

# WATER AND ITS PROPERTIES: AN UNUSUAL MOLECULE



Fill a glass with 18 cm<sup>3</sup> water, and divide it in two parts. Keep splitting it and 18 times later you will get a water droplet. After 79 operations a single water molecule would be obtained.

*Tip for the calculation*: Avogadro number (number of molecules per mol) is approximately  $2^79$ . Molecular weight of water = 18 gr/mol.



Internal energy is approximately 500 kJ per mol. This is high as compared to other molecules.

 $1pm = 10^{-12} m$ ; 1 A (Angstrom)= $10^{-10} m$ . Then 96 pm is approximately one Anstrong.

Objective: make sure that you remember what bond energies mean. Why the energy bonding the oxygen and hydrogen atoms of one single water molecule is the same as the energy contained in half a litre of semi-skimmed milk?



Due to electronegativity differences between oxygen and hydrogen, there is a different charge density in the oxygen and hydrogen atoms, so that the water molecule is a dipole.

The dipolar character of the water molecule explains many of its macroscopic features.



One consequence of the uneven distribution of charge (O vs. H) water molecules are oriented following quadrupolar interactions, known as hydrogen bonds.

Water hydrogen bonds are high when compared to other intermolecular interactions, but even so, they are approximately 50 times smaller than intramolecular water bonds.



Water can be found in three aggregation states solid, liquid and gas.

Note that the fact that water fusion and evaporation temperatures at a 1 atmosphere pressure are so exactly zero and one hundred degrees is not a coincidence: water is the reference substance to define the 0 and 100 marks of the Celsius scale.



Water density presents an anomalous behaviour because at temperatures close to freezing it increases with temperature, as opposed to the behaviour of most substances, whose density decreases when temperature increases. In fact this behaviour only occurs in a short temperature interval.

This is caused by the hydrogen bonds. When ice is liquefied, water molecules increase their mobility (going from a fluid to a rigid phase), thus allowing dipoles to be reoriented and therefore the number of hydrogen-bond interactions increases. This produces a higher molecular packing density, thus decreasing the volume and increasing density. If we keep increasing the kinetic energy of the molecules (increasing the temperature), the dipole-dipole interaction energy can be reached (Temp > 4 °C) and then the cohesion energy among them decreases, the distance increases and volume decreases, which is the conventional behaviour at other temperature ranges and for most substances.

Note: the 1 kg/L value of density is also exact, because water was used as a weight standard in the International System (IS)



Surface tension decreases when temperature increases.

Contact angles depend on differences between liquid-liquid versus liquid-surface interactions. The surface tension changes when salts are dissolved in a liquid, and therefore related effects like contact angles and wetting change as well.



The solubility of most salts increases with water temperature, but there are important exceptions, like calcium carbonate which is responsible of incrustations, typical of heating systems.

The solubility of gases decreases when the temperature increases, as can be seen in the graph above.

The behaviour of water as a good solvent influences the transport of pollution and the design and operation of water treatment systems.



Heat capacity: the amount of heat that is needed to increase one degree centigrade (from 13,5 to 14,5  $^{\circ}$ C) the temperature of 1 gr.

The heat capacity of water, 1 calorie per gram, is among the highest of all natural solvents, and is responsible of its special thermal properties. For instance climatic regulation of the sea. Temperature fluctuations in areas close to large water volumes (i.e. coastal areas) are smaller than inland, due to the fact that for the same received radiation the sea temperature has a smaller increase.



# Heat of Vaporization = 0,54 kcal·g<sup>-1</sup>





# TRANSPARENCY





If we observe earth from space, it looks as a sphere mainly covered by water (71%). This implies that the total volume of water, 1387 million  $\text{km}^3$ , would form a thin layer of approximately 2,7 km thickness (0,04 % of the terrestrial radius), if it was evenly distributed.

