

## GENERAL CHEMISTRY OF SEAWATER

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**Keywords:** advection, aeolian, carbon dioxide, carbon monoxide, colloid, composition, conservative property, dielectric constant, electric conductivity, gas, heat of fusion, heat of vaporization, humic material, latent heat, leaching, major elements, methane, minor elements, nitrogen, nitrous oxide, organic matter, oxygen, residence time, salinity, speciation, specific heat, surface tension, temperature of maximum density, trace elements, viscosity.

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### Summary

The oceans are filled with  $1.348 \times 10^9$  km<sup>3</sup> of seawater, a dilute aqueous electrolytic solution. The major component of seawater, as the name suggests, is water, which constitutes 96.5 per cent with the remaining 3.5 per cent composed of NaCl, MgSO<sub>4</sub> and a great number of other elements and compounds. Water is not only the major component of seawater, but it also accounts for over 85 per cent of the mass of most marine organisms.

Water has many unique properties as a result of the shape of the molecule, which is composed of two hydrogen atoms and one oxygen atom. The shape of H<sub>2</sub>O causes it to have a dipolar distribution of electrical charge with the hydrogen end having a partial positive charge, and the oxygen end having a partial negative charge. The dipolar nature results in the hydrogen bond which plays a major role in giving water many of its unique properties, one of the most important being the tremendous dissolving power.

Most substances can be dissolved by water and this is especially true with inorganic salts which makes seawater salty. The average salinity of the oceans is 34.7, meaning that there are 34.7 grams of dissolved solids in one kilogram of seawater. Over 99 per cent of the salinity is accounted for by six ions, which are in order of decreasing abundance: chloride (Cl<sup>-</sup>), sodium (Na<sup>+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), magnesium (Mg<sup>2+</sup>), calcium (Ca<sup>2+</sup>) and potassium (K<sup>+</sup>). These ions remain in the same relative proportions everywhere in the oceans.

Gases in the atmosphere readily dissolve in seawater at the air-sea interface. That plants and animals living in the oceans require some of the gases to survive is not surprising, but despite the abundant oxygen atom in the form of  $\text{H}_2\text{O}$  in seawater, no animal can break down the water molecule to obtain oxygen needed for breathing. Life-sustaining oxygen must come from the atmosphere or from photosynthesis, that process whereby plants convert carbon dioxide ( $\text{CO}_2$ ) to organic carbon and, in the meantime, release oxygen. Some plants, notably *cyanobacteria*, are able to 'fix' the nitrogen molecule ( $\text{N}_2$ ). In this process the very stable  $\text{N}_2$  is converted to organic plant tissue. The eventual decomposition of the organic material consumes oxygen but releases  $\text{CO}_2$  into the water column, mostly at depth. As a result, oxygen concentration is usually lower but  $\text{CO}_2$  concentration is higher in the subsurface. In areas of low oxygen content, anaerobic processes may result in the release of methane ( $\text{CH}_4$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ), nitrous oxide ( $\text{N}_2\text{O}$ ) or  $\text{N}_2$ .

In spite of nitrogen fixation and the denitrification processes (see Nutrient Cycling in the Oceans), the amount of  $\text{N}_2$  involved is very small, and the changes are too minor to detect in the large  $\text{N}_2$  background either in the atmosphere or in seawater. Many other gases, such as Ne, Ar, Kr and Xe, do not show much variation in seawater either because of their inertness or lack of biogeochemical activities.

## 1. Introduction

'From a drop of water, a logician could infer the possibility of an Atlantic or a Niagara, without having seen or heard of one or the other', said Sherlock Holmes, in *A Scarlet*, by Sir Arthur Conan Doyle.

For all the hundreds of millions of years following the cooling of the Planet Earth, liquid water has poured from the atmosphere, or flowed from land, to the sea. And now, the oceans cover 70.8 per cent of the surface of the Earth with the seawater composition remain unchanged for thousands of years prior to the present.

Water, the compound composed of two hydrogen atoms and one oxygen atom, is the major component of seawater. The polar nature of the water molecular produces many unique physical and chemical properties, one of the most important of which is water's remarkable ability to dissolve more substances than any other natural solvent. As a result, seawater contains millions and millions of chemical compounds aside from the most abundant and well known  $\text{NaCl}$  and  $\text{MgSO}_4$ . In addition to inorganic salts, seawater contains dissolved gases and organic material, as well.

