Introduction

Prof. Dr. Chiara Valsecchi

Course Goals

- Characterize Water quality
- Calculate solute presence at equilibrium
- Use thermodynamics to understand equilibria and if the reaction is favorable
- Understand reaction kinetics
- Describe air and water pollution
- Characterize atmosphere and its stability

Calendar

	hours	Date
Water properties and measurements	2	08/03
Reaction Equilibrium	4	15-22/03
Reaction Kinetics	2	29/03
MIDTERM 40%	2	**12/04**
Reaction Energetics	2	19/04
Redox reaction	2	26/04
Atmosphere stability and air pollution	2	10/05
FINAL 40%		**24/05**

Assignment 20%

Contacts

I am available to answer quick questions and doubts anytime.

Contact me to reserve a time if you require more time

Office: Room 4512B

Water

Class Goals

- Review on measurements
- Water composition and distribution
- Water properties
- Concepts of water pollution

Concentration Units

Describe presence of particulate/solute in a solution, independent of its phase

1. **Percentages:**
   - wt/wt % = mass of solute / mass of solvent
   - wt/v % = mass of solute / volume of solvent (100 mL)

2. **Molarity:** moles of solute / Volume of solvent (in L)

Exercise: the concentration of Na^+ in water is 1.06 %
What is its molarity ?

Concentration Units

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What is its molarity ?

1. Calculate the total grams of Na^+ in the solution:

$$1.06\% = \frac{1.06 \text{ g } Na^+}{100 \text{ mL}}$$

Concentration Units

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What is its molarity ?

1. Calculate the total grams of Na^+ in the solution:

$$1.06\% = \frac{1.06 \text{ g } Na^+}{100 \text{ mL}} \longrightarrow \quad 10.6 \text{ g in } 1 \text{ L}$$

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2. Calculate the number of moles of Na^+ :

Concentration Units

<u>Exercise</u>: the concentration of Na^+ in water is 1.06 wt/v %
What is its molarity ?

1. Calculate the total grams of Na^+ in the solution:

$$1.06\% = \frac{1.06\ g\ Na^+}{100\ mL} \longrightarrow 10.6\ g\ \text{in}\ 1\ L$$

2. Calculate the number of moles of Na^+ :

$$\text{Moles } Na^+ = \frac{10.6\ g}{23.0\ g/mol} = 0.46\ \text{mole}$$

3. Calculate Molarity: 0.46 M

Concentration Units

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3. **ppm:** 1 part of solute in 1 million part of solvent. Diluted solutions

$$1\ \text{ppm} = \frac{1\ \text{g of solute}}{1\ \text{million g of water}} \xrightarrow{\text{Water density}} 1\ \text{ppm} = \frac{1\ \text{mg}}{1\ \text{L}}$$

<u>CAREFUL</u> ! We assume here water density of 1.00 g/mL

But sea water density is 1.025 g/mL !

Sometimes is better to just keep ppm as mg/Kg

Concentration Units

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4. **ppb:** 1 part of solute in 1 Billion part of solvent. Very diluted solutions

$$1\ \text{ppb} = \frac{1\ \mu\text{g}}{1\ \text{L}}$$

Concentration Units

ppb: 1 part of solute in 1 Billion part of solvent. Very diluted solutions

$$1 \text{ ppb} = \frac{1\,\mu\text{g}}{1\text{ L}}$$

Exercise: Pb

The U.S. EPA set a limit for the concentration of lead in drinking water at 15 ppb. A laboratory finds the concentration of lead in a sample taken from a water fountain to be 18 μg/100 mL. Is this above or below the EPA limit? By how much?

Concentration Units

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1. Grams of lead in 1L: 18µg x 10 = 180 µg

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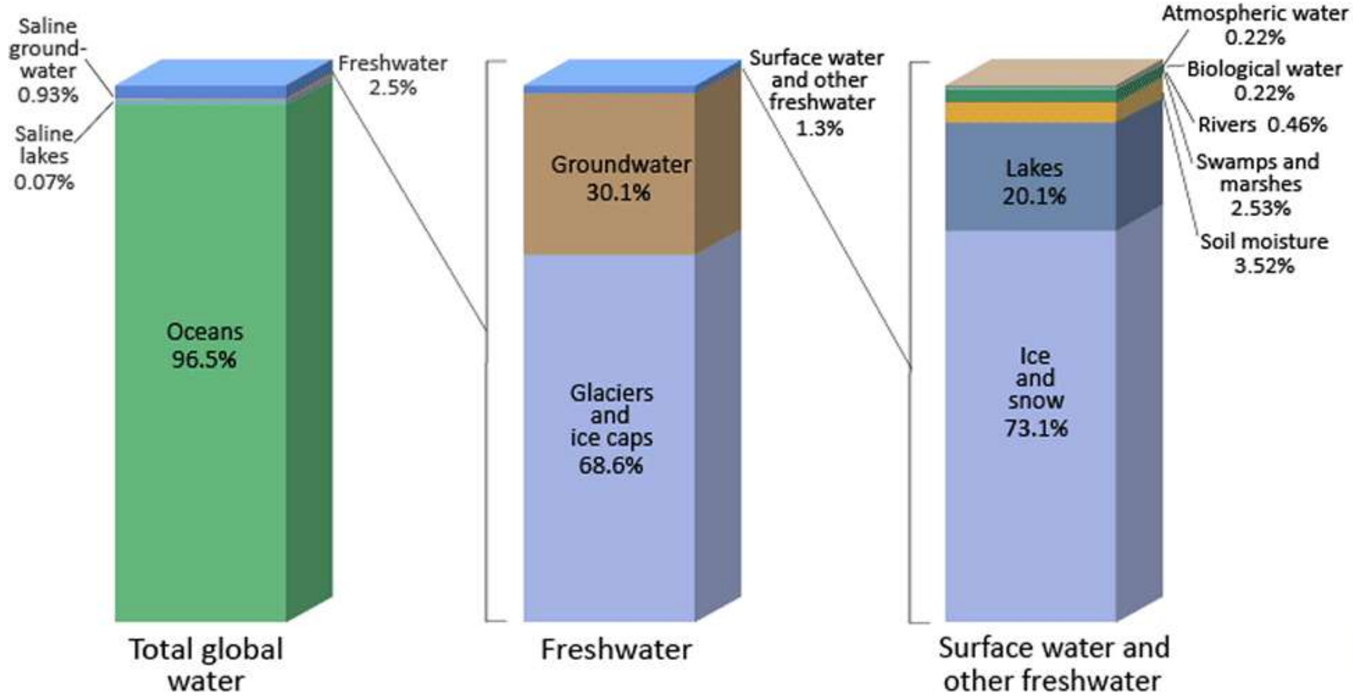
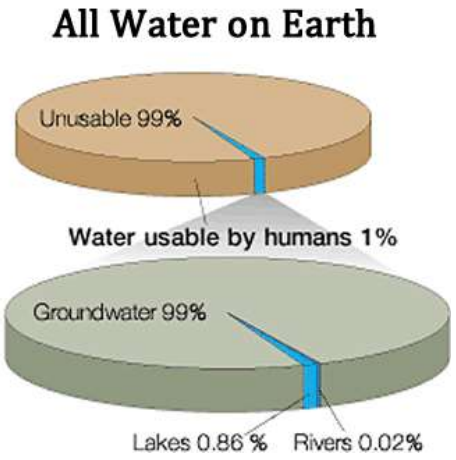
1. Grams of lead in 1L: 18µg x 10 = 180 µg
2. Express in ppb: 180 ppb
3. Answer: yes, the amount of lead exceed the limit by 165 ppb

Water Distribution





Less than **0.01 %** of Earth's total water is **drinking water** !

