Chapter 5

The Properties of Seawater

LEARNING OBJECTIVES

1. Understand the nature of the water molecule and its unique properties and how these are altered by the presence of salt in solution.
2. Know the types of materials that are dissolved in sea water, their importance and how they vary with time.
3. Explain variations in salinity, temperature, and pressure within the sea and how they alter the chemical and physical properties of the ocean.

CHAPTER OUTLINE

5-1. Basic Chemical Notions

A. **Atoms** are the smallest unit which display all of the properties of the material.
   1. Atoms are composed of:
      a. **Nucleus**—the center of the atom consisting of positively charged particles called **protons** and neutrally charged particles called **neutrons.**
      b. **Electrons**—negatively charged particles, which orbit the nucleus in discrete **electron shells.**
   2. Electrically stable atoms have the same number of electrons as protons.
   3. **Ions** are atoms with either more or less electrons than protons and are therefore electrically charged.
   4. **Isotopes** are atoms containing the same number of protons, but different numbers of neutrons and therefore have different weights.
   5. **Molecules** are chemically combined compounds formed by two or more atoms.

5-2. Basic Physical Notions

B. **Heat** results from the vibrations of atoms (**kinetic energy**) and can be measured with a **thermometer**.
   1. In **solids**, the atoms or molecules vibrate weakly and are rigidly held in place.
   2. In **liquids**, the atoms or molecules vibrate more rapidly, move farther apart, and are free to move relative to each other.
   3. In **gases**, the atoms or molecules are highly energetic, move far apart, and are largely independent.
   4. **Melting** is the transition from solid to liquid; **freezing** is the reverse.
   5. **Evaporation** (**vaporization**) is the transition from liquid to gas; **condensation** is the reverse.
   6. Temperature controls density. As temperature increases, atoms or molecules move farther apart and density (mass/volume) decreases because there is less mass (fewer atoms) in the same volume.

5-3. The Water Molecule

C. The water molecule is unique in structure and properties.

1. H_2O is the chemical formula for water.
2. Unique properties of water include:
    a. Higher melting and boiling point than other hydrogen compounds.
    b. High **heat capacity**, amount of heat needed to raise the temperature of one gram of water 1^oC.
    c. Greater solvent power than an other substance.
3. Water molecules are asymmetrical is shape with the two hydrogen molecules at one end, separated by 105^o when in the gaseous or liquid phase and 109.5^o when ice.
4. Asymmetry of a water molecule and distribution of electrons result in a **dipole structure** with the oxygen end of the molecule negatively charged and the hydrogen end of the molecule positively charged.
5. Dipole structure of water molecule produces an electrostatic bond (**hydrogen bond**) between water molecules that cluster together in a **hexagonal** (six-sided) pattern.
6. Ice floats in water because all of the molecules in ice are held in hexagons and the center of the hexagon is open space, making ice 8% less dense than water.
7. Water reaches its maximum density at 3.98^oC.
    a. Below this temperature increasing numbers of water molecules form hexagonal polymers and decrease the density of the water.
    b. Above this temperature water molecules are increasingly energetic and move farther apart, thereby decreasing density.
8. Hydrogen bonding is responsible for many of the unique properties of water because more energy is required to break the hydrogen bonds and separate the water molecules.

9. Water dissolves salts by surrounding the atoms in the salt molecule and neutralizing the **ionic bond** holding the molecule together. Dissolved salts form **cations** (positively charged ions) and **anions** (negatively charged ions).
    - The process of water surrounding an ion is called **hydration**.

D. Sea water consists of water with various materials dissolved within it.
1. The **solvent** is the material doing the dissolving and in seawater it is the water.
2. The **solute** is the material being dissolved.
3. **Salinity** is the total amount of salts dissolved in the water.
    - It is measured in parts of salt per thousand parts of salt water and is expressed as **ppt** (**parts per thousand**) or abbreviated **o/oo**.
4. Average salinity of the ocean is about 35 o/oo.

E. 99% of all the salt ions in the sea are sodium (Na^{+}), chlorine (Cl^{-}), sulfate (SO_4^{-2}), Magnesium (Mg^{+2}), calcium (Ca^{+2}) and potassium (K^{+}).
1. Sodium and chlorine alone comprise about 86% of the salt in the sea.
2. The major constituents of salinity display little variation over time and are a **conservative property** of seawater.

F. **Nutrients** are chemicals essential for life.
1. Major nutrients in the sea are compounds of nitrogen, phosphorus, and silicon.
2. Because of usage, nutrients are scarce at the surface and their concentrations are measured in **parts per million** (**ppm**).
3. Concentrations of nutrients vary greatly over time and because of this they are considered a **nonconservative property** of the sea.