## 2. Physical Parameters

The oceans consist mainly of water, and the water molecular itself is fascinating owing to its simplicity. A water molecular ( $\text{H}_2\text{O}$ ), containing two hydrogen atoms and one oxygen atom, is extremely stable because of the large heat of formation ( $285.9 \text{ k J m}^{-1}$ ). If one were to put a water molecule into a cube (Figure 1) with the oxygen occupying the center, the two hydrogens would occupy opposite corners of one face of this cube at an angle of  $105^\circ$ . Two of the oxygen's eight electrons would be near its nucleus, one each being involved in the bonding of each hydrogen, and pairs of unshared electrons

would form limbs directed toward opposite corners of the cube face opposite the one containing the hydrogens. These unshared electrons would attract the positive partial charges of the hydrogen atoms of other water molecules nearby and thus form the so-called hydrogen bonds. Pointing positive charges in one direction but negative charges in the other would give the water molecule its polar properties.

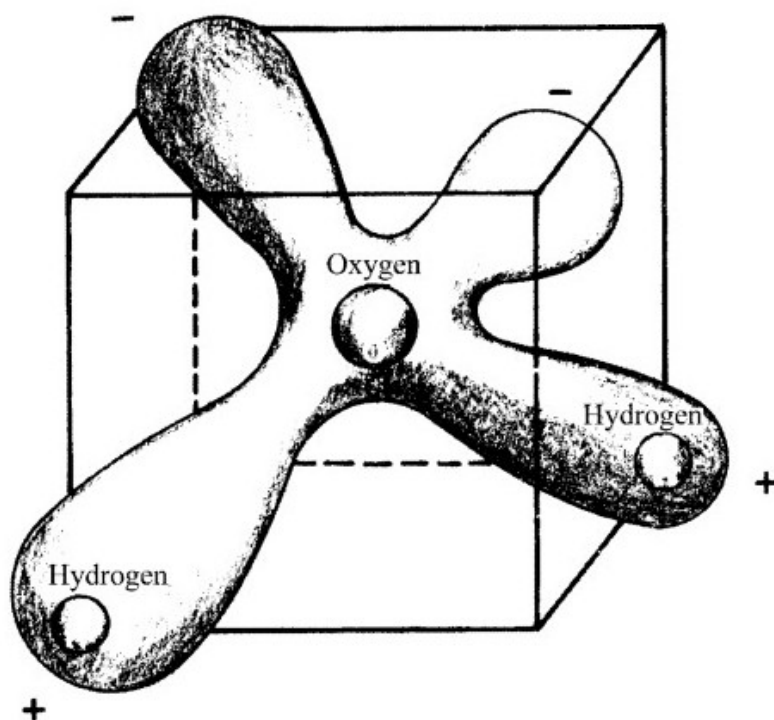


Figure 1. Electronic cloud of the water molecule (modified from Horne, 1969).

These unique electrical properties (electronegativity) make water anomalous in many ways. For instance, the heat capacity of water (about  $4.18 \times 10^3 \text{ J kg}^{-1} \text{ }^\circ\text{C}^{-1}$ ) is the highest of all solids and liquids except liquid  $\text{NH}_3$ . This is because part of the energy that is normally used to raise temperature is now diverted to break the hydrogen bond. This unique property helps to prevent extreme ranges in temperature on Earth because heat transfer by water movements is very large. High heat capacity also tends to maintain a mostly uniform body temperature in living organisms. Water's latent heat of fusion ( $3.33 \times 10^5 \text{ J kg}^{-1}$ ) is the highest except for  $\text{NH}_3$ . This has a thermostatic effect at freezing point due to the absorption or release of latent heat. Latent heat from the evaporation of water ( $2.25 \times 10^6 \text{ J kg}^{-1}$ ) is also the highest of all substances. The large latent heat from evaporation is extremely important in the heat and water transfer in the atmosphere and helps to keep the climate mild.

Another one of the most peculiar properties of water is its unusual thermal expansion capacity. The density of most solids is greater than that of their corresponding liquids, and the density of liquids typically decreases progressively when heated from the melting point—but ice is less dense than water, and the maximum density of pure water is reached at  $4^\circ\text{C}$ . As the temperature of pure water is raised above its melting point ( $0^\circ\text{C}$ ), the energy of the molecules increases, counteracting the tendency to form partly

ordered groups by breaking progressively more hydrogen bonds. Individual molecules can then fit together more closely, occupying less space and increasing the density of the water. However, raising the temperature also causes thermal expansion of the free, individual molecules, which results in decreased density. At temperatures between 0°C and 4°C, the 'ordering effect' predominates, whereas at higher temperatures thermal expansion is more important. The combination of these two effects means that the density of pure water is greatest at 4°C. Water below 4°C actually shrinks in volume when heated, and the temperature of maximum density decreases with increasing salinity. Since fresh water and dilute seawater have their maximum densities at temperatures above the freezing points (Figure 2), this property is important in controlling temperature distribution and vertical circulation in lakes in winter at temperatures below 4°C. This is because in such environment, water becomes lighter at lower temperature. Thus, it stays on the surface until it freezes over, forming an ice cover which serves as a layer of insulation. Beneath ice, the denser, warmer water remains in its liquid form to sustain living organisms. Many physical properties of seawater, such as density, specific volume, compressibility, expansibility, sound speed, heat capacity, etc., can be calculated using an equation of state (Table 1).