Water Composition

Fresh water: water body with less than 1,000 ppm of dissolved solid

Drinking Water: less than 450 ppm of dissolved solid (China), 500 ppm (USA), 300 ppm (WHO)

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Major ion content (% of the total)

Ion	Freshwater	Seawater
HCO_3^-	41.0	0.2
Ca^{2+}	16.0	0.9
Mg^{2+}	14.0	4.9
Na^+	11.0	41.0
Cl^-	8.5	49.0

Major Constituents of Seawater

Ion	Concentration (ppm)
Chloride, Cl^-	19,000
Sodium, Na^+	10,600
Sulfate, SO_4^{2-}	2,600
Magnesium, Mg^{2+}	1,300
Calcium, Ca^{2+}	400
Potassium, K^+	380
Bicarbonate, HCO_3^-	140
Bromide, Br^-	65
Other substances	34
Total	34,519

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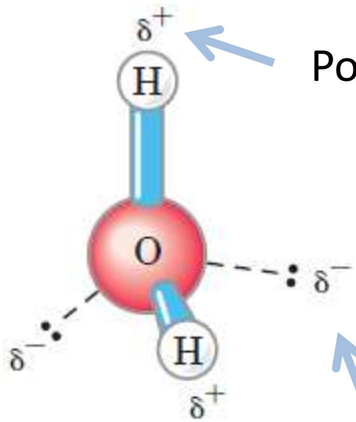
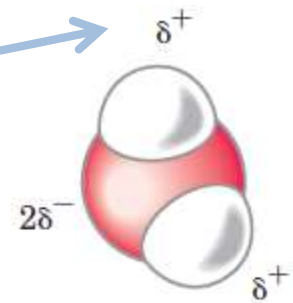
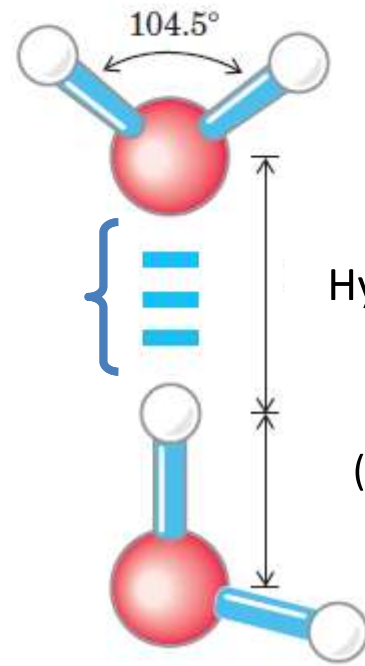
Water Properties p.1



Positive parcial charges

Negative parcial charges

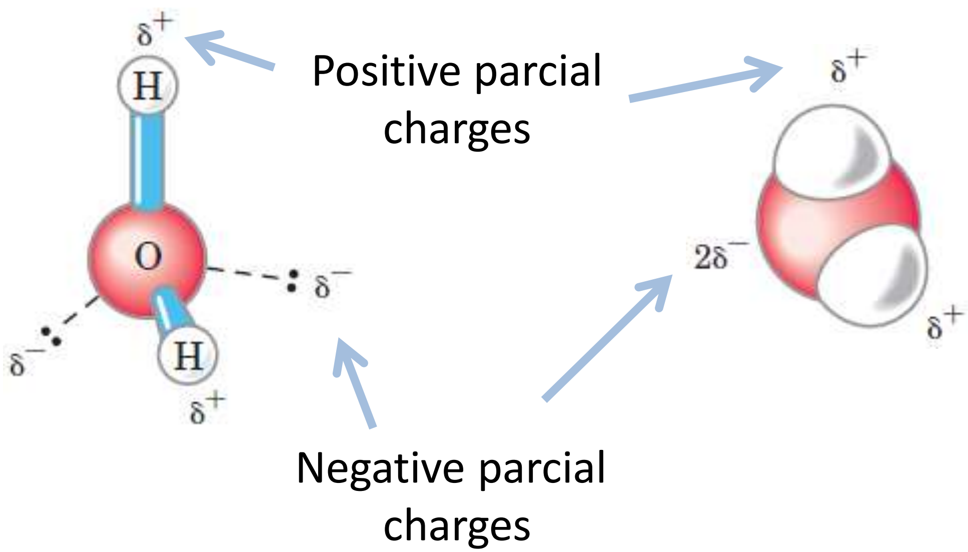


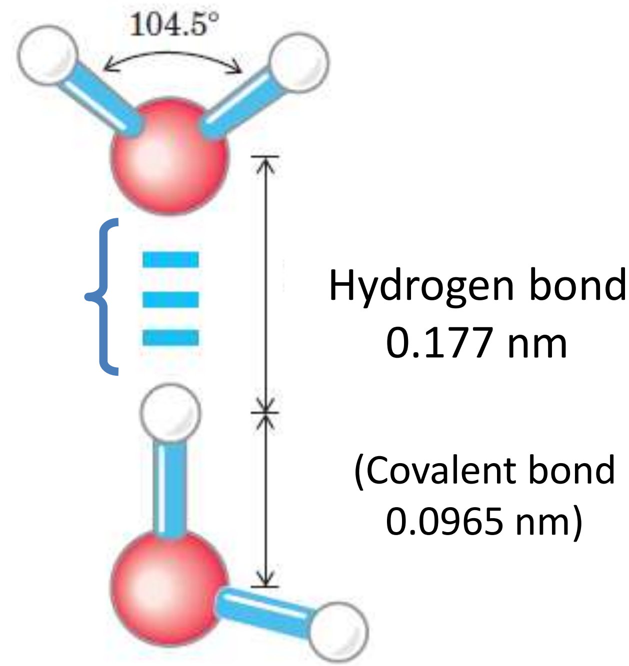


Hydrogen bond 0.177 nm

(Covalent bond 0.0965 nm)

Water Properties p.1





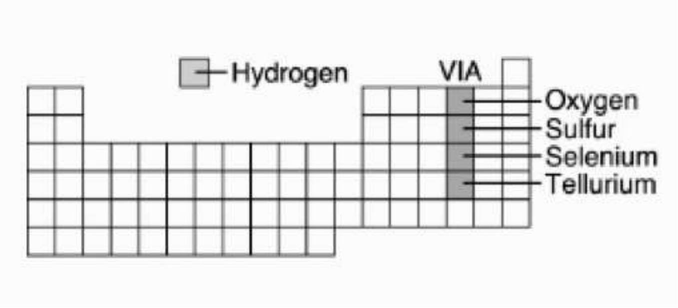
Hydrogen bond formation is the cause for water special properties:

1. Higher fusion and boiling point
2. Density: solid is less dense than liquid phase
3. Large specific heat: the capacity to raise 1°C for 1g of material
4. Capillarity by cohesive forces: transportation in trees
5. Elevated surface tension