G. In order of decreasing abundance the major gases in the sea are nitrogen, oxygen, carbon dioxide and the **noble gases**, argon (Ar), neon (Ne) and helium (He).
- Nitrogen and the noble gases are considered to be **inert** because they are chemically non-reactive.

H. **Trace elements** occur in minute quantities and are usually measured in parts per million (ppm) or **parts per billion** (**ppb**).
- Even in small quantities they are important in either promoting life or killing it.

I. Marine organic compounds occur in low concentrations and consist of large complex molecules, such as fat, proteins, carbohydrates, hormones and vitamins, produced by organisms or through decay.

5-4. Salinity

J. **Salinity** is the total mass, expressed in grams, of all substances dissolved in one kilogram of sea water when all carbonate has been converted to oxide, all bromine and iodine has been replaced by chlorine and all organic compounds have been oxidized at a temperature of 480^{o}C.

1. **Principle of constant proportion** states that the absolute amount of salt in seawater varies, but the relative proportion of the ions is constant.
   - Because of this principle, it is necessary to test for only one salt ion, usually chlorine, to determine the total amount of salt present.
2. **Chlorinity** is the amount of **halogens** (chlorinity, bromine, iodine, and fluorine) in the seawater and is expressed as **grams/kilogram** or **o/oo**.
3. Salinity is equal to 1.8065 times chlorinity.
4. **Salinometers** determine salinity from the electrical conductivity produced by the dissolved salts.

K. Salinity in the ocean is in a **steady-state condition** because the amount of salt added to the ocean (**input** from **source**) equals the amount removed (**output** into **sinks**).

1. Salt sources include weathering of rocks on land and the reaction of lava with seawater.
   - **Weathering** mainly involves the chemical reaction between rock and acidic rainwater, produced by the interaction of carbon dioxide and rainwater forming **carbonic acid**.
2. Salt sinks include the following:
   a. Evaporation removes only water molecules.
      - Remaining water becomes increasingly saline until it producing a salty **brine**.
      - If enough water evaporates, the brine becomes supersaturate and salt deposits begin to precipitate forming **evaporite** minerals.

   b. Wind-blown spray carries minute droplets of saltwater inland.

   c. Adsorption of ions onto clays and some authigenic minerals.

   d. Shell formation by organisms.
3. Lack of similarity between relative composition of river water and the ocean is explained by **residence time**, average length of time that an ion remains in solution in the ocean.

   a. Ions with long residence times tend to accumulate in the sea, whereas those with short residence times are removed.

   b. Rapid mixing and long residence times explain constant composition of seawater.

L. Addition of salt modifies the properties of water.

1. Pure water freezes at 0^{o}C. Adding salt increasingly lowers the freezing point because salt ions interfere with the formation of the hexagonal structure of ice.
2. Density of water increases as salinity increases.
3. **Vapor pressure** is the pressure exerted by the gaseous phase on the liquid phase of a material. It is proportional to the amount of material in the gaseous phase.
   - Vapor pressure decreases as salinity increases because salt ions reduce the evaporation of water molecules.

5-5. Chemical and Physical Structure of the Oceans

M. Ocean surface temperature strongly correlates with latitude because **insolation**, the amount of sunlight striking Earth's surface, is directly related to latitude.
   1. Ocean **isotherms**, lines of equal temperature, generally trend east-west except where deflected by currents.
      - Ocean currents carry warm water poleward on the western side of ocean basins and cooler water equatorward on the eastern side of the ocean.
   2. Insolation and ocean-surface water temperature vary with the season.
   3. Ocean temperature is highest in the tropics (25^{o}C) and decreases poleward.
   4. Tropical and subtropical oceans are permanently layered with warm, less dense surface water separated from the cold, dense deep water by a **thermocline,** a layer in which water temperature and density change rapidly.
      - Temperate regions have a seasonal thermocline and polar regions have none.

N. Salinity displays a latitudinal relationship related to precipitation and evaporation.
   1. Highest ocean salinity is between 20-30^{o} north and south or the equator.
   2. Low salinity at the equator and poleward of 30^{o} results because evaporation decreases and precipitation increases.
   3. In some places surface water and deep water are separated by a **halocline**, a zone of rapid change in salinity.
   4. **Water stratification** (layering) within the ocean is more pronounced between 40^{o}N and 40^{o}S.

O. Density of seawater is a function of temperature, salinity, and pressure.
   1. Density increases as temperature decreases and salinity increases as pressure increases.
   2. Pressure increases regularly with depth, but temperature and salinity are more variable.
   3. Higher salinity water can rest above lower salinity water if the higher salinity water is sufficiently warm and the lower salinity water sufficiently cold.
   4. **Pycnocline** is a layer within the water column where water density changes rapidly with depth.

