EPSS 15 Introduction to Oceanography Fall 2019

# The Physical and Chemical Properties of Seawater

The focus of the Lab this week is seawater--its composition, physical and chemical properties. Seawater is a complex solution containing dissolved inorganic salts (3.5%), dissolved gases, and traces of dissolved organic molecules. Chemical and physical exchanges at the interface between the ocean and atmosphere have profound effects on the heat budget and climate of the Earth. In addition, seawater forms the basic environment of marine organisms. Its various properties (temperature, salinity, oxygen and nutrient content, degree of penetration of sunlight) strongly affect the distribution of marine species. The abundance of dissolved nutrients in seawater provides a fundamental control on biological productivity within the shallow surface layer of the oceans. Thus, understanding how the properties of seawater vary spatially and temporally in the oceans is a fundamental part of oceanography. The Lab this week will introduce you to some of the important chemical and physical properties of seawater.

## Water - A Unique Compound

Earth is the third planet from the Sun. The "Blue Planet." As far as we know, it is a unique environment in our solar system, because it provides the necessary conditions for life. At a fundamental level, this uniqueness is attributable to temperatures and pressures that permit water to exist in all three states (solid, liquid, and vapor) at the Earth's surface.

Table 1 provides a summary of some of the important and unique properties of water. Many of the unusual features of water are related to the dipolar structure of the water molecule, and the tendency for water molecules to bond with one another by hydrogen bonds (Figure 1). The formation of hydrogen bonds results in unusually high melting (0˚C) and boiling (100˚C) points for such a light compound. Without hydrogen bonds, water would be expected to boil at –68˚C! The formation of hydrogen bonds also results in high latent heats of melting and vaporization (Figure 2). Water also has an extremely high heat capacity (the amount of energy it can store/release relative to changes in temperature). These properties of water not only allow the oceans to exist on the Earth, but they result in oceans that have a major moderating effect on the climate.

## Temperature

Temperature is an important physical property of seawater. It is a measure of the amount of heat stored in the oceans. Because of the high heat capacity of water, the oceans store large amounts of energy. Temperature also has a great effect on the density of seawater. The higher the temperature of seawater, the lower its density (or conversely, cold seawater has a high density). Temperature also has an effect on the chemical activity of water. For example, gases from the atmosphere (i.e., nitrogen, oxygen and carbon dioxide) are most soluble in cold water.

## Salinity

Seawater is a complex mixture of salts in solution that have been derived from the chemical weathering of the crust and from volatiles released by volcanic gases. The salt content of seawater is typically expressed as the concentration of ions in seawater, or grams of dissolved solids per kilogram (1000 grams) of seawater. A kilogram of average seawater contains 34.7 grams of dissolved salts, and therefore has a salinity of 34.7‰ (parts per thousand) or 3.47% (percent). The remaining 96.53% is water. The composition of seawater salts is given in Table 2. Most of the inorganic components in seawater are accounted for by only six ions. These are chloride ($Cl^-$), sodium ($Na^+$), sulfate ($SO_4^{2-}$), magnesium ($Mg^{2+}$), calcium ($Ca^{2+}$), and potassium ($K^+$). Analysis of seawater samples from many different places in the oceans reveals that the relative proportions of the major ions are remarkably constant. In other words, the open oceans are well mixed, and although salinity may vary from place to place due to the evaporation or precipitation of water, the proportions of ions in the solution does not vary significantly from place to place. This concept is embodied in the Principle of Constant Proportions. Application of this principle provides a useful means for estimating salinity: by measuring the abundance of one ion, we can calculate the total abundance of dissolved salts based on the assumption of constant proportions. If you were asked to determine salinity, which ion would you choose? Obviously the most abundant, chloride ($Cl^-$), would be the easiest and most accurate to measure. This, in fact, has been the traditional ion of choice by oceanographers. Once the total chloride content, or chlorinity, of seawater is known, we can calculate salinity using the formula:

$$\text{Salinity (‰)} = 1.80555 \times \text{Chlorinity (‰)}$$

Determining the chlorinity of a seawater sample is time consuming, and in recent years more convenient methods have been developed. Many modern salinometers utilize the relationship between the electrical conductivity of a solution and its ion concentration. The conductivity of water is a function of the number of ions present. As the ion concentration increases, electrical conductivity increases. Conductivity meters are first calibrated against standards of known salinity (determined by chlorinity), and then electrical conductivity of the water sample is determined directly. The accuracy is about 20 parts per million, the accuracy of the standard used. Modern salinometers are direct-reading devices that function in situ to depths of more than 6,000 meters.