Water Properties p.1

Hydrogen bond formation is the cause for water special properties:

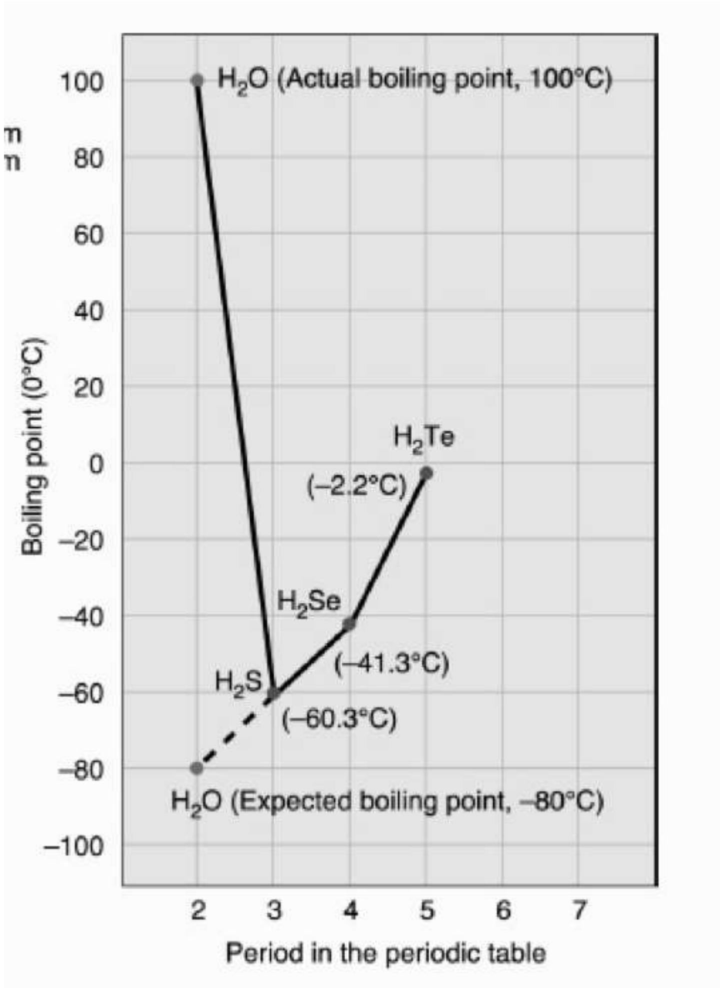
1. Higher fusion and boiling point (**bp**):



Inside the same group the ***bp*** should increase.

The theoretical **bp** of water is -80 C !!!

With water, we need more energy to break **H** bond.



Water Properties p.1

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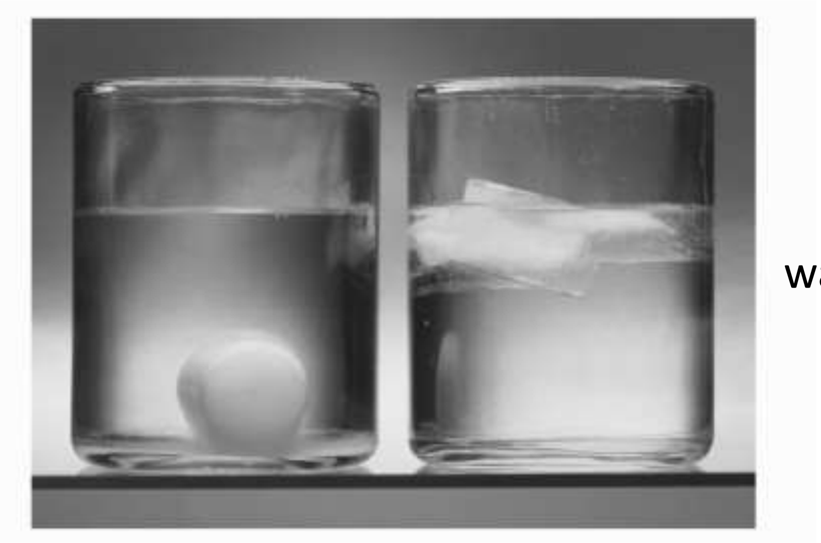
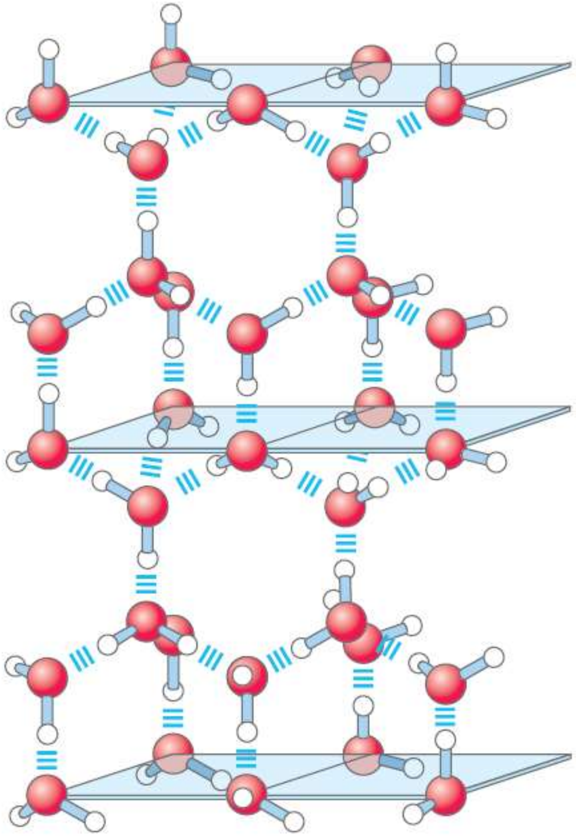
wax  water



The presence of tridimensional Hydrogen bonds expand the ice structure, leading to less density

