

## MOLAR AMOUNT OF WATER

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### Abstract

When modeling body fluids using physical chemistry, we encountered a contradiction. We proceeded from the erroneous assumption that the molar amount of water in an aqueous solution is the molar amount of  $\text{H}_2\text{O}$  molecules (mass divided by the mass of one  $\text{H}_2\text{O}$  molecule). Thus, in one kilogram of pure water, we calculated 55.508 moles of water because the molar mass of  $\text{H}_2\text{O}$  is 18.01528 g / mol. When calculating the molar fractions as the molar amount of the substance divided by the solution's total molar amount, we thus obtained numerically completely different values than for molalities or molarities. According to the theory, these values should be substitutable. However, it turned out that using these values in the calculations of the solubility of gases in aqueous solutions showed us an error of about 55 mol/kg. Similar errors began to be reported for chemical processes with different numbers of reactants and products (at the same number, the error is annulled algebraically). So is the water molality really about 55 mol/kg? No. This is because water forms bonds with each other, which cluster more  $\text{H}_2\text{O}$  molecules into larger particles. From the required molar amount of water, we derived the dissociation constant and enthalpy of this bond. The results are compatible with data from the National Institute of Standards and Technology (NIST) and the data of formation energies of individual substances. Using these constants, we can derive the molar amount of water in aqueous solutions and subsequently make calculations over molar fractions, the results of which begin to coincide with the measured and published experiments.

### 1 Introduction

In physical chemistry, there is often the only talk of very dilute solutions [1], while this is not the case with body fluids in physiology. For example, intracellular fluid has only approx. 70% water. Conventional calculations cease to apply here because the shift from the standard state of an aqueous solution is so significant that it is necessary to extend the theory of physical chemistry to these conditions as well. One of our experiments is the extension using hypotheses about the molar amount of water, in which we replace the constants of standard molality and standard molarity.

Our research into the molar amount of aqueous solutions began unconsciously in April 2015 with a question published on the website [www.researchgate.net](http://www.researchgate.net): "What is the concentration of hydroniums ( $\text{H}_3\text{O}^+$ ) or free protons ( $\text{H}^+$ ) as the equivalent of  $\text{pH} = 7.4$  in the aqueous solution?". Although this question had about 20,000 views on this international scientific network, 38 public answers and other private communications followed, its clear answer was not found here. One way of calculating the result from the dissociation of water showed a molar fraction of  $10^{-7.4}$  mol/mol. However, directly from the definition of pH, it should be a molality of  $10^{-7.4}$  mol/kg. The contradiction of these physical units at that time led to the fact that both can be true only if, under the given conditions, there will be exactly one mole of all particles in one kilogram of water.

Our laboratory has been dealing with calculating the acidity (pH) of blood and other body fluids within the acid-base balance for many years. Only by integrating several models into one whole does everything begin to be formalized so that it is necessary to solve all redundant and opposing relationships so that the resulting mathematical model clearly defines the course of the described variables in time. However, this formalization requires interconnection ideally up to the level of a

fundamental theory such as physics or physical chemistry [2]. The use of physical chemistry for simulations in physiology or medicine is not very widespread today. Calculations in these fields remain mainly for empirical relations or fundamental physics, often with an enormous tolerance for error. But modern computer technology can handle robust physical systems of equations both algebraically and numerically. However, from experience with empirical equations, it might seem that a large number of equations will be associated with a large number of unknown parameters. However, this may not be true when using physical relations correctly because physics is based on eliminating "unknown parameters" or, in extreme cases, even "unknown constants". It does this elimination precisely through the relations by which it defines these values. Therefore, it is theoretically possible to create even very complex and complex physical-mathematical models that need only a small number of well-known (i.e., derivable or measurable) parameters and constants.

In creating our human physiology models [3-6], we describe body fluids in detail: blood plasma, interstitial fluid, intracellular fluid, cerebrospinal fluid, urine, etc. In describing these aqueous solutions, we are interested in the relationships of individual substances and their processes. These processes are closely related to heat, charge, acidity, water solubility in water, and other properties described by physical chemistry. In 2015, we implemented the Modelica library for Physical Chemistry [7], which we use to calculate these processes in or between aqueous solutions. At that time, this software library contained components for the equilibrium of chemical processes such as chemical reactions, diffusion, the solubility of gases in solutions, electron transfer between different media, Donnan equilibria on the membrane, according to Nernst relations, etc.