P. The water column in the ocean can be divided into the surface layer, pycnocline, and deep layer.
   1. The **surface layer** is about 100m thick, comprises about 2% of the ocean volume, and is the most variable part of the ocean because it is in contact with the atmosphere.
      - The surface layer is less dense because of lower salinity or higher temperature.
   2. The **pycnocline** is transitional between the surface and deep layers and comprises 18% of the ocean basin.
      - In the low latitudes, the pycnocline coincides with the thermocline, but in the mid-latitudes it is the halocline.
   3. The **deep layer** represents 80% of the ocean volume.
      - Water in the deep layer originates at the surface in high latitudes where it cools, becomes dense, sinks (**convects**) to the sea floor and flows outward (**advects**) across the ocean basin.

5-6. Gases in Seawater

Q. The solubility and saturation value for gases in seawater increase as temperature and salinity decrease and as pressure increases.

1. **Solubility** is the ability of something to be dissolved and go into solution.
2. **Saturation value** is the equilibrium amount of gas dissolved in water at an existing temperature, salinity, and pressure.
    a. Water is **undersaturated** when under existing conditions it has the capacity to dissolve more gas. Gas content is below the saturation value.
    b. Water is **saturated** when under existing conditions it contains as much dissolved gas as it can hold in equilibrium. Gas content is at saturation value.
    c. Water is **supersaturated** when under existing conditions it contains more dissolved gas than it can hold in equilibrium. Gas content is above saturation value and excess gas will come out of solution.
3. The surface layer is usually saturated in atmospheric gases because of direct exchange with the atmosphere.
4. Below the surface layer, gas content reflects relative importance of respiration, photosynthesis, decay, and gases released from volcanic vents.

R. Oxygen tends to be abundant in the surface layer and deep layer bottom, but lowest in the pycnocline.

1. Surface layer is rich in oxygen due to photosynthesis and contact with the atmosphere.
2. **Oxygen minimum layer** occurs at about 150 to 1500m below the surface and coincides with the pycnocline.
    a. There is an ample food supply in the pycnocline. The food draws large numbers of organisms that respire, consuming oxygen.

b. Decay of uneaten material consumes additional oxygen.
c. Density difference prevents mixing downward of oxygen-rich water from the surface or upward from the deep layer.
3. The deep layer is rich in oxygen because its water is derived from the cold surface waters that sank (**convect**) to the bottom. Consumption is low because there are fewer organisms and less decay consuming oxygen.
4. **Anoxic** waters contain no oxygen and are inhabited by **anaerobic** organisms (bacteria).

S. Carbon dioxide is of major importance in controlling acidity in the sea water.
1. Major sources of carbon dioxide are respiration and decay.
2. Major sinks are photosynthesis and construction of carbonate shells.
3. Carbon dioxide controls the acidity of sea water.
a. A solution is **acid** if it has excess H^+ (**hydrogen**) ions and is a **base** if it has excess OH^- (**hydroxyl**) ions.
b. **pH** measures how acid or base water is.
- pH of 0 to 7 is acid.
- pH of 7 is neutral.
- pH of 7 to 14 is base.
c. pH is related to the amount of CO_2 dissolved in water because it combines with the water to produce carbonic acid which releases H^+ ions.

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

d. H_2CO_3 is **carbonic acid**, HCO_3^- is the **bicarbonate ion,** and CO_3^{-2} is the **carbonate ion**.
e. Changing the amount of CO_2 shifts the reaction to either the right or left of the equation.
1. Adding CO_2 shifts the reaction to the right and produces more H^+ ions making the water more acid.
2. Removing CO_2 shifts the reaction to the left, combining H^+ ions with carbonate and bicarbonate ions reducing the acidity.
f. Dissolved CO_2 in water acts as a **buffer**, a substance that prevents large shifts in pH.
g. Dissolution of carbonate shells in deep water results because cold water under great pressure has a high saturation value for CO_2 and the additional CO_2 releases more H^+ ions making the water acid.
h. Warm, shallow water is under low pressure, contains less dissolved CO_2 and is less acidic. Carbonate sediments are stable and do not dissolve.

5-7. The Ocean as a Physical System

T. Water is recycled from the ocean to the land and returned to the sea.

1. The reservoirs of water include:
   a. Oceans—cover 60% of the Northern Hemisphere and 80% of the Southern Hemisphere and contain 97% of Earth's water.
   b. Rivers, lakes and glaciers.
   c. **Groundwater —**contains a larger volume of water than all of the water in lakes and rivers.
2. The **hydrologic cycle** describes the exchange of water between ocean, land, and atmosphere.
   a. On land precipitation exceeds evaporation.
   b. In the ocean evaporation exceeds precipitation.
3. The ocean is part of a biogeochemical system in which land undergoes weathering and weathered products are transported to the sea where they may be deposited directly or used by organisms and later deposited as organic remains or organic wastes. Deposits are buried, lithified, and recycled by plate tectonics into new land that is weathered and the cycle repeats.