Water Properties p.1

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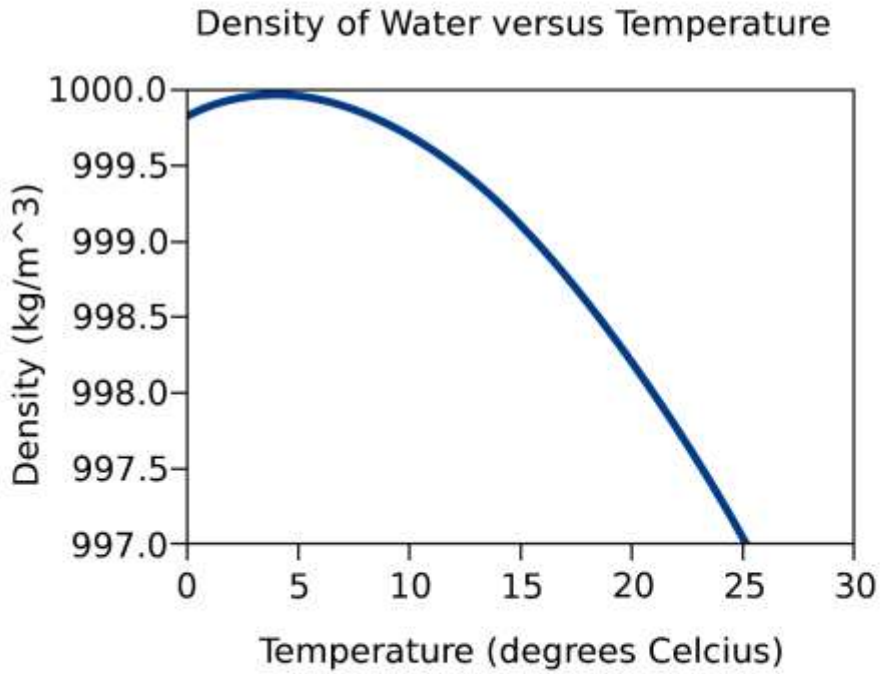
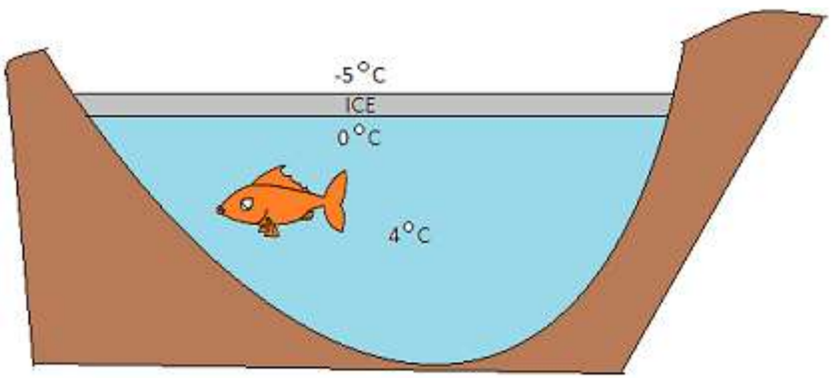


LIFE is maintained in lakes during winter, because the ice cap insulate the rest of the water body !



Water Properties p.1

Hydrogen bond formation is the cause for water special properties:

3. Large specific heat:

Specific Heat is the quantity of heat that is required to raise the temperature of 1g of substance by 1°C.

It takes 1 calorie of heat to raise the temperature of 1 g of liquid water by 1°C.

The larger the Specific Heat, the less the temperature will rise when it absorbs a given amount of heat.

Specific Heat	(J/gC°)
H_2O (l)	4.184
H_2O (s)	2.03
Al (s)	0.89
C	0.71
Fe	0.45

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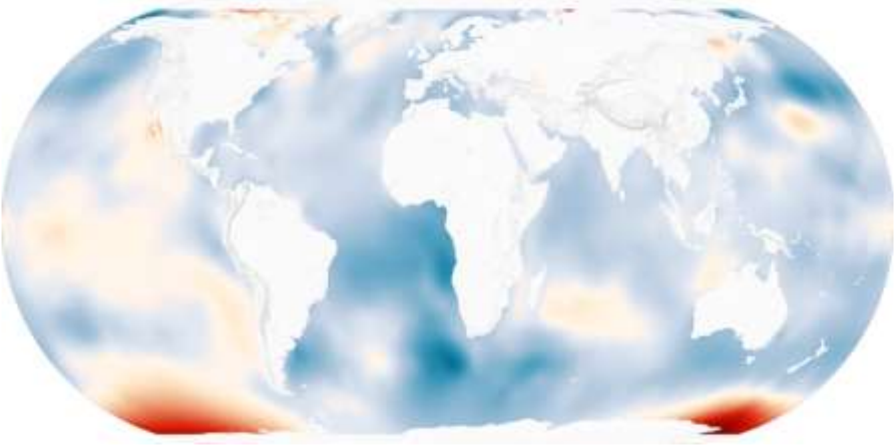
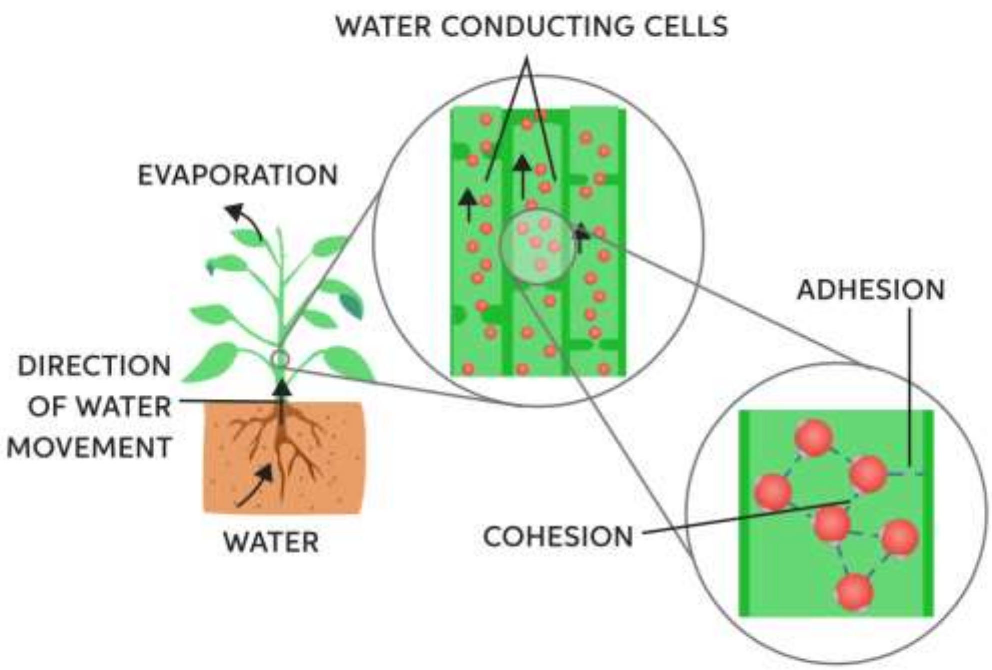


Oceans absorbs during the day (summer) and release during the night (winter): They control the Earth’s Climate!!

Water Properties p.1

Hydrogen bond formation is the cause for water special properties:

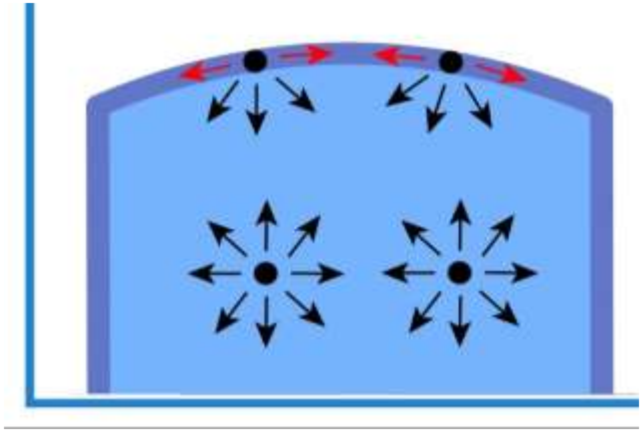
4. Capillarity by cohesive forces: transportation in trees