One of the other issues arising from implementing this software library was the necessary correction in expressing the solubility of gases in water. The calculated value of Henry's constant for gas solubility in water was not the same as the measured value published using the National Institute of Standards and Technology (NIST) tables. This problem was described in detail in 2015 in the dissertation [8] on page 38. At that time, we compared Henry's constants for different gases with their derived values. We found that the coefficient by which the values differ is the same for each gas. But then we didn't know why. By further investigating the properties of liquid water, we found that the explanation can be relatively simple. The calculations depend on the molar fraction of a given gas in water. The molar fraction of a substance is the ratio of the molar amount (number of particles) of a given substance to the molar amount of all particles in a given solution. It didn't take long, and we realized that if we adjusted the molar amount of water, it is possible to agree with the measured values of dissolved gas. This is because the molar amount of water is not equal to the molar amount of  $\text{H}_2\text{O}$  molecules.  $\text{H}_2\text{O}$  molecules form dynamically weak hydrogen bonds with each other [9]. These bonds in liquid water form clusters of  $\text{H}_2\text{O}$  molecules and each such cluster must be considered one particle at a given point in time.

### 2 Methods

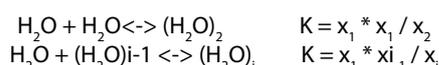
As a possible hypothesis, we chose the following statement: "In liquid water,  $\text{H}_2\text{O}$  molecules bind to each other in clusters by bonds so that these bonds do not form cycles and each of these bonds has the same properties."

The bond cycle is the joining of two  $\text{H}_2\text{O}$  molecules that are already part of one cluster. The assumption that bonds do not form cycles is relatively strong, and in many articles, on the contrary, there are structures where these cycles exist. In contrast, we have remained with the idea that the bonds between

individual clusters (with any number of water molecules) are much more likely to be the same as between individual water molecules and are independent of each other.

If the bonds are independent of each other, they have the same properties as the enthalpy and entropy of hydrogen bonds between H<sub>2</sub>O molecules. Thus, the dissociation constant (**K**) at the junction of two clusters is the same as the dissociation constant between two free H<sub>2</sub>O molecules.

Based on these statements, we constructed a mathematical model that accurately derives the molar fractions (**x<sub>i</sub>**) of cluster sets from a given number of H<sub>2</sub>O molecules (**i**). Simultaneously, it is not important how long this state of specific clusters will last because the number of individual clusters remains the same even if the links change rapidly dynamically.



This chemical reaction defines a geometric series for  $x_i = x_{i-1} * x_1 * K$ , which can also be written as

$$x_i = x_1 * (x_1 * K)_{i-1}$$

The sum of all molar fractions in pure water if we neglect OH<sup>-</sup> and H<sup>+</sup> ions, which are 10<sup>-7</sup> mol/mol, expressed as the sum of  $x_i$  through  $i$  from 1 to infinity, is equal to 1.

$1 = \sum_{i=1}^{\infty} x_1 \cdot (x_1 \cdot K)^{i-1} = \frac{x_1}{(1-x_1 \cdot K)}$	Sum of all molar fractions
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Assuming that  $x_1 * K$  is positive and less than 1, it is possible to use the relation for the geometric sequence

$$\sum_{k=0}^{\infty} a r^k = \frac{a}{(1-r)}$$

The size of the individual members decreases exponentially here (Fig. 1), and therefore the total sum of this infinite series is finite.

