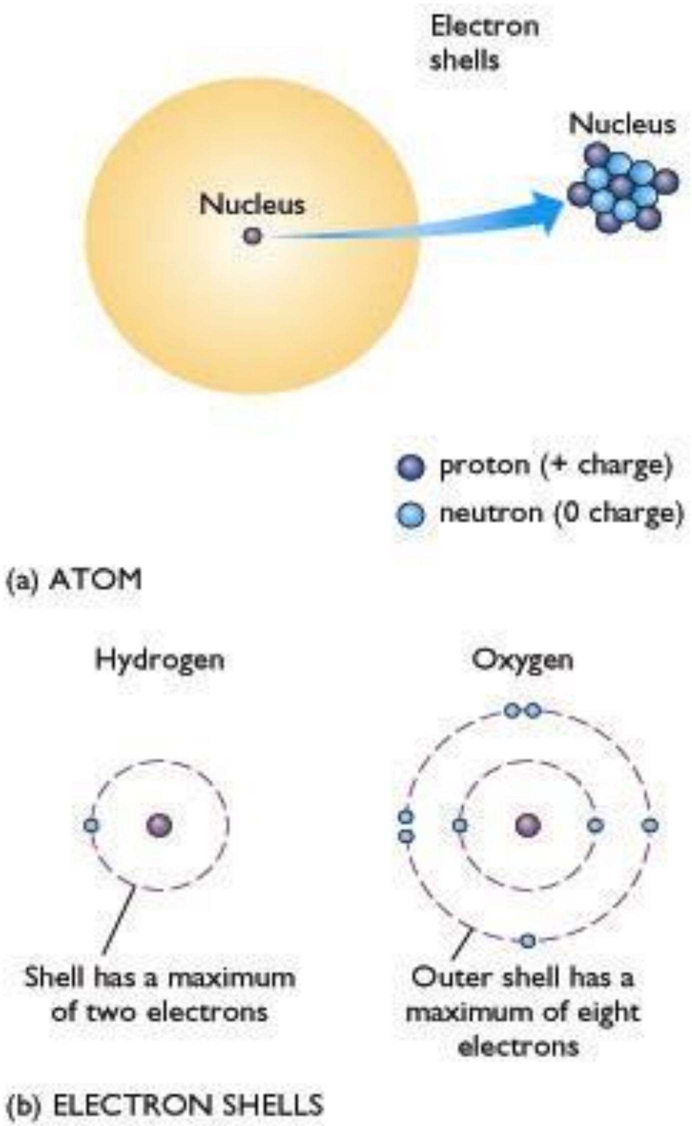
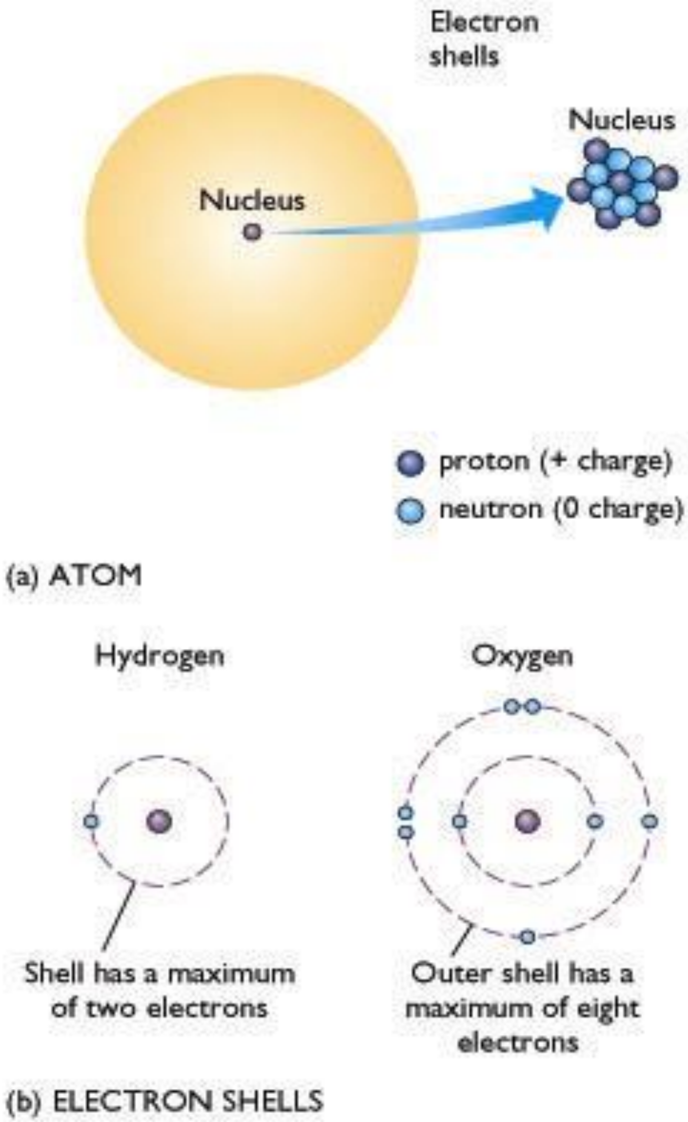
Atoms are the smallest unit which display all of the properties of the material.