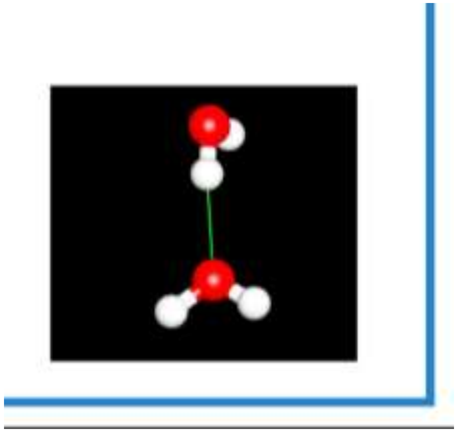


Water Properties p.1

Hydrogen bond formation is the cause for water special properties:

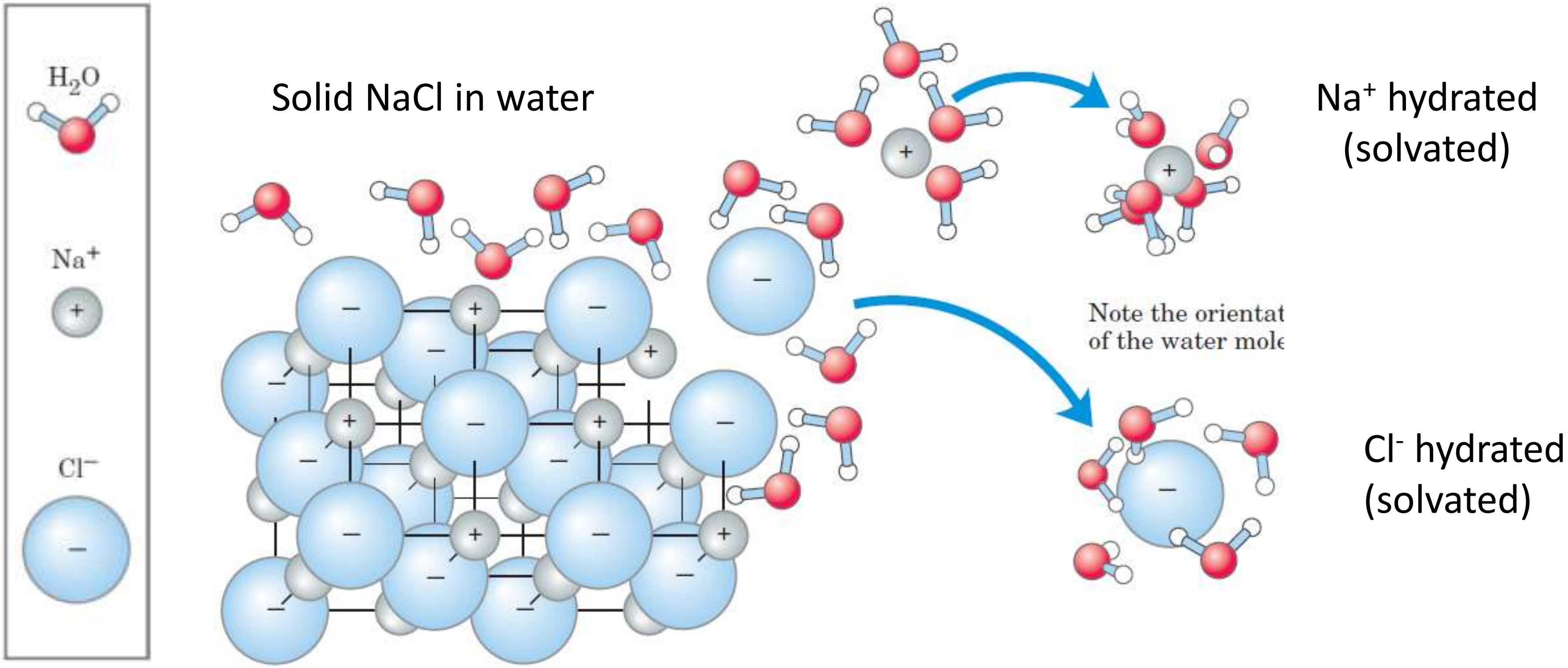
4. High Surface Tension





Water Properties p.1

Hydration or Solvation:



Dissolution: the sum of all the charges interaction with the water molecule is enough to break ionic bond.

Water Properties p.2

Properties based on the ION content:

Normally less discussed, but extremely important!

Major ion content (% of the total)

Ion	Freshwater
HCO_3^-	41.0
Ca^{2+}	16.0
Mg^{2+}	14.0
Na^+	11.0
Cl^-	8.5

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1. Salinity

Water Properties p.2

Properties based on the ion content:

Normally less discussed, but extremely important!

2. Alkalinity

Major ion content (% of the total)		
Ion	**Freshwater**	**Seawater**
HCO_3^-	41.0	0.2
Ca^{2+}	16.0	0.9
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Na^+	11.0	41.0
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Water Properties p.2

Properties based on the ion content:

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3. Hardness

Major ion content (% of the total)		
Ion	**Freshwater**	**Seawater**
HCO_3^-	41.0	0.2
Ca^{2+}	16.0	0.9
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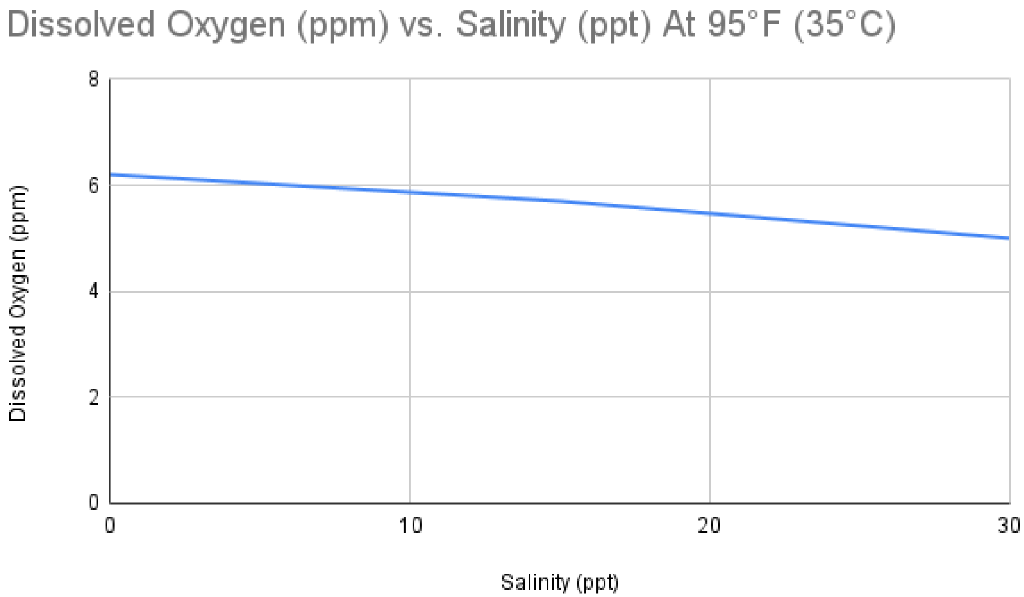
Na^+	11.0	41.0
Cl^-	8.5	49.0

1. SALINITY

Salinity is the total amount of dissolved salts in water; grams of salts per kilogram of water (g/kg) or as parts per thousand (ppt).

