Introduction to Oceanography

Physical Properties of Pure Water

- **Sea water is a mixture of 96.5% pure water and 3.5% other material, such as salts, dissolved gases, organic substances, and undissolved particles.**

- **Its physical properties are mainly determined by the 96.5% pure water.**

- **The physical properties of pure water will therefore be discussed first.**

Pure water, when compared with fluids of similar composition, displays most uncommon properties.

- **This is the result of the particular structure of the water molecule H2O: The hydrogen atoms carry one positive charge, the oxygen atom two negative charges, but the atom arrangement in the water molecule is such that the charges are not neutralized**

- **(See Figure ; the charges would be neutralized if the angle were 180° rather than 105°).**

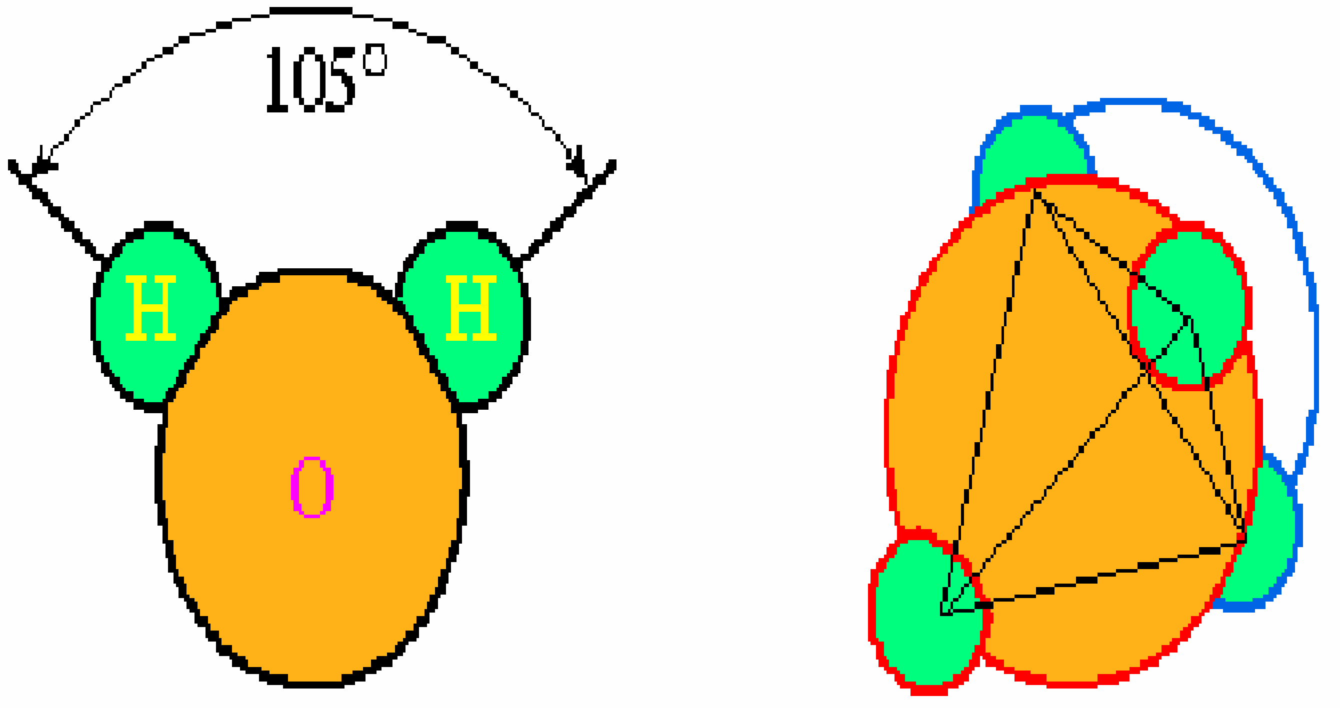


Fig. Left diagram: Arrangement of the oxygen atom (O) and the two hydrogen atoms (H) in the water molecule. The angle between the positively charged hydrogen atoms is 105°, which is very close to the angles in a regular tetrahedron (109° 28'). Right diagram: Interaction of two water molecules in the tetrahedral arrangement of the *hydrogen bond*. The hydrogen atoms of the blue water molecule attach to the red water molecule in such a way that the four hydrogen atoms form a tetrahedron.