- **Atoms are composed of:**
  - *Nucleus - the center of the atom consisting of positively charged particles called protons and neutrally charged particles called neutrons.*
  - *Electrons - negatively charged particles which orbit the nucleus in discrete electron shells.*



- Electrically stable atoms have the same number of electrons as protons.
- Ions are atoms with either more or fewer electrons than protons and are therefore electrically charged.
- Isotopes are atoms containing the same number of protons, but different numbers of neutrons and therefore have different atomic weights.
- Molecules are chemically-combined compounds formed by two or more atoms.

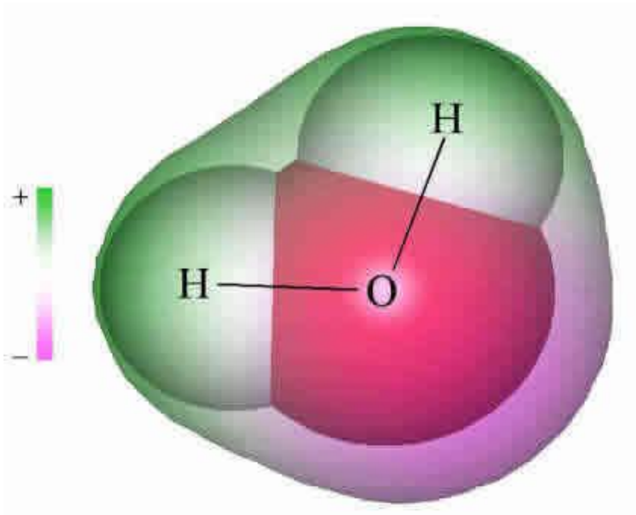


Basic Physical Notions

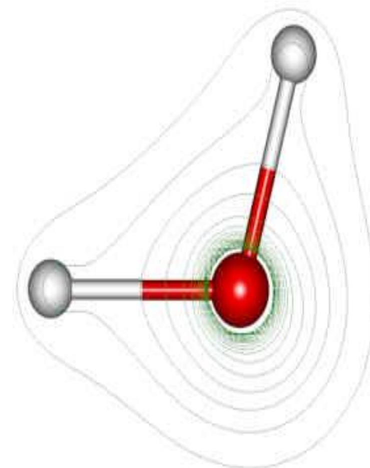
Heat results from the vibrations of atoms (kinetic energy) and can be measured with a thermometer.

- In solids, the atoms or molecules vibrate weakly and are rigidly held in place.
- In liquids, the atoms or molecules vibrate more rapidly, move farther apart and are free to move relative to each other.
- In gases, the atoms or molecules are highly energetic, move far apart and are largely independent.