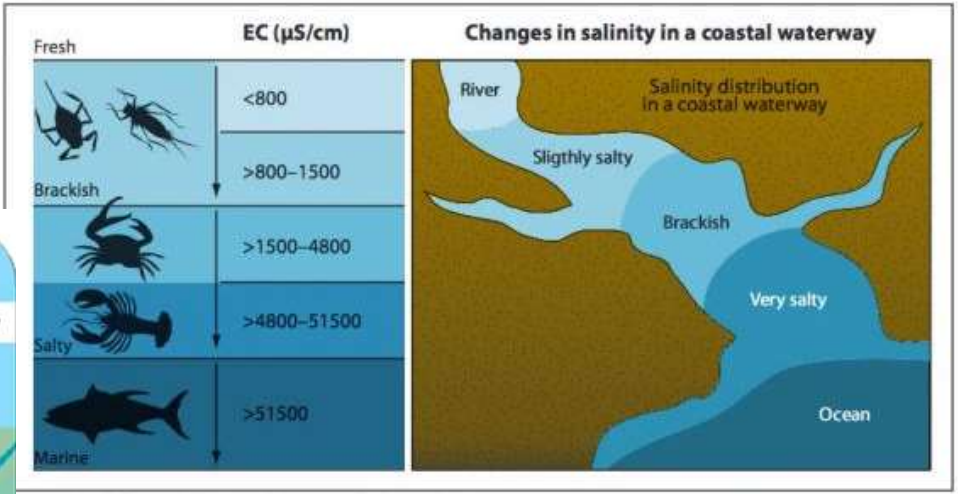
Cl^- Na^+ SO_4^{2-} and Mg^{2+}

Affects other properties of seawater, such as its density and the amount of dissolved oxygen.

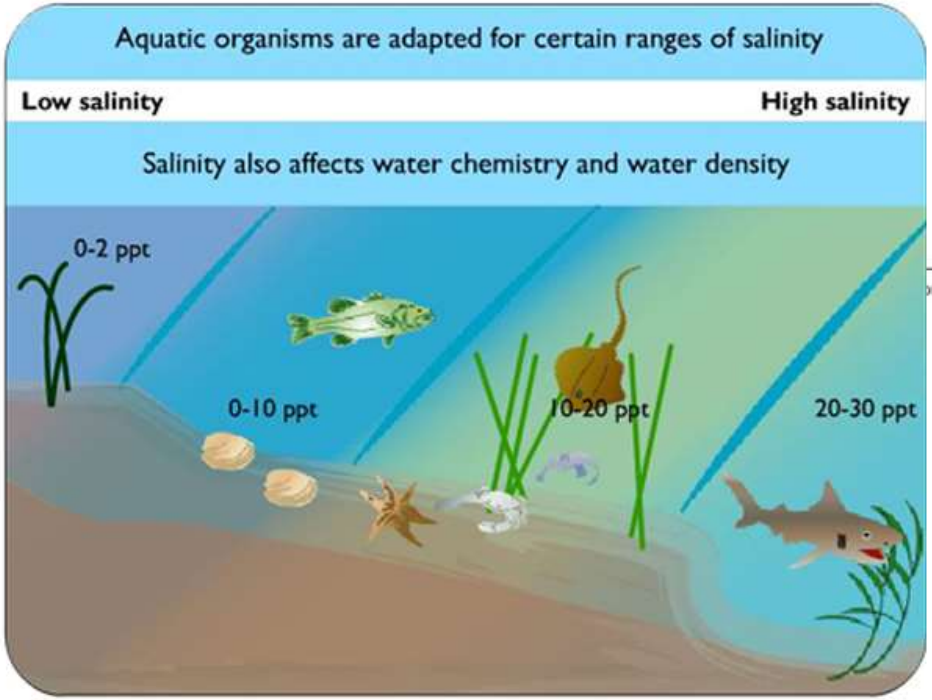


1. SALINITY

Determines the distribution of plants and animals that live in the ocean.



ource: Adapted from Oz Estuaries – *Changes in salinity in an estuary*



The average salinity of the world's oceans is 35 ppt.

Freshwater has a salinity of <1 ppt.

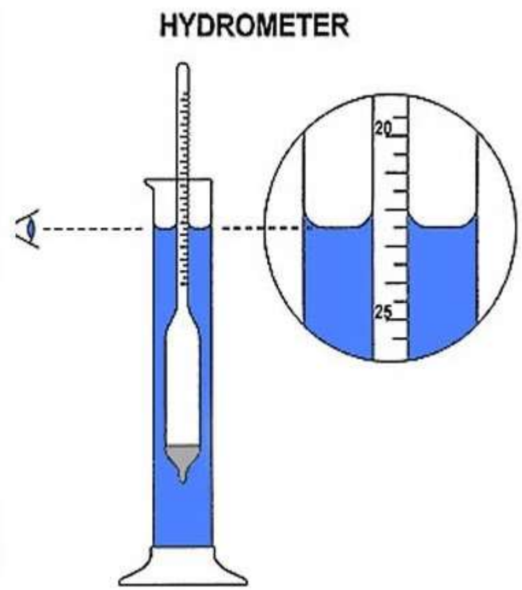
1. SALINITY

How to <u>measure</u> salinity:

- <u>hydrometer</u>: addition of salts to pure water causes an increase in density. Salinity can be calculated by measuring the specific gravity of a water sample:

$$\text{Specific Gravity} = \frac{\text{density of sample}}{\text{Density of pure water}}$$

Tables to convert to salinity



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- <u>Silver nitrate titration</u> method: the amount of chloride (chlorinity)

Salinity (ppt) = 1.80655 x Chlorinity (ppt)

2. HARDNESS

Hardness: capacity of water to form the lather of soap

It is the total concentration of calcium and magnesium ions

Temporary – Bicarbonates of Ca^{2+} and Mg^{2+}
Permanent – Sulphates and chlorides of Ca^{2+} and Mg^{2+}

Temporary hardness can be removed by boiling water

2. HARDNESS

Temporary – Bicarbonates of Ca^{2+} and Mg^{2+} → Soluble
Permanent – Sulphates and chlorides of Ca^{2+} and Mg^{2+} → Insoluble

Temporary hardness can be removed by boiling water

↓

Forms a white solid

$$Ca(HCO_3)_2 \xrightarrow{\text{Heat}} \underset{\text{(Insoluble)}}{CaCO_3}\downarrow + H_2O + CO_2\uparrow$$

bicarbonate carbonate

Temporary – Bicarbonates of Ca^{2+} and Mg^{2+} $\rightarrow$ Soluble

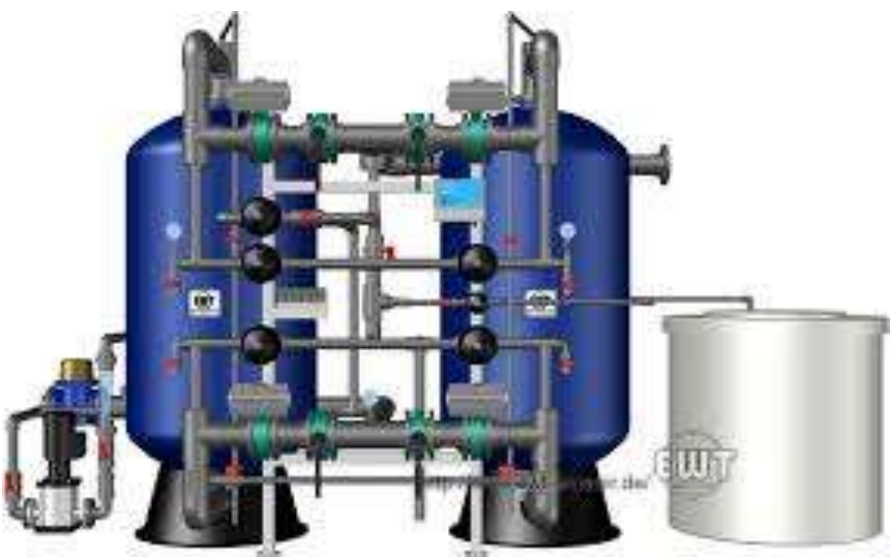
Permanent – Sulphates and chlorides of Ca^{2+} and Mg^{2+} $\rightarrow$ Insoluble