Salinity of ocean surface waters typically falls between 34‰ and 37‰ (see Figure 4). The salinity of seawater increases whenever pure water is removed by evaporation or formation of ice. The salinity of seawater decreases whenever water is added by precipitation (rain) or melting of ice. The salt content of water has an important effect on its physical properties. Addition of salt to water increases its density and lowers its freezing point.

How are dissolved salts added to and removed from the oceans? The sources of dissolved salts include river waters, gases from volcanic eruptions, and fluids from hydrothermal vents at the Ridge and Rise System. There are two primary sinks (processes that remove salts). Many dissolved elements eventually get incorporated into deep-sea sediments as a result of biological or inorganic processes. Some dissolved salts get removed from seawater by fluids that circulate into ocean ridges. Thus ridges are a sink for some elements as cold fluids circulate into them, and later a source for others, as hot fluids leave through hydrothermal vents.

## Density

Density of seawater is an important property that controls deep-ocean circulation. Dense seawater formed at the surface will sink to great depths, driving the internal circulation of the oceans. Density is primarily a function of temperature and salinity. High density is favored by low temperature and high salinity. In general, the coldest waters are usually the most dense (see Figure 3).

Carbon Dioxide ($CO_2$)

Carbon dioxide is highly soluble in seawater because it reacts chemically with water to produce a weak acid, carbonic acid. Carbonic acid dissociates to form hydrogen and bicarbonate ions. Some of the bicarbonate even dissociates further to form hydrogen and carbonate ions.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

[carbon dioxide] [water] [carbonic acid] [hydrogen ion] [bicarbonate ion] [hydrogen ion] [carbonate ion]

All of these forms of $CO_2$ ($CO_2$, $H_2CO_3$, $HCO_3^-$, and $CO_3^{2-}$) exist in seawater. It turns out that 90% of the total carbon dioxide in the oceans is stored in bicarbonate ions. All of these reactions are reversible. Thus if carbon dioxide is used up by photosynthesizing plants, these reactions will go to the left, consuming bicarbonate and carbonic acid to make more carbon dioxide available. Carbon dioxide is a fundamental ingredient in photosynthesis. The carbon atom in a $CO_2$ molecule is used by plant cells to manufacture complex organic molecules, such as sugars, starches, proteins and lipids:

$$6H_2O + 6CO_2 + \text{Energy} \underset{\text{Respiration}}{\overset{\text{Photosynthesis}}{\rightleftharpoons}} C_6H_{12}O_6 + 6O_2$$

[water] [carbon dioxide] [sunlight] [sugar] [oxygen]

Acidity and Alkalinity (pH)

We have just seen how carbon dioxide dissolves in seawater to produce carbonic acid. To understand the significance of this requires a discussion of acidity, alkalinity and the pH scale. An acid is any compound that, when dissolved in water, releases hydrogen ions ($H^+$), increasing their concentration in solution. Water molecules constantly dissociate and reform:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Because the concentrations of the H+ and OH- are equal in a solution of pure water, the solution is, by definition, neutral. However, if we dissolve an acid in water, the hydrogen ion concentration will increase as the acid dissociates. For example:

$$HCl + H_2O \rightleftharpoons H^+ + Cl^- + H_2O$$

[hydrochloric acid] [water] [hydrogen ion] [chloride ion] [water]

In contrast, an alkaline substance (a base) is one that dissociates in water releasing hydroxyl ions ($OH^-$) into solution. If we dissolve a strongly alkaline substance in water (e.g., sodium hydroxide), the concentration of $OH^-$ ions in solution will increase. For example:

$$NaOH + H_2O \rightleftharpoons Na^+ + OH^- + H_2O$$

[sodium hydroxide] [water] [sodium ion] [hydroxyl ion] [water]

The acidity or alkalinity of a solution is described relative to pure water by the pH scale. pH is defined as the inverse of the logarithm of the concentration of $H^+$:

$$pH = -\log_{10}[H^+]$$

pH ranges from about 0 to 14 (see Table 3). Pure water, by definition, has a neutral pH with a value of 7 on the pH scale. Acidic solutions have extra $H^+$ (i.e., a higher concentration than pure water). The minus sign in the definition of pH means that extra $H^+$ lowers the pH. So acidic solutions have pH values less than 7 and alkaline (basic) solutions have pH values greater than 7. Remember that the pH scale is not linear. Each unit change in pH is a ten-fold change in hydrogen-ion concentration.