The major consequences of the molecular structure of pure water are:

1. The water molecule is **an electric dipole**, forming aggregations of molecules (polymers), of on average 6 molecules at 20°C. Therefore, water reacts slower to changes than individual molecules; for example the **boiling point** is shifted from -80°C to 100°C, the **freezing point** from -110°C to 0°C.

2. Water has an unusually strong **disassociative power**, i.e. it **splits dissolved material** into electrically charged ions (Figure). As a consequence, dissolved material greatly **increases** the **electrical conductivity** of water.

- The **conductivity** of **pure water** is relatively **low**, but that of **sea water** is midway between **pure water** and **copper**.

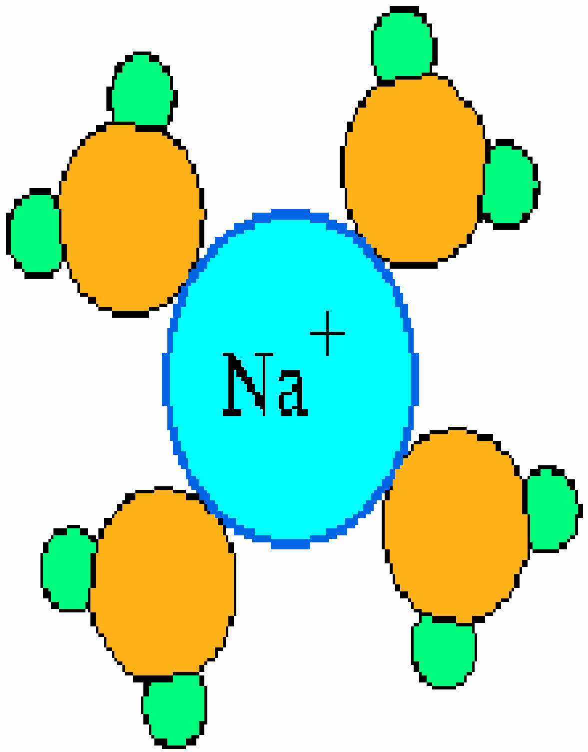
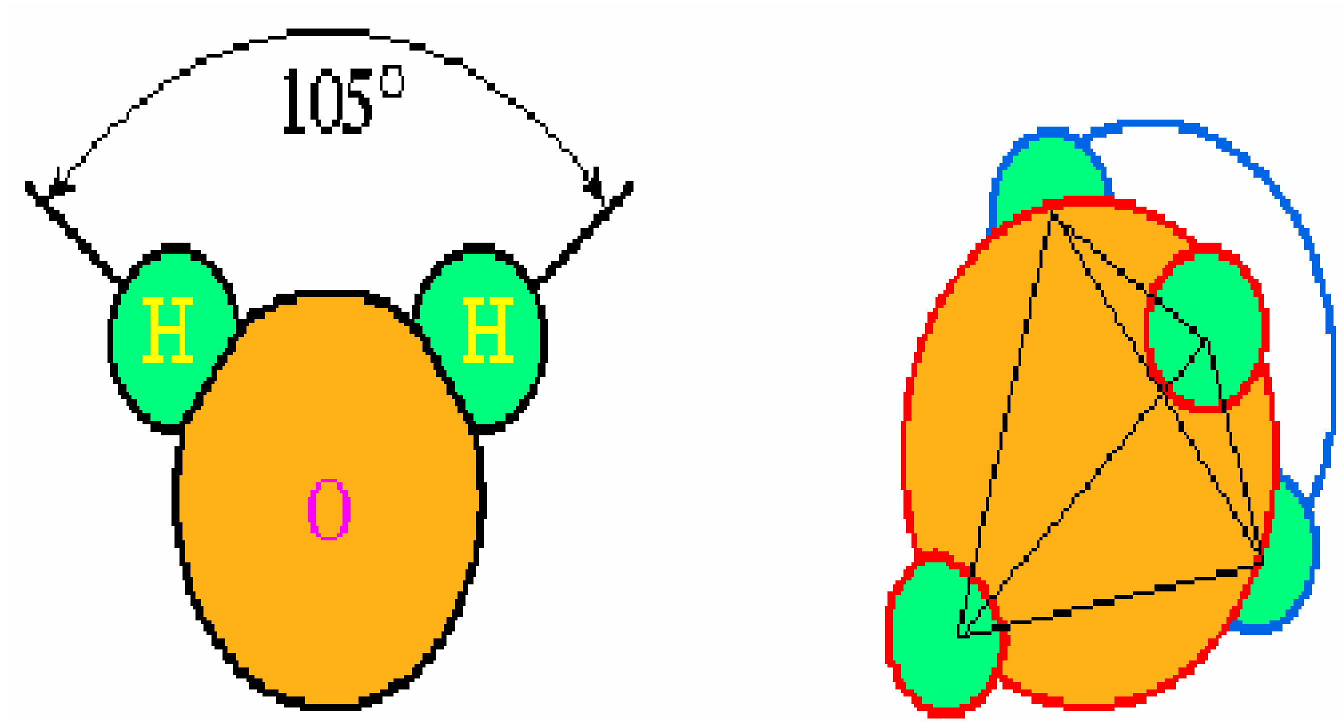