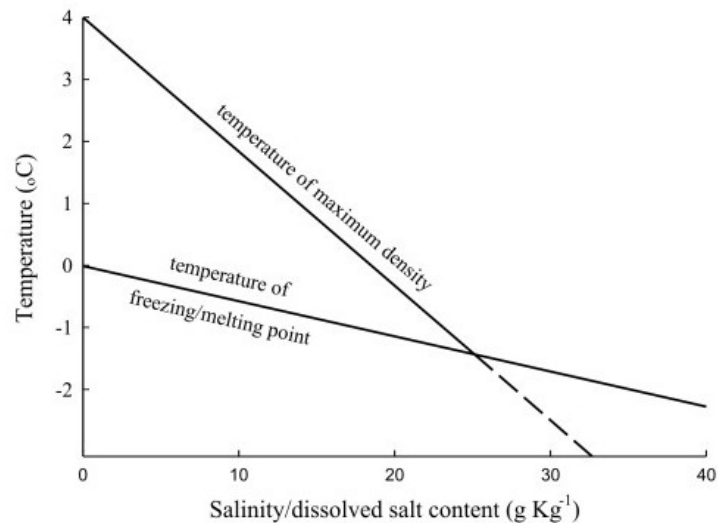


Figure 2. Temperatures of freezing and melting point and maximum density of seawater as functions of dissolved salt content.

$$V^P = V^0 (1-P/K) \tag{1}$$

$$\rho^P = \rho^0 [1/(1-P/K)]$$

where: V and P are the specific volume and density, respectively, of seawater; superscripts P and 0 denote, respectively, applied pressure P and 0 (the applied pressure is the absolute pressure minus one atmosphere, expressed in bars; i.e. the applied pressure at sea level is zero); t is degree Celsius; and S is salinity.

$$\begin{aligned} \rho^0 = & 999.842594 + 6.793952 \times 10^{-2} t - 9.095290 \times 10^{-3} t^2 \\ & + 1.001685 \times 10^{-4} t^3 - 1.120083 \times 10^{-6} t^4 \\ & + 6.536336 \times 10^{-9} t^5 + (8.24493 \times 10^{-1} \\ & - 4.0899 \times 10^{-3} t + 7.6438 \times 10^{-5} t^2 \\ & - 8.2467 \times 10^{-7} t^3 + 5.3875 \times 10^{-9} t^4) S \\ & + (-5.72466 \times 10^{-3} + 1.0227 \times 10^{-4} t \\ & - 1.6546 \times 10^{-6} t^2) S^{3/2} + 4.8314 \times 10^{-4} S^2 \\ \\ K = & 19652.21 + 148.4206t - 2.327105t^2 + 1.360477 \times 10^{-2} t^3 \\ & - 5.155288 \times 10^{-5} t^4 + S(54.6746 - 0.603459t \\ & + 1.09987 \times 10^{-2} t^2 - 6.1670 \times 10^{-5} t^3) - S^{3/2} (7.944 \times 10^{-2} \\ & + 1.6483 \times 10^{-2} t - 5.3009 \times 10^{-4} t^2) + P[3.239908 \\ & + 1.43713 \times 10^{-3} t + 1.16082 \times 10^{-4} t^2 - 5.77905 \times 10^{-7} t^3 \\ & + S(2.2838 \times 10^{-3} - 1.0981 \times 10^{-5} t - 1.6078 \times 10^{-6} t^2) \\ & + S^{3/2} (1.91075 \times 10^{-4})] + P2[8.50935 \times 10^{-5} - 6.12293 \times 10^{-6} t \\ & + 5.2787 \times 10^{-8} t^2 + S(-9.9348 \times 10^{-7} + 2.0816 \times 10^{-8} t + 9.1697 \times 10^{-10} t^2)] \end{aligned}$$

The thermal expansibilities of seawater can be determined by differentiating equation (1) with respect to temperature

$$\alpha = \frac{1}{V^P} \left( \frac{\partial V^P}{\partial T} \right)_P$$

The isothermal compressibilities of seawater can be obtained by differentiating equation (1) with respect to pressure

$$\beta_T = \frac{-1}{V^P} \left( \frac{\partial V^P}{\partial P} \right)_T$$

Table 1. The International Equation of State for Seawater (m<sup>3</sup> kg<sup>-1</sup>).