Permanent hardness can be removed by more complex techniques:

- Ion exchange
- Distillation $\rightarrow$ Occurs naturally in the water-circle:
- Reverse Osmosis

$\downarrow$

Rain water is always soft



How it is expressed?

As equivalent of $CaCO_3$ in ppm

Salt/ion	Molar mass	Multiplication factor for converting into equivalents of $CaCO_3$
$Ca(HCO_3)_2$	162	100/162
$Mg(HCO_3)_2$	146	100/146
$CaSO_4$	136	100/136
$CaCl_2$	111	100/111
$MgSO_4$	120	100/120
$MgCl_2$	95	100/95
$CaCO_3$	100	100/100
$MgCO_3$	84	100/84
CO_2	44	100/44
$Ca(NO_3)_2$	164	100/164
$Mg(NO_3)_2$	148	100/148
HCO_3^-	61	100/122
OH^-	17	100/34
CO_3^{2-}	60	100/60
$NaAlO_2$	82	100/164
$Al_2(SO_4)_3$	342	100/114
$FeSO_4.7H_2O$	278	100/278
H^+	1	100/2
HCl	36.5	100/73

2. HARDNESS

Calculate the temporary and permanent hardness of water sample containing $Mg(HCO_3)_2$= 7.3mg/L, $Ca(HCO_3)_2$= 16.2mg/L, $MgCl_2$= 9.5mg/L, $CaSO_4$=13.6mg/L).

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$Mg(HCO_3)_2$= 7.3mg/L	100/146	
$Ca(HCO_3)_2$= 16.2mg/L	100/162	
$MgCl_2$= 9.5mg/L	100/95	
$CaSO_4$=13.6mg/L	100/136	

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Constituent	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$= 7.3mg/L	100/146	7.3X100/146= 5mg/L
$Ca(HCO_3)_2$= 16.2mg/L	100/162	16.2X100/162=10mg/L
$MgCl_2$= 9.5mg/L	100/95	9.5X100/95= 10mg/L
$CaSO_4$=13.6mg/L	100/136	13.6X100/136= 10mg/L

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Constituent	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$= 7.3mg/L	100/146	7.3X100/146= 5mg/L
$Ca(HCO_3)_2$= 16.2mg/L	100/162	16.2X100/162=10mg/L
$MgCl_2$= 9.5mg/L	100/95	9.5X100/95= 10mg/L
$CaSO_4$=13.6mg/L	100/136	13.6X100/136= 10mg/L

Permanent Hardness: $MgCl_2$ + $CaSO_4$ = 10 + 10 mg/L = 20 mg/L

2. HARDNESS

Calculate the temporary and permanent hardness of water sample containing $Mg(HCO_3)_2$= 7.3mg/L, $Ca(HCO_3)_2$= 16.2mg/L, $MgCl_2$= 9.5mg/L, $CaSO_4$=13.6mg/L).

Constituent	Multiplication factor	$CaCO_3$ equivalent
$Mg(HCO_3)_2$= 7.3mg/L	100/146	7.3X100/146= 5mg/L
$Ca(HCO_3)_2$= 16.2mg/L	100/162	16.2X100/162=10mg/L
$MgCl_2$= 9.5mg/L	100/95	9.5X100/95= 10mg/L
$CaSO_4$=13.6mg/L	100/136	13.6X100/136= 10mg/L

Permanent Hardness: $MgCl_2$ + $CaSO_4$ = 10 + 10 mg/L = 20 mg/L

Temporary Hardness: $Mg(HCO_3)_2$ + Ca $(HCO_3)_2$ = 5 + 10 mg/L = 15 mg/L

How to determine the amount of Ca^{2+} e Mg^{2+} from soluble salts?

Titration with EDTA and Eriochrome Black-T (EBT)

Indicator: red to blue

Chelating agent:
removes up to 4 cations from solution forming stable complexes

3. ALKALINITY

Capacity to neutralize acid:

$$\text{Alkalinity} = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-]$$

Presence of carbonates (CO_3^-), bi-carbonates (HCO_3^-), and hydroxide (OH^-) of Ca, Mg, Na and K.

Alkalinity: the amount of acid needed to lower the pH to 4.5

Units: - milligrams CaCO3 per liter (ppm)
- mmol of H+ per L

Natural waters have alkalinity of 1 mmol/L (1mM)

3. ALKALINITY

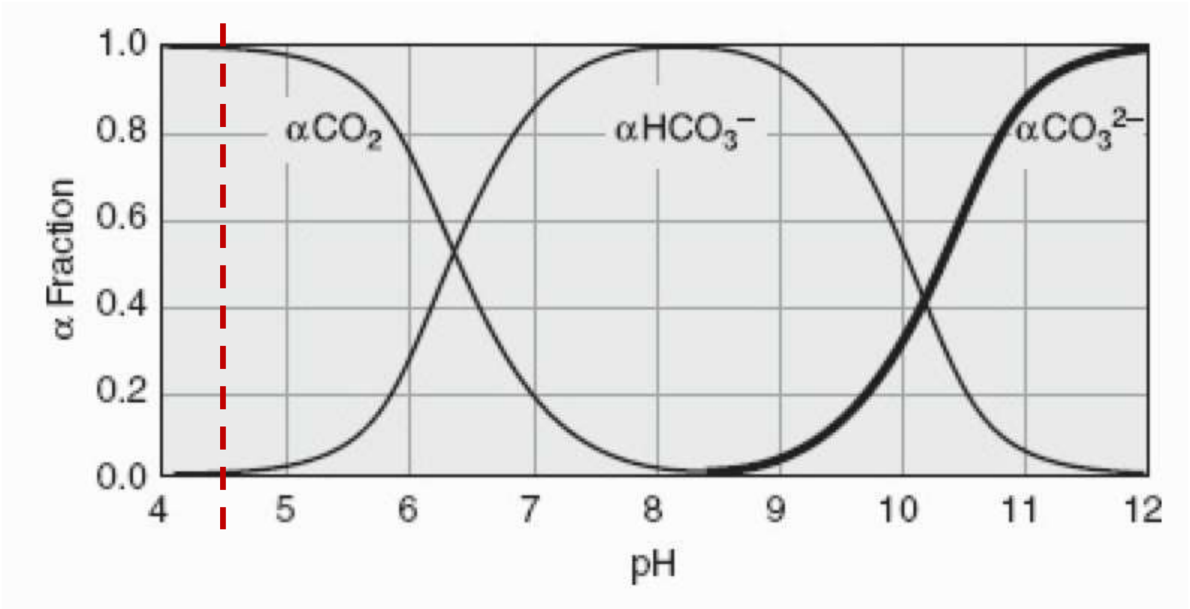
Capacity to neutralize acid: the amount of acid needed to lower the pH to 4.5

★4.5 is the value where all carbonate species are neutralized.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

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

Weak acid



Parenthesis: **HENRY`S LAW**

Allow to calculate the concentration of a gas in a solution.