Fig. Sodium chloride Na+Cl- is the main component of salinity in the ocean. The diagram shows how in hydrated form it causes water molecules to attach themselves with the positive hydrogen charges to the chloride and with the negative oxygen charge to the natrium.

3. The angle **105°** is close to the angle of a **tetrahedron**, i.e. a structure with four arms emanating from a centre at equal angles (109° 28′).

- As a result, oxygen atoms in water try to have four hydrogen atoms attached to them in **a tetrahedral arrangement** (Figure). This is called a "**hydrogen bond**", in contrast to the (**ionic**) **molecular** bond and **covalent** bonding. Hydrogen bonds need a bonding **energy 10 to 100 times smaller** than **molecular bonds**, so water is very flexible in its reaction to changing chemical conditions.



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4. Tetrahedrons are of a more wide-meshed nature than the molecular closest packing arrangement. They form **aggregates** of **single**, **two**, **four** and **eight** molecules.

- **At high temperatures** the one and two molecule aggregates dominate.
- **As the temperature falls** the larger clusters begin to dominate .
- The larger clusters occupy less space than the same number of molecules in smaller clusters.
- As a result, the density of water shows a maximum at 4°C.

When freezing, all water molecules form tetrahedrons. This leads to a sudden expansion in volume, i.e. a decrease in density. The solid phase of water is therefore lighter than the liquid phase, which is a rare property.

Some important consequences are:

1. Ice floats. This is important for **life** in **freshwater lakes**, since the ice acts as an **insulator** against further heat loss, preventing the water to freeze from the surface to the bottom.

2. Density shows a rapid decrease as the freezing point is approached. The resulting expansion during freezing is a major cause for the weathering of rocks.

3. The freezing point decreases under pressure. As a consequence, melting occurs at the base of glaciers, which facilitates glacier flow.

4. Hydrogen bonds give way under pressure, i.e. ice under pressure becomes plastic. As a consequence, the inland ice of the Antarctic and the Arctic flows, shedding icebergs at the outer rims. **Without this process all water would eventually end up as ice in the polar regions.**

The anomalous properties of water:

Water has many unusual properties that indicate **strong intermolecular associations**. The structure of the H_2O molecule and the hydrogen bonding of water explain many of these unique physical properties.

1-high heat capacity

- Heat Capacity **(Cp)** is the thermal energy it takes to raise 1 gm of a substance by 1° C.
- Water has the **highest heat capacity** of all solids and liquids except liquid NH_3.
- This is because it takes **a lot of energy** to break the hydrogen bonds and change the structure of water.
- Thus water has a large thermal buffer capacity and acts as **a climate buffer.**

2- high heat of evaporation

- Mammals cool by **sweating**! - it takes energy (.H = 540 calg-1) to break the hydrogen bonds.
- Water has the **highest heat of** evaporation of all liquids.