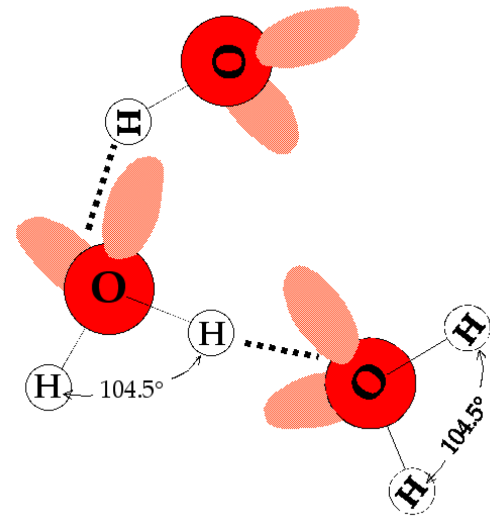
The Water in Seawater

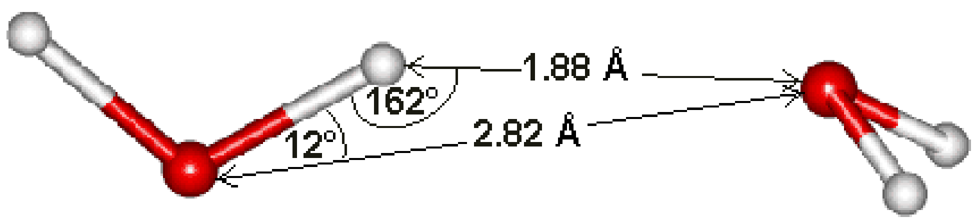


Shape and Charge Distribution
(Small H-atom; electronegative O-atom)

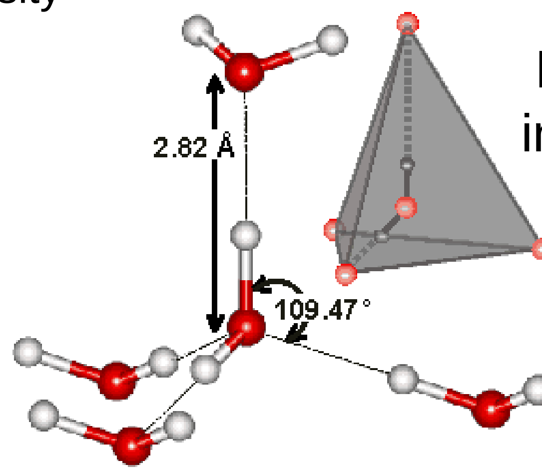


Electron Density





Hydrogen bond:
10-30 times weaker than covalent bonds
(O-H covalent bond length ~1Å)
H-bond length varies strongly with T,P



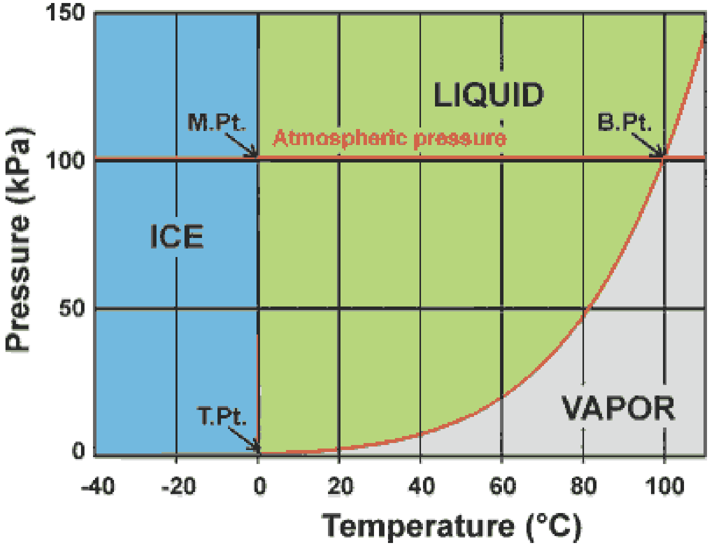
Bond angle in e.g. liquid; solid