The Carbonate Buffer System

In general, the pH of the oceans ranges from 7.5 to 8.4 (slightly alkaline). The pH of seawater is remarkably stable within this range, being "buffered" by bicarbonate ions in solution. This resistance to change in pH can be simply understood as the sensitivity of the carbonate reactions discussed previously to changes in hydrogen-ion concentration. If the carbon dioxide concentration of seawater increases, some of the carbon dioxide will react with water and most of it will be converted to bicarbonate. However, as can be seen from this reaction, for every bicarbonate ion produced, one hydrogen ion is also produced, thus increasing the acidity of the water.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

| | | | | | | |
|---|---|---|---|---|---|---|
| [carbon dioxide] | [water] | [carbonic acid] | [hydrogen ion] | [bicarbonate ion] | [hydrogen ion] | [carbonate ion] |

However, if seawater becomes too acidic, this reaction is not favored and bicarbonate tends to combine with hydrogen ions to make carbonic acid, carbon dioxide, and water (the reaction goes to the left). Constant adjustments to pH occur by forward (to the right) and back (to the left) reactions in this buffer system to keep pH within the range 7.5 to 8.4. In general, however, the higher the total carbon dioxide content of seawater, the more acidic it is. Stability in pH is very important in the oceans for the proper functioning of biological systems. All enzymes have optimal pH ranges for efficient functioning.

# Table 1. Properties of Seawater

| PROPERTY | COMPARISON WITH OTHER SUBSTANCES | IMPORTANCE IN OCEAN |
|---|---|---|
| Heat capacity | Highest of all solids and liquids except ammonia | Prevents extreme ranges in ocean temperature |
| Latent heat of fusion | Highest except ammonia | Acts as thermostat at freezing point owing to uptake or release of latent heat |
| Latent heat of evaporation | Highest of all substances | Extremely important in heat and water transfer to atmosphere |
| Thermal expansion | Temperature of maximum density decreases with increasing salinity. For pure water, it is at 4°C. | Freshwater and dilute seawater reach maximum density at temperatures above freezing point |
| Surface tension | Highest of all liquids | Controls drop formation and behavior; also certain surface phenomena, such as capillary waves |
| Dissolving power | Dissolves more substances and in greater quantities than any other liquid. | |
| Transparency | Relatively great | Absorption of radiant energy is large in infrared and ultraviolet. In visible portion of energy spectrum there is relatively little selective absorption which makes water colorless. |

Table 2. Major constituents of seawater.

| ION | PERCENT BY WEIGHT |
|---|---|
| Chloride ($Cl^-$) | 55.07 |
| Sodium ($Na^+$) | 30.62 |
| Sulfate ($SO_4^{2-}$) | 7.72 |
| Magnesium ($Mg^{2+}$) | 3.68 |
| Calcium ($Ca^{2+}$) | 1.17 |
| Potassium ($K^+$) | 1.10 |
| TOTAL | 99.36 |