3-high boiling point

- The boiling points and freezing points of most substances are **decreasing** with **decreasing molecular weight** except **water** .
- The expected **B.P**. of H2O should be **68°** C while the real value is **100 C**.

4-high freezing point

- It is easier to **freeze** water than **convert** it to **a gas**.
- The freezing point of 0° C is **anomously high**. The expected F.P. , based on the other elements of its group in the Periodic Table, is **-90°** C.
- Water exists in 3 phases within the critical temperature range that accommodates life.

5-low heat of freezing

- The water structure can **move easily** to the **ice** structure.
- The heat of freezing is only **1/7** that of **evaporation** implying that there is a relative **small difference** in the number of **bonds** between **water** and **ice**.

6-high surface tension

- Water likes itself relative to most other surfaces and because of this water **tends** to **minimize** its **surface area**. When air bubbles break at the **sea surface** the **high surface tension causes** the surrounding water to **snap back** into the **depression** left by the bubble resulting in injection of a small droplet of surface seawater into the atmosphere (**Fig.**). The water soon evaporates leaving a small aerosol of sea salt. This is the mechanism by which **sea salt** is **transferred from** the **ocean** to **land**.

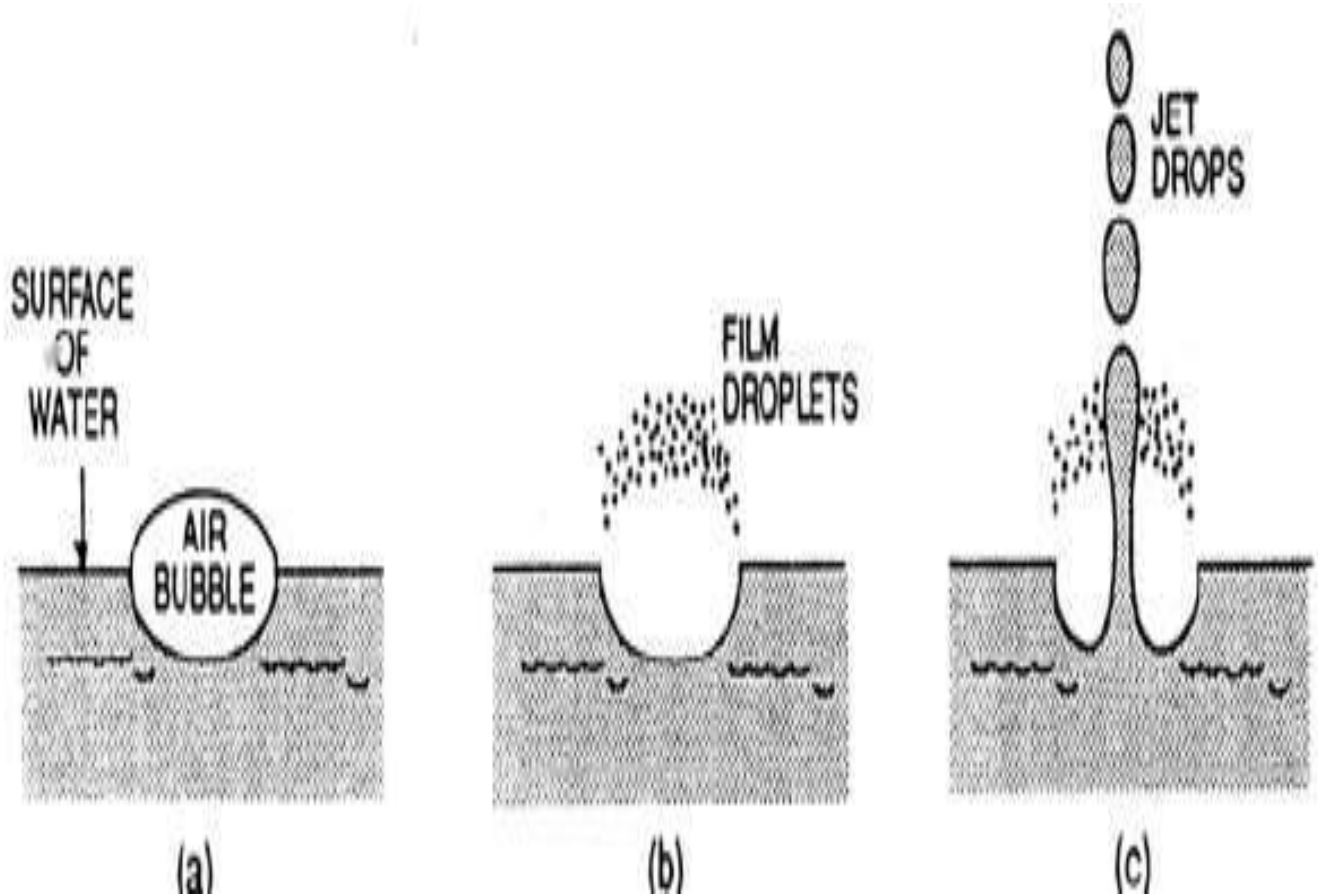

Fig. Aerosol formation after an air bubble comes to the sea surface

7-high dielectric constant

Water has the **highest dielectric constant** of all substances except H_2O_2 and HCN.

Water has a **high dissolving power** because the water molecules **reduce** the **forces** of **attraction** between **ions**.

- **The high heat capacity and heats of fusion and evaporation provide huge thermo- stating capacity in the critical temperature range that accommodates most life (-50 to 100 ° C).**

- It takes **766 calories** to raise the temperature of **1 gram** of water from **-50° C** (as ice) to **+150 °** C (as steam). The same number of calories would elevate the temperature of **10 grams** of granite to **383 ° C.**

❖ The Effect of Adding Salt To pure Water:

- Water is called the **universal solvent** because of its ability to dissolve many substances. Water is a particularly good solvent for substances held together by **polar** or **ionic bonds**. Indeed, the most abundant substances dissolved in seawater are ionic solids (salts such as sodium chloride). When we add salt to pure water to make seawater, what happens?

1-The density is increased:

- Any substance dissolved in a liquid has the effect of **increasing** the **density** of that **liquid**.
- The greater the amount of solute, the greater the effect.

2- The freezing point is depressed:

- This is why salt is spread on frozen roads.
- Salts also **lower the temperature** at which water reaches its maximum density.
- That is because **dissolved salts inhibit the tendency of water molecules** to form direct bonds with other water molecules.

3- The boiling point is elevated:

- The salts have the effect of making the water molecules cluster and become more ordered, thus harder to pull apart and evaporate.

4- The conductivity is increased:

If an electromagnetic field is applied to seawater, the ions will migrate, producing an electric current.

• Conductivity

- Conductivity is an important property of seawater.

- Conductivity **increases** almost **linearly** with **temperature** and **slightly less linearly** with **concentration**.
- It is one measurement commonly used to determine the **salinity** of **seawater** (Cox *et al*., 1967). In addition, it provides insight into **solvent structure**.
- The **electrical mobility** of an ion in solution is related to the **ionic conductivity**.

• Viscosity

- Viscosity is defined as the **internal fluid friction** or the **forces** of **drag** which its **molecular** and **ionic constituents** exert on one another. We expect that the ease with which water molecules can move about should be strongly dependent on the extent to which they are bound (i.e., on the amount of structure present).

- The **effect** of **ions** on the **viscosity** gives us **clues** regarding the **effect** of the **ions** on the **structure**.

- For most liquids, the **viscosity** normally **increases** with **pressure** as the **molecules get compressed**.

- Pure water is clearly anomalous because the viscosity goes through a **minimum** with **increasing pressure**. With **small increase** in **pressure**, water **molecules** move about more **easily**.

- The initial decrease in **viscosity** is a result of the **breaking down** of the "**structured**" **cluster units**.

- Once the structures are **broken down**, **compression increases** the relative **viscosity** as found for normal liquids.

❖ **The viscosity of pure water and seawater also decreases with increasing temperature.**

- The effect of increasing temperature is to decrease cluster size and this parallels the viscosity of pure water and seawater.

- seawater has a higher viscosity at all temperatures, suggesting that the salts in seawater have a net effect of enhancing the structure of water. Thus, **temperature and ions** have an opposite effect