In one kilogram of pure water, is 1 / MM (55,508 mol/kg, where MM is the molar mass of H<sub>2</sub>O) moles of H<sub>2</sub>O molecules, while the number of particles is according to the measured data N:

$\frac{1}{MM} = \sum_{i=1}^{\infty} i \cdot N \cdot x_1 \cdot (x_1 \cdot K)^{i-1} = \frac{N \cdot x_1}{(1-x_1 \cdot K)^2}$	Number of H <sub>2</sub> O molecules in 1kg of water
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So we have two equations for two unknowns, which allows their direct derivation:

$x_1 = MM \cdot N$	The molar fraction of free H <sub>2</sub> O molecule
$K = \frac{1}{MM \cdot N} - 1$	Dissociation constant of hydrogen bonding of water

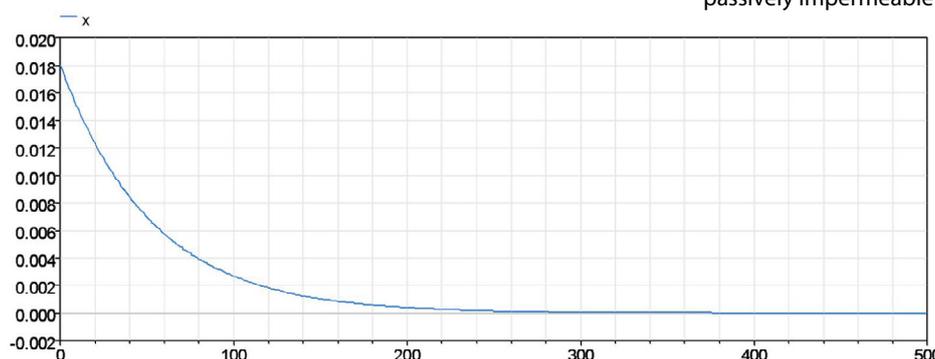


Figure 1 – Distribution of molar fractions according to the number of H<sub>2</sub>O molecules in the cluster. The frequency of a cluster of a given size decreases exponentially with its size. The larger the cluster, the lower the concentration.

In conclusion, it is sufficient to verify that the product  $x_1 * K$  is less than 1. The number of clusters (N) must be less than the number of H<sub>2</sub>O molecules (1 / MM) and therefore  $MM * N < 1$ , and therefore the product  $x_1 * K = 1 - MM * N < 1$ . Therefore, the use of the calculation of a geometric series is justified for each possible measured value of N.

One way to estimate the number of water particles (N) is to measure the solubility of gases (A) in water and then compare it with this chemical process's energy equilibrium. From the balance of chemical potentials of gaseous and dissolved substance A, it is possible to derive the relationship between the difference of formation Gibbs energies ( $\Delta_{dis} G^\circ$ ) and Henry's coefficient (kH):

$kH = \frac{a_{A(aq)}}{a_{A(g)}} = e^{-\frac{\Delta_{dis} G^\circ}{(R \cdot T)}}$	Henry's coefficient for molar fractions
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From the table values of formation energies for gaseous ( $\Delta_f G^\circ_{A(g)}$ ) and dissolved substance in water ( $\Delta_f G^\circ_{A(aq)}$ ) it is, therefore, possible to determine the value  $\Delta_{dis} G^\circ = \Delta_f G^\circ_{A(aq)} - \Delta_f G^\circ_{A(g)}$ .

At the same time, it is possible to measure the molar fraction of substance A in the gas ( $a_{A(g)}$ ) as well as the molar amount of substance A that dissolved in water ( $n_{A(aq)}$ ). Then N can be expressed from the relation:

$N = \frac{n_{A(aq)}}{a_{A(g)}} e^{\frac{(\Delta_f G^\circ_{A(aq)} - \Delta_f G^\circ_{A(g)})}{(R \cdot T)}}$	Number of particles in 1 kg of pure water
$N = \frac{n_{A(g)}}{a_{A(g)} \cdot kH_{(aq)}}$	Number of particles in 1 kg of aqueous solution

### 3 Results

The first estimate of the number of water particles per kilogram of pure water is 1 mol (standard molality). For this value, it is possible to express

$$N \approx 1 \text{ mol}$$

$$x_1 \approx 0.018 \frac{\text{mol}}{\text{mol}}$$

$$K \approx 54.5$$

$$x_1 \cdot K \approx 0.98 \frac{\text{mol}}{\text{mol}}$$

According to NIST (National Institute of Standard and Technology, see <https://www.nist.gov/>), Henry's constant for the solubility of CO<sub>2</sub> in water is 0.035 mol/kg/bar in pure water, where 1 kg of water contains 1 mol of all particles. At a partial pressure of pCO<sub>2</sub> = 40 mmHg = 40/760 bar in the intracellular fluid, the concentration of freely dissolved CO<sub>2</sub> is measured as 1.24 mmol / L. Thus, the total number of intracellular fluid particles is 0.67 mol / L. This is roughly confirmed by measuring the volume fraction of water or the measurement of solubility for O<sub>2</sub> or even isoosmolarity expressed in the sum of molar fractions of passively impermeable substances.