Universidad Carlos III de Madrid www.uc3m.es	Earth dis	stribu	ition
•]	Rivers:	0,0001%	1387 km <sup>3</sup>
a	Atmospheric humidity :	0,001%	13870 km <sup>3</sup>
	Lakes:	0,016%	222·10 <sup>3</sup> km <sup>3</sup>
	Groundwater:	0,61%	8,46·10 <sup>6</sup> km <sup>3</sup>
	Glaciers and polar caps :	2,24%	31,1·10 <sup>6</sup> km <sup>3</sup>
	Oceans:	97,1%	1346,8·10 <sup>6</sup> km <sup>3</sup>

•Water from rivers, one millionth of total water.

•Atmospheric humidity is 10 times higher.

•Water contained in lakes is 16 times higher than in the atmosphere.

•Groundwater amounts 6 in one thousand of the total water.

•Ice (polar caps, glaciers, etc.) in a significantly higher quantity, a 2,3 %, nearly four times more than in soil.

•But when oceans and seas are taken into account, we see that almost all of it can be found there (97,1%).

*Conclusion*: available fresh water (even with reservoirs), so important for life on the planet, represents a tiny fraction of the total water mass.

Translation:

- •Groundwater: aguas subterráneas
- •Fresh water: agua dulce
- \* Polar caps: casquetes polares



Water does not stay in a place or state, it moves around the globe. This movement is called "hydrological cycle".

Translation of some technical words :

Runoff: escorrentía. Water flows on land surfaces.

Infiltration: water is transferred to groundwater.

Meteors: water from the atmosphere is deposited on the land or on the sea.

Outcrop: *afloramiento*. Water from groundwater is transferred to earth surfaces.



The figure presents the estimated (average) time that water stays in different media.

Averages may change greatly with geological and climatic conditions. For instance, in tropical regions, the cycle can be closed in hours while in arid areas like polar caps and deserts, the cycle can last for a hundred thousands years.



The global balance of water for the hydrological cycle is as follows:

•1.347 millions km<sup>3</sup> water are concentrated in seas and oceans,

•13.800 km<sup>3</sup> in the atmosphere,

•In solid state, as snow and ice, 31 millions km<sup>3</sup>,

•223.000 km<sup>3</sup> in lakes and rivers and

•8,5 millions km<sup>3</sup> in the underground as GROUNDWATER.

This is approximately the amount of water that stays in each situation as an average. There is a continuous transfer from one medium into another:

•430.000  $\text{km}^3$  water are evaporated per year from the seas, and

•70.000  $\text{km}^3$  are evaporated from the land surface and due to evapotranspiration of living beings.

The  $\frac{1}{2}$  million total water evaporated per year is compensated by an equal amount of water going back to the surface, both to the oceans (390.000 km<sup>3</sup>) and to the dry land (110.000 km<sup>3</sup>) through rainfall.

Mass balance between input (precipitation) and output (evaporation) of each subsystem yields a  $40.000 \text{ km}^3$  water deficit in the ocean /atmosphere system, that corresponds to the net water transfer from dry land to the oceans, called runoff. This also allows the existence of rivers and water flows.



The "hydrological cycle" also transports substances other than water.

This is enhanced by the fact that water is a very good solvent, so many salts are dissolved. Salts can then reach the oceans and become involved in the carbon cycle.

Note: the hydrological cycle is closely related to the carbon cycle and the nitrogen cycle (not studied in this course).



Pollution can be classified according to different criteria: the source of pollution, the medium in which it occurs, etc.



**Natural pollution:** Water dissolves gases present in the atmosphere ( $CO_2$ ,  $O_2$ ,  $N_2$ , etc.), soil salts by lixiviation ( $Na^+$ ,  $Ca^{2+}$ ,  $HCO_3^-$ ,  $Cl^-$  etc.), compounds coming from living beings and their degradation (urea, humic acids, etc.) and drags suspended solids (soil particles, microorganisms, etc.). In some cases, the concentration of these substances is so high that water cannot be used (brine water, large avenues, swamps, ...).

**Antropic pollution:** Water whose properties have been modified by the action of man. Generally the term "polluted water" is reserved to this type of pollution.

Swamp: pantanoso



### b) Activity causing pollution

•Industrial production (20%):

Raw materials, intermediate products, heat transfer, cooling

•Discharge of municipal and domestic wastewater (10%): Food, faecal, cleaning wastes...

•Farming and fishing activities (70%):

Pesticides, herbicides, industrial waste, farming wastes (load may be low, but higher number of substances)

#### **ACTIVITY CAUSING POLLUTION.**

**Industrial products:** Consume around 20% of the total water used by men, with an estimated 2% of water used in the industry allocated to the products, and 98 % released back to the environment as liquid water or steam. In most cases this water is discharged after modifying to a large or small extent its characteristics. Pollutant content is characteristic of each industrial activity and may originate both from the raw material used and from the transformation and finishing products or from the heat transfer and cooling operations performed along the process.

**Domestic and municipal wastewater discharges:** Represent a 10% of the world water consumption. This water contains substances coming from human activity wastes (food, excrements, domestic and urban cleaning , etc.) of an organic, inorganic and microbial nature. More that 3.000 wastewater treatment plants operate in Spain, with around 200 under construction...

**Farming and agricultural activities:** approximately 70% of the world fresh water consumption corresponds to farming and agriculture. Though its pollutant load is low, that amount of different substances emitted to the environment is the highest absolute value. It usually consists in pesticides, herbicides, fertilizers, faecal and liquid excretions and industrial waste.



## c) Geographical origin

- Point sources. Eg: localized industrial discharges
- Non-point sources. Eg.: fertilizers or herbicides

## d) Type of effluent flow

• White or rainwater (high volume but low load after 15 min): Atmospheric pollution, Human activity waste, Traffic waste, Vegetal waste, Leaks

#### • Domestic wastewater:

Discharge to municipal sanitary system: households, commercial and large facilities (hospitals...), Cleaning, Faecal (black waters)

• Industrial wastewater

• Black or urban water (quantified per equivalent population)

#### **GEOGRAPHICAL ORIGIN.**

Knowing the location where pollution is produced is not always easy, but nonetheless it is sometimes important to find the source. For instance, think in pollution found in a river. Note that usually non-point sources are more difficult to locate.

#### TYPE OF EFFLUENT.

The origin of the wastewater flow defines some of the most of the important features that have to be taken into account when designing a treatment plant, both in terms of composition and in terms of flow oscillations. For instance domestic wastewater flows follow a 24 hour cycle, while industrial wastewater may change in holyday periods.



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# Water quality parameters

Physical-chemical parameters	
– Solids	Temperature
<ul> <li>Color, odor and taste</li> </ul>	Dissolved Oxygen
– Biochemical Oxygen Demand	Chemical Oxygen Demand
– Total Organic Carbon	Oxidability
– Oil and grease	Phenols
– Acidity	Alkalinity
– Conductivity	Hardness
– Chloride (Cl <sup>-</sup> ), chlorine (Cl <sub>2</sub> ), hypochlorite (ClO <sup>-</sup> )	
– Sulfurs (S <sup>=</sup> ), sulfites (SO <sub>3</sub> <sup>=</sup> ), sulfates (SO <sub>4</sub> <sup>=</sup> )	
- Ammonium ( $NH_3$ ), nitrites ( $NO_2^{-}$ ) and nitrates ( $NO_3^{-}$ )	
– Total phosphorus	Heavy metal ions
– Toxicity	Detergents
Radiological parameters	
General Parameters	





# **IMHOFF TEST**

To determine settleable solids in wastewater: Solids that accumulate in the bottom of the cone after 60 min, reported in mL/L.

• Settleable solids cause turbidity:

-Drinking water: colloidal particles with pathogens

- Nature: influence of penetration of light for fauna and flora



Imhoff cone used to determine settleable solids in wastewater. Solids that accumulate in the bottom of the cone (1 L) after 60 min are reported as mL/L.

Standard: UNE 77032:1982

Settleable: sedimentables



Turbidity: a measure of the light-transmitting properties of water, a test used to indicate the quality of water discharges with respect to colloidal and residual suspended matter.

Settleable solids are responsible of water turbidity due to the scattering of the light that goes through water. Turbidity is quantified, following the standard, semi-quantitatively by observation of the depth at which a label is not visible any more, or quantitatively by using optical turbidimeters. The unit is called Formacine Nephelometric Unit (FNU).

Turbidity is an important parameter of fresh water quality, because small colloidal particles can carry pathogenic microorganisms. In rivers or lakes turbidity decreases light transmission and alters subaquatic flora and fauna.

Standard: UNE-EN 27027:1995



Water temperature is very important for the development of many processes. Water temperature increases modify the solubility<sup>[1]</sup> of substances, increase the solubility of dissolved solids, decrease gas solubility, and double (approximately) biological activity every 10 degrees ( $Q_{10}$  law), though above a given value characteristic of each species, any increase would cause lethal effects to the organisms.

An abnormal increase (not due to climatic causes) of water temperature usually has an origin in discharges of water used in industrial heat exchange processes.

Temperature is measured by "in situ" thermometry.

According to the present legislation discharge temperatures should not exceed 40°C, and the river average temperature increase downstream cannot cause an average temperature increase higher than 1,5 or 3 °C in river beds where salmon type and carp type fishes live (respectively).

*Solubility*: maximum amount of a substance that can be dissolved in a given solvent volume at a set temperature.



Subjective tests, of importance in domestic consumption waters
• COLOUR:

Apparent (raw water), true (without suspended solids). Measure within 24 hours from sampling: scattered daylight, on a white background, successive dilution or visible spectroscopy

Perception threshold 1/40, 1/20

• ODOUR:

Organic (VOCs) and inorganic substances (H2S, NH3) Industrial waters, treated waters, etc.

#### • TASTE:

- Highly related to odor
- Only for sanitary waters approved for human consumption

Organoleptic properties are detected with senses. No precise measure of the pollution level is provided with these properties, butt their existence points to the fact that water treatment is not working properly.

They are very important in water for consumption because consumers may refuse water with colours, smells or taste not (subjectively again) "associated" with "pure" water. Sometimes this is.

**Colour.** Colour can provide some clues on what type of pollution water has. Typical colours are: •greyish brown: degradation of organic matter

•green (phytoplankton and chlorophyll)

•other colours (inorganic ions and organic dyes).

No direct relation exists between colour and pollution degree, as interferences among coloured substances may take place. Many coloured substances are degraded after some time, so colour has to be measured within 24 hours after sampling, and samples must be kept in a cool (2-5 °C), dark place. Colour is measured visually with the UNE-EN ISO 7887:1995 standard or with a visible un spectrophotometer.

**Odour:** Generally odours are produced by volatile organic compounds (VOCs) or by inorganic gases (H<sub>2</sub>S, NH<sub>3</sub>, etc.), and are usually due to degrading organic matter or to chemical products (phenols, chlorine and their derivates, etc.) produced or used in the industry, besides wastewater treatment water. Odour is measured by diluting (Temp  $\approx$  40 °C) until the perception threshold is reached. Samples must be kept in glass containers a maximum of 6 h at 2-5 °C.

**Taste:** Some compounds, like cooper, zinc or iron salts, may modify the taste without changing the effluent colour.



DO is measured by electrometric or iodometric methods, the units are mg/L (i.e. mg of oxygen dissolved in 1 litre of water).

Some care has to be taken so that no oxygen is dissolved from the air after the sample is taken, that it does not react with whatever substances are present in the sample or that no oxygen is consumed by microorganisms in the sample. This can be achieved by measuring "in situ" or by "fixing" it, sealing the samples in dark, glass containers for less than 4 days.

Note: Maximum DO value is a parameter that changes with water temperature and decreases with temperature decreases. Maximum DO concentration within the normal temperature range is approximately 9 mg/L. When oxygen concentration drops below, water cannot be considered suitable for life.



## BIOCHEMICAL OXYGEN DEMAND (BOD)

Measures the pollutant load due to biochemically degradable substances by analysing the oxygen consumed by aerobic bacteria





## CHEMICAL OXYGEN DEMAND (COD)

#### Measures the pollutant load due to all substances capable of being oxidized (organic or inorganic)

•Determined by treating in strong oxidation conditions: dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) and reflux •Method faster than BOD<sub>5</sub>

•Analyzes all organic substances that can be oxidized. (Includes Bio-refractory and toxic).

# 0,2< BOD<sub>5</sub>/COD < 0,5 Not biodegradable COD (urban wastewater): 150-800 mg/l



# TOTAL ORGANIC CARBON (TOC)

- Instrumental method
  - Combustion with CO2 atr 900°C
  - Ultraviolet oxidation with persulphate
- Fast
- Difference  $C_{\text{organic}}$ ,  $C_{\text{inorganic}}$ ,  $CO_2$
- Not allowed by present legislation.
- Expensive.







#### HARDNESS AND CONDUCTIVITY

· Related to the water capacity to form insoluble salts (incrustations) => \_ Measured by titration · lons causing hardness (carbonates and hydroxides): Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SiO<sub>3</sub><sup>2-</sup>. 0-75 mg/l soft 75-150 mg/l moderately hard 150-300 mg/l hard > 300 mg/l very hard CONDUCTIVITY Ability of water to conduct electrical current. Max. authorised value: 5000 μS·cm<sup>-1</sup>

Pure water Λo = 0,5-2 µS·cm<sup>-1</sup>

Aerated pure water  $\Lambda o = 2.4 \ \mu S \ cm^{-1}$ Measures concentration of dissolved solids DS (mg/L) =  $\mathbf{k} \cdot \Lambda \mathbf{0} \ (\mu \mathbf{S} \cdot \mathbf{cm}^{-1})$ k = 0,55-0,8

#### SALINITY

• soluble inorganic salt content

**Conductivity (Ao):** ability of water to conduct electrical current. Standard yields microsiemens- cm<sup>-1</sup> ( $\mu$ S cm<sup>-1</sup>) (UNE EN 27888-1993). Indirectly it measures the amount of dissolved solids (though it also depends on the specific ions present in the sample). The following empirical formula can be used to estimate the amount of dissolved solids (DS):

#### DS (mg/L) = $0.8 \cdot \Lambda o (\mu S \text{ cm}^{-1})$

According to the present legislation, the maximum punctual (i.e. not time averaged) allowed value in a discharge is  $5000\mu$ S cm<sup>-1</sup>.

Samples must be preserved in polyethylene containers (not sodium glass), in a cool (2-4 °C), dark place and must be measure before 24 h, though an "in situ" measure is recommended. Heating to 25 °C is required before measuring.

**Hardness:** A measure of the ionic content of water, referred to the total concentration of ions calcium, magnesium, strontium and barium ions (mainly due to the first two ones). The presence of these ions has usually a natural origin. Measured according to (UNE 77040-1983), the results are given in equivalent Ca2+ mg/l.

Hard water problems are due to the formation of carbonate and hydroxides precipitates that are insoluble and when deposited on pipes and equipment may caused working problems in heating and cooling towers, heat exchangers, filters, etc.



#### Chloride (Cl<sup>-</sup>), chlorine (Cl<sub>2</sub>) and hypochlorite (ClO<sup>-</sup>):

Chlorides are measured by titration or with potentiometer (UNE 77041-1983 and UNE 77042-1983). Free and combined chlorine is quantified with an spectrophotometer (UNE 77064-1990).

**Total phosphorous:** Phosphorous and nitrogen are two of the main nutrients of all living beings, so that abnormally high contents in water may cause an uncontrolled growth of the aquatic biomass (eutrophication). Measuring is accomplished with an spectrophotometer (UNE 77047-1983 and UNE EN 1189-1997), but a previous digestion of the polyphosphates (found in detergents) into phosphates is required. Polyphosphates are analysed later.



# NITROGEN AND DETERGENTS

AMMONIUM (NH<sub>4</sub><sup>+</sup>), NITRITES (NO<sub>2</sub><sup>-</sup>), NITRATES (NO<sub>3</sub><sup>-</sup>) AND N<sub>organic</sub>:



Kjeldhal's method is an analytical method for determination of nitrogen in certain organic compounds.

Ammonium  $(NH_3)$ , nitrites  $(NO_2)$  and nitrates  $(NO_3)$ : Ammonium is not an ion and is found in water as ammoniac  $(NH_4^+)$ , but is linked to the evolution of nitrites and nitrates. Ammoniac is an intermediate compound produced in the biodegradation of nitrogenated organic compounds (aminoacids, proteins, nucleic acids, etc.). Together with organic nitrogen is an indicator of water flows that have suffered a recent pollution. Both are measured n a single step (Kjeldhal method UNE 77028-1983 and UNE EN 25663-1994). Aerobic oxidation of ammoniac and nitrogenated organic compounds leads to the formation of nitrites which later become nitrates, so that a high content of nitrates together with a low ammonium content proves that water has been polluted time ago.

Ammonium, nitrites and nitrates can be measured by adsorption spectrophotometry (UNE 77027-1982, UNE EN 26777-1994 and UNE EN ISO 13395-1997) or using the ion selective electrode method.

Detergents: Usually anionic, but also cationic or neutral exist. (UNE EN 903-1994).





- Most harmful pollutants.
- Industrial discharge
- Interfere with treatment processes (alter biodegradation processes )
- Essential to life (Fe, ...), high toxicity (Cd, Cr, Hg, Pb, etc.)

	Maximum concentration	
Metal	to water drinking treat. (mg/L)	Observations
Cd	0,005	Highly toxic. Originated in the electrolytic metallization industry
Hg	0,001	Highly toxic. Chlorine-hydroxide industry, catalysers, paints.
Pb	0,01	Toxic. Metallurgy wastes, pipe corrosion
Cu	0,05	Toxic. Mining, metallurgy, corrosion of pipes and heaters.
Cr (VI)	0,05	Highly toxic. Electrolytic metal industry, stainless steel, leather industries.
As	0,05	Highly toxic. Mining, sanitary products, combustion cinders.

#### Heavy metal ions:

Their presence in water generally indicated an industrial discharge. Due to their large toxicity and to the fact that they interfere with wastewater treatment process (altering biodegradation) it is necessary to remove them before biodegradation treatments.



# TOXICITY

Synergies with other substances • Biodiversity studies.



•Eg. Ensayo de toxicidad aguda en dafnias (UNE-EN ISO 6341:1996). Determination of the inhibition of the Daphnia Magna Strauss mobility (OECD Guideline 202 and CEE 84/449)



# RADIOLOGICAL PARAMETERS





# BIOLOGICAL PARAMETERS

Based in the presence of species related to the contamination level (indicator organisms).

•Easy to isolate and grow in a laboratory.

Relatively innocuous for humans and animals.
Relates qualitative and quantitatively with other pathogens

**Analytical methods:** 

•Dilution in tubes

•Membrane filtration

ntitatively with other E.Coli Coliformes

Presence of coliform does not imply the existence of pathogenic, only indicates probability.