The surface tension of water (7.2×10<sup>9</sup> N m<sup>-1</sup>, where N is Newton, a unit of force in kg m s<sup>-2</sup>) is also the highest of all liquids. This is important in the physiology of the cell and modulates such surface phenomena as droplet formation. Because of high surface tension, certain small animals can actually stand on water. Water also has a tremendous dissolving power. In general, water dissolves more substances and in greater quantities

than any other liquid. This has obvious implications in both physical and biological phenomena, and a bit of everything can be found in the oceans because of this.

Pure water has the highest dielectric constant (87 at 0°C, 80 at 20°C) of all liquids except H<sub>2</sub>O<sub>2</sub> and HCN. This is of the utmost importance in the behavior of inorganic dissolved substances because of the resulting high dissociation. Water's electrolytic dissociation is very small (ionic dissociation constant is only 10<sup>-14</sup> M<sup>-1</sup> at 25°C), so water is essentially a neutral substance even though it contains both H<sup>+</sup> and OH<sup>-</sup> ions. These ions make the water somewhat conductive to electrical current (electrical conductivity <10<sup>-8</sup> ohm<sup>-1</sup> cm<sup>-1</sup> at 25°C).

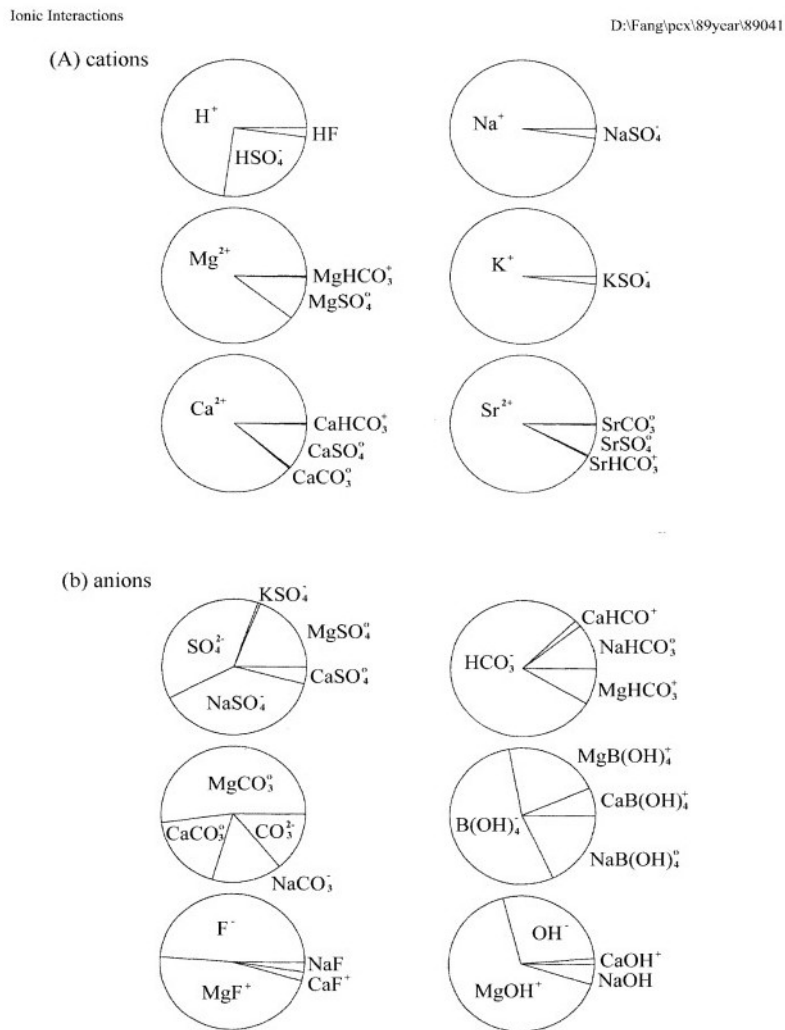


Figure 3. The speciation of (a) cations and (b) anions in seawater (after Millero, 1996).

