011) 89.

[14] R. Feistel, Thermodynamic Properties of Seawater, Ice and Humid Air: TEOS-10, Before and Beyond, Ocean Sci, **14** (2018) 471.

[15] A G Dickson, M F Camoes, P Spitzer, P Fisicaro, D Stoica, R Pawlowicz and R Feistel, Metrological challenges for measurements of key climatological observables. Part 3: Seawater pH, Metrologia **53** (2016) 26.

[16] W. Ebeling, K. Scherwinski, On the estimation of theoretical individual activity coefficients of electrolytes. Hard sphere model, Z. phys. Chem.(Leipzig) **264** (1983) 1-14 .

[17] H. Sakaida, T. Kakiuchi, Determination of single -ion activities of H^+ and Cl^-, J. Phys. Chem. B **115** (2011) 13222.

[18] F. J. Millero, R. Feistel, D. G. Wright, T. J. McDougall, The Composition of Standard Seawater and the Definition of the Reference-Composition Salinity Scale, Deep-Sea Research I, **55** (2008) 50.

[19] A. Ulfsbo, Z. Abbas, D. Turner, Activity coefficients of a simplified seawater electrolyte using Monte Carlo simulations, Marine Chemistry, **171** (2015) 78.

[20] M.C. Justice, J.C. Justice, J. Solution Chemistry, **6** (1977) 819; **7** (1978) 859 ; J.C. Justice, W. Ebeling, J. Solution Chemistry, **8** (1977) 809.

[21] W. Ebeling, H. Reinholz, G. Röpke, Hydrogen, Helium and Lithium plasmas at high pressures, Eur. Phys. J. ST, to appear (2020)

[22] W. Ebeling, M. Grigo, MSA - MAL Theory of Ionic Solutions, Ann. d. Physik **37**(1980) 21 -30, J. Solution. Chem. **11** (1982) 151-167.

[23] R. Pawlowicz, Calculating the conductivity of natural waters, Limnol. Oceanogr.: Methods **6** (2008) 489501