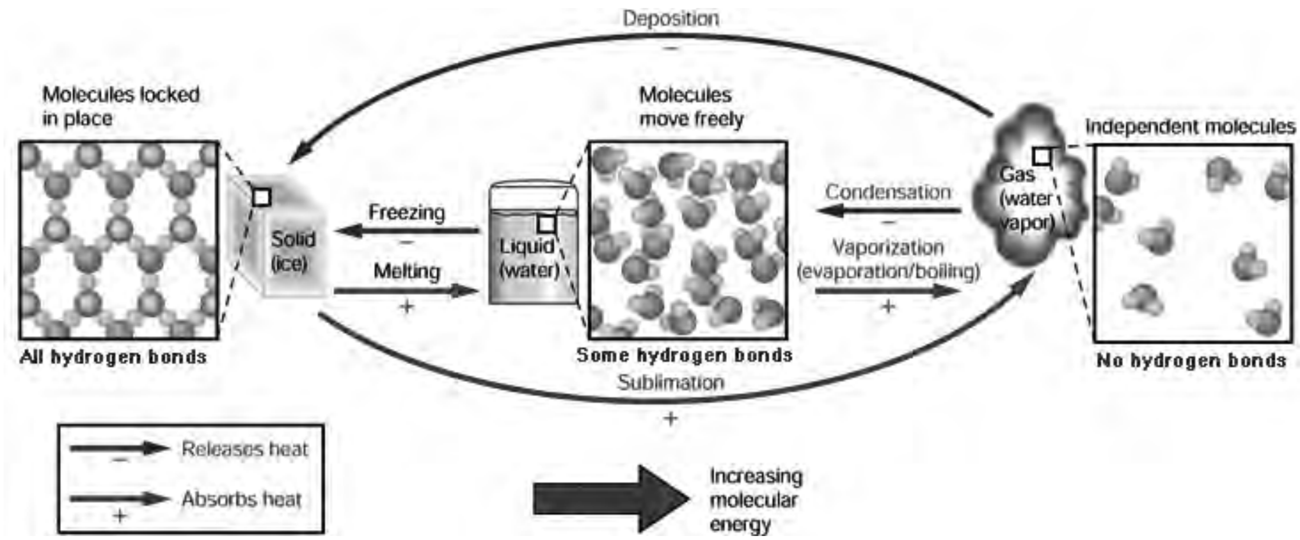


Figure 1. The phases of water.

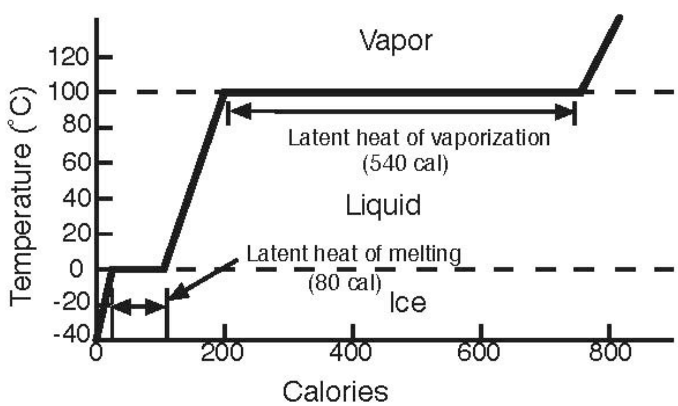


Figure 2. The latent heat of melting (80 cal/g) is much less than the latent heat of vaporization (540 cal/g) because only a few hydrogen bonds must be broken to convert ice to liquid, while all remaining hydrogen bonds must be broken to convert liquid to gas

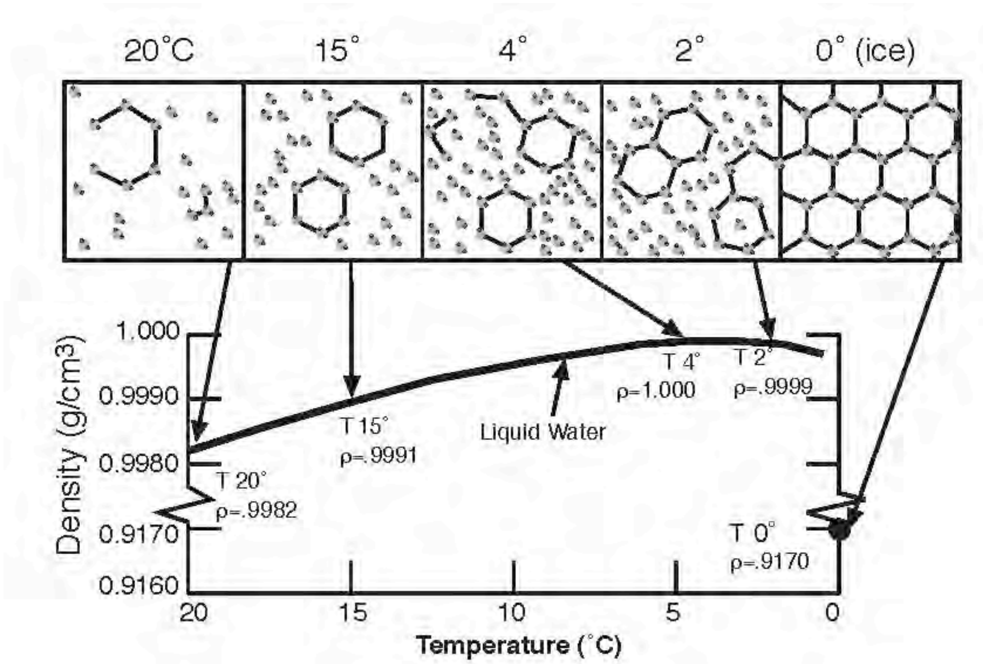


Figure 3. Density of liquid water and ice is related to hydrogen bonding

Increasingly Acid ↑

Neutral ($H^+ = OH^-$)