The transparency of water is relatively high. Although the absorption of radiant energy is large with regard to infrared and ultraviolet, in the visible portion of the energy spectrum, there is relatively little selective absorption; hence, water appears colorless. The great transparency makes the euphotic zone relatively thick to allow for photosynthesis. The conduction of heat in water is the highest of all liquids (0.006 watt cm<sup>-1</sup> °C at 20°C). Although important on a small scale, as in living cells, in the water

column advection is far more important. Finally, the molecular viscosity of water ( $10^{-3}$  N s m<sup>-2</sup>) is less than most other liquids so water flows readily to equalize pressure differences. Adding salt, or heat or pressure, makes water lose its uniqueness by breaking the ordering effect or reducing the number of hydrogen bonds.

Dissolving most substance in a liquid has the effect of increasing the density of that liquid. The greater the amount dissolved, the greater the density. The density of freshwater is close to  $1.00 \times 10^3$  kg m<sup>-3</sup>, while the average density of seawater is about  $1.023 \times 10^3$  kg m<sup>-3</sup>. One important effect of dissolved salts in water is to depress the freezing point of liquids. This is why salt is spread on icy roads. It also lowers the temperature at which water reaches its maximum density (Figure 2). This is because dissolved salts inhibit the tendency of water molecules to form ordered groups, so that density is controlled more by the thermal expansion effect. When seawater first begins to freeze, relatively pure ice is formed by extruding salts so that the salinity of the surrounding seawater is increased, which both increases its density and depresses its freezing point. Sea ice has a density of about  $0.92 \times 10^3$  kg m<sup>-3</sup>. Most of the salt remaining in sea ice is in the form of concentrated brine droplets trapped within the ice as it forms. Gradually, the heavier brine droplets travel downward, while air replaces the brine in the cavities. Finally, the sea ice becomes 'rotten'. By shaking off rotten sea ice, which may be soaked in seawater which is easy to get rid of, sea ice may become potable. When sea ice is first formed, nutrients are trapped in it, which may support algae and other micro-organisms.

Once salts are dissolved in water, they frequently form ions, which are seldom free and often interact with water molecules or with ions to form ion pairs. There are four classes of ion pairs: a) complexes – when the ions are held tightly in contact by strong covalent bonds; b) contact ion pairs – when the ions are held in contact by electrostatical force, or ionic bonds; c) solvent – shared ion pairs – when the ions are linked by electrostatical force but separated by a single water molecule; d) and solvent – separated ions pairs when ions are linked loosely by electrostatical force but separated by more than one molecule. These ion pairs affect the separation of the chemicals in seawater. Once an ion forms ion pairs its chemical activity is reduced, and frequently, so is toxicity. Take hydrogen ion as an example. Its activity in seawater is only about 70 per cent of that in freshwater because 30 per cent of it forms HSO<sub>4</sub><sup>-</sup> and HF<sup>0</sup> ion pairs. In other words, 30 per cent of H<sup>+</sup> is no longer H<sup>+</sup>. The speciation of common cations and anions in seawater are given in Figure 3.

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## Biographical Sketch

Born in Changhua, Taiwan, on 22 April 1949, **Prof. Chen-Tung Arthur Chen**, his wife and two daughters are currently residing in Kaohsiung, where he has been Professor at the Institute of Marine Geology and Chemistry since 1986. After receiving his B.Sc. degree in Chemical Engineering from National Taiwan University in 1970, Prof. Chen was awarded his Ph.D. degree in Chemical Oceanography from the University of Miami in 1977. In the same year, he was appointed Assistant Professor in the College of Marine Sciences of Oregon State University, where he was later promoted to Associate Professor in 1981. He served as visiting professor at National Sun Yat-Sen University (NSYSU) in Kaohsiung, Taiwan, and as Chargé de recherche (CNRS), Université Pierre et Marie Curie in Paris during 1984-1985. During this period, he founded the Institute of Marine Geology at NSYSU, and served as its director until 1989 when he was made Dean of the College of Marine Sciences, a position he held until 1992.



Prof. Chen has sat on numerous international committees, including the Scientific Committee on Oceanic Research and the World Ocean Circulation Experiment. He also served as one of the executives of the Scientific Steering Committee of the Joint Global Ocean Flux Study (JGOFS) between 1992-1995. Just prior to that, he had helped to form the Joint JGOFS / LOICZ Marginal Seas Task Team in 1991, and served as its chairman until 1995. Prof. Chen is at present one of the editors of *Oceanography Journal* and associate editor of *Marine Chemistry*. Besides having more than 150 of his own scientific papers published, Professor Chen was awarded the highly-coveted Biowako Prize for Ecology from Japan in 1997.

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