We then support these and many other physiological calculations using a software library designed for physiology [10-13].

Similarly, it is possible to express all body fluids' molar density and then switch to counting over molar fractions instead of molality or molarity [14]. In physical chemistry, counting over molar fractions is directly linked to calculating energies and electrochemical potentials. Therefore, it is then possible to express the end states of elementary processes as equalizing electrochemical potentials. This will allow using physical chemistry to derive dissociation constants, Henry coefficients, electrical potentials, Nernst voltages, Donnan equilibria on the cell membrane, osmolarity, and other electrochemical processes.

#### 4 Discussion

Unfortunately, many books on physical chemistry equate molality, molarity, and molar fractions in aqueous solutions (either directly or through activities or through chemical potential). At the same time, they are aware that this equality only applies under specific conditions and at low solute concentrations. In order to make it all right in terms of physical units, the constants "standard molality" and "standard molarity" were introduced, which will convert moles into kilograms or liters. Unfortunately, these constants have also become part of the definitions. One of them is the definition of pH. However, today's pH measurement via a hydrogen electrode does not measure molality but the electrical voltage in redox reactions and thus the activity of hydrogen ions. The conversion to the molality of these positively charged water particles' activity should depend on the total number of particles in one kilogram or in one liter. As a result, the theoretical balance using the current pH definition cannot fully coincide with measurements in environments such as intracellular fluid (where it is not true that 1 mol of all particles has one kilogram of solvent or 1 mol of all particles is in one liter of solution). In principle, the current definition of pH works where the "standard molality" works, i.e., in solutions where the total molar density of 1 mol of all particles per 1 kg of solvent applies.

Our idea of water is based only on macroscopic properties that interest us. Although the model derives the abundance of individual water clusters, only the total number is relevant to us. Thus, our hypothesis was only partially confirmed, and further measurements and experiments of already molecular properties of H<sub>2</sub>O and their hydrogen bonds are necessary for its full confirmation.

For example, if we relax from this assumption and allow more cyclic hydrogen bonds within one cluster, it is possible to reformulate the calculation to the molar fraction of the cluster as

$$x_{ij} = x_1 * (x_1 * K)^{i-1} * K_{(int)}^j,$$

assuming that all internal bonds would have the same dissociation constant  $K_{(int)}$ . The added index  $j$  here expresses the number of internal links that are missing in the original model. However, it is necessary to omit the first members when summing these fractions because these internal cyclic bonds can exist only from a certain cluster size. For example, the smallest cluster with one internal bond must have at least 4 H<sub>2</sub>O molecules, with two 6, with three 8, four 9, etc. However, these complexities come into play only when conflicting data requires the theory to be extended by another degree of freedom. So far, according to the Occam razor pattern, a simpler model where  $j = 0$  will suffice.

#### 5 Conclusion

Water forms bonds with each other that cluster more H<sub>2</sub>O molecules into larger particles. We assume that in liquid water, H<sub>2</sub>O

molecules bind to each other in clusters by bonds so that these bonds do not form cycles, and each of these bonds has the same properties as the enthalpy and entropy of the hydrogen bonds between the H<sub>2</sub>O molecules. The dissociation constant when joining two clusters is the same as the dissociation constant between two free H<sub>2</sub>O molecules. We constructed a mathematical model that accurately derives the molar fractions of cluster sets from a certain number of H<sub>2</sub>O molecules based on these assumptions. Simultaneously, it does not matter how long this state of specific clusters lasts because the number of individual clusters in the steady-state remains the same even if the bonds change rapidly dynamically.

From the required molar amount of water, we derived the dissociation constant and enthalpy of hydrogen bonds between H<sub>2</sub>O molecules to be compatible with data from the National Institute of Standards and Technology (NIST) and data on the formation energies of individual substances. Using these constants, it is possible to derive the molar amount of water in aqueous solutions and then make calculations over molar fractions, the results of which begin to coincide with published experiments.

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