Increasingly basic ↓

| pH Value | Example Solutions |
|---|---|
| 0 | Hydrochloric Acid (HCl) |
| 1 | Battery Acid<br>Stomach Acid |
| 2 | Gastric Juice (1-3)<br>Lemon Juice |
| 3 | Vinegar, wine, soft drinks, beer<br>orange juice |
| 4 | Tomatoes, grapes |
| 5 | Black coffe, most shaving lotions<br>Bread<br>Normal rainwater |
| 6 | Urine (5-7)<br>Milk (6.6)<br>Saliva (6.2-7.4) |
| 7 | Pure Water<br>Blood (7.3-7.5) |
| 8 | Eggs **Seawater (7.5-8.4)** |
| 9 | Baking Soda<br>Phosphate detergents<br>Chlorox, Tums |
| 10 | Soap solutions<br>Milk of Magnesia |
| 11 | Household Ammonia (10.5-11.9)<br>Nonphosphate detergents |
| 12 | Washing soda (Na2CO3) |
| 13 | Hair remover |
| 14 | Oven cleaner<br>Sodium hydroxide (NaOH) |

pH Value

# Table 3. The pH scale.

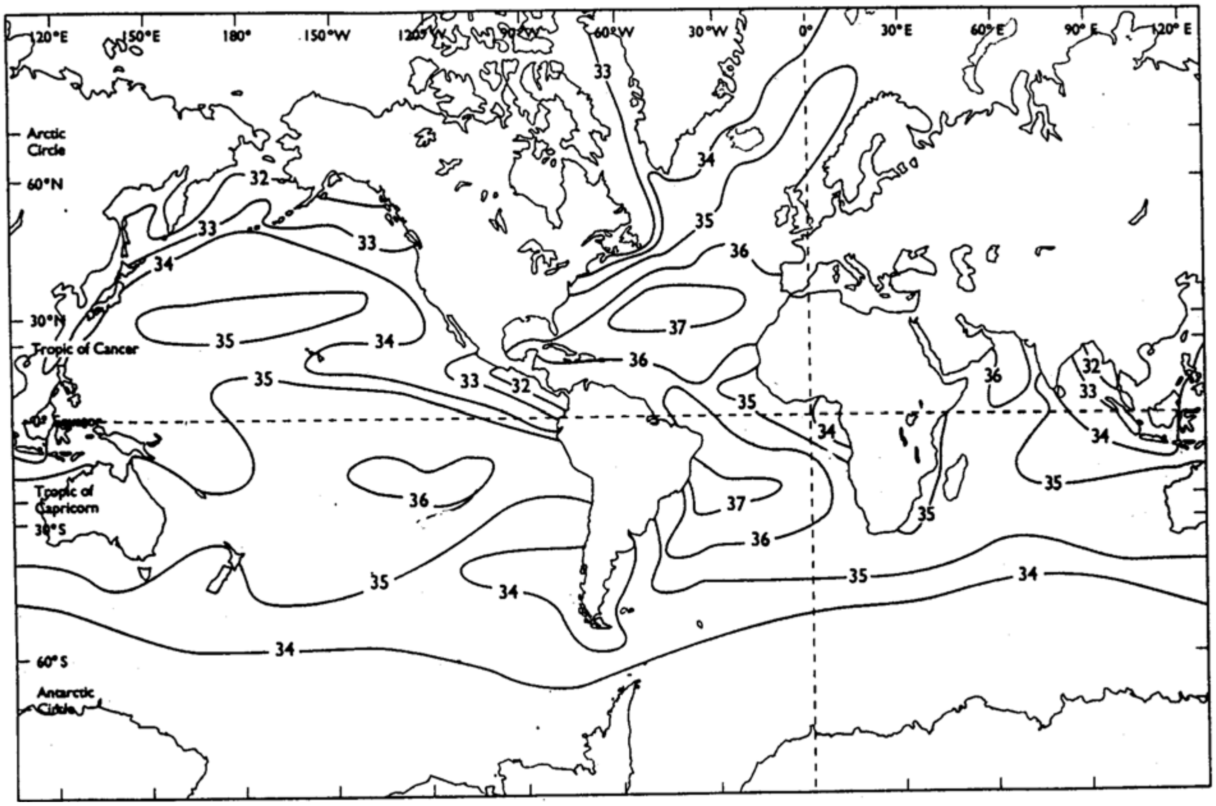

Figure 4. Sea surface salinity (‰) in August (From Pinet, 1998)