“ The solubility of a gas in a liquid is proportional to the partial pressure of the gas that is in contact with the liquid ”

$$\left[CO_2\ (aq)\right] = K_{CO_2} P_{CO_2}$$

Henry’s constant:

$$K_{CO_2} = 3.38 \times 10^{-2}\ \text{mol/atm-L}$$

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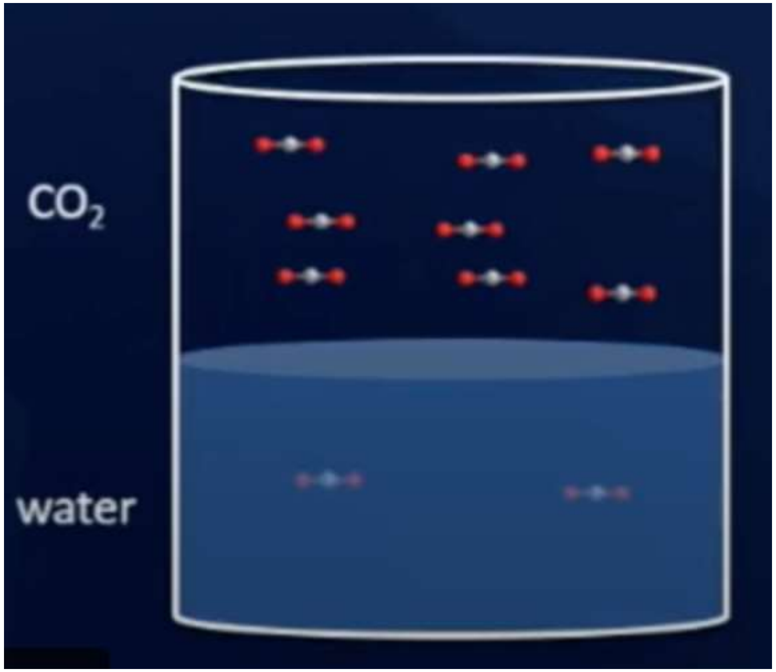
Exercise 1. In a bottle of soda, the partial pressure of CO_2 is 4 atm. How much of CO_2 is dissolved inside the liquid if the bottle is left open?



Inside the closed bottle:

$[CO_2]$ = 0.0338 mol/(atm L) * 4 atm = 0.135 M

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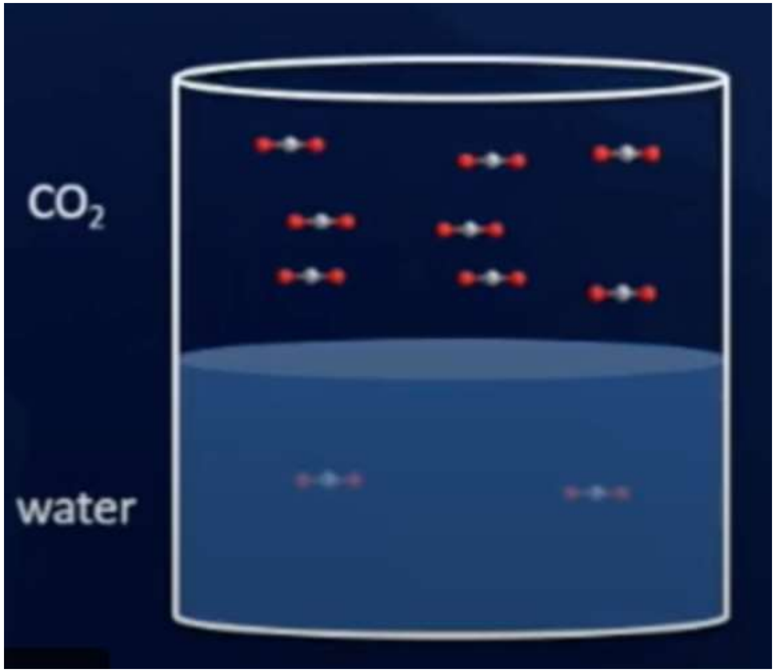

Inside the closed bottle:

$[CO_2]$ = 0.0338 mol/(atm L) * 4 atm = 0.135 M

Open bottle:

$[CO_2]$ = 0.0338 mol/(atm L) * 0.04 atm

= 0.00135 M = 1.35 mM

3. ALKALINITY

Parenthesis: **HENRY`S LAW**

Exercise 2. What is the average CO_2 concentration at the surface of the ocean, given the following data:

- Temperature of 25 °C
- CO_2 concentration in air: 370 ppm
- Water Vapor partial pressure: 0.0313 atm

$$\left[CO_2\ (aq)\right] = K_{CO_2} P_{CO_2}$$

$P_{CO2} =$

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$$P_{CO2} = (\text{air pressure} - \text{water vapor}) * \%\text{ of } CO_2$$

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370 ppm = 370 mg/Kg = 0.370 g/kg = 0.037 g/100g

0.037 %

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$$[CO_2] = 0.0338\ \text{mol/(atm L)} * 3{,}5 \cdot 10^{-4}\ \text{atm} = 1{,}18 \cdot 10^{-5}\ \text{M}$$

3. ALKALINITY

Carbonate ions acts as buffer and reservoir for inorganic carbon. Alkalinity is a measure to see if water can support aquatic life.

Alkalinity vs. Hardness

Alkalinity = Hardness
– Ca and Mg salts are present $Ca\ (HCO_3)_2$

Alkalinity > Hardness
– presence of basic salts, Na, K along with Ca and Mg $[OH^-]$

Alkalinity < Hardness
– neutral salts of Ca & Mg present $CaCl_2$

POLLUTANTS

List of type of pollutants in water:

1. Disease-causing agents: **coliform bacteria** count

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2. Oxygen-consuming wastes: decomposition of organic waste
3. Plant nutrients: nitrogen (ammonia, nitric acid), phosphorous

eutrophication, dense mats of rooted and floating plants are formed

POLLUTANTS

List of type of pollutants in water:

1. Disease-causing agents: coliform bacteria count
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5. Dissolved solids: increase salinity, by irrigation
6. Thermal pollution (heat) : the hotter, the less soluble oxygen

POLLUTANTS

List of type of pollutants in water:

1. Disease-causing agents: coliform bacteria count
2. Oxygen-consuming wastes: organic waste
3. Plant nutrients: nitrogen, phosphorous
4. Suspended solids and sediments: block light
5. Dissolved solids: increase salinity
6. Thermal pollution (heat): less dissolved oxygen
7. Toxic materials
8. Radioactive substances
9. Oil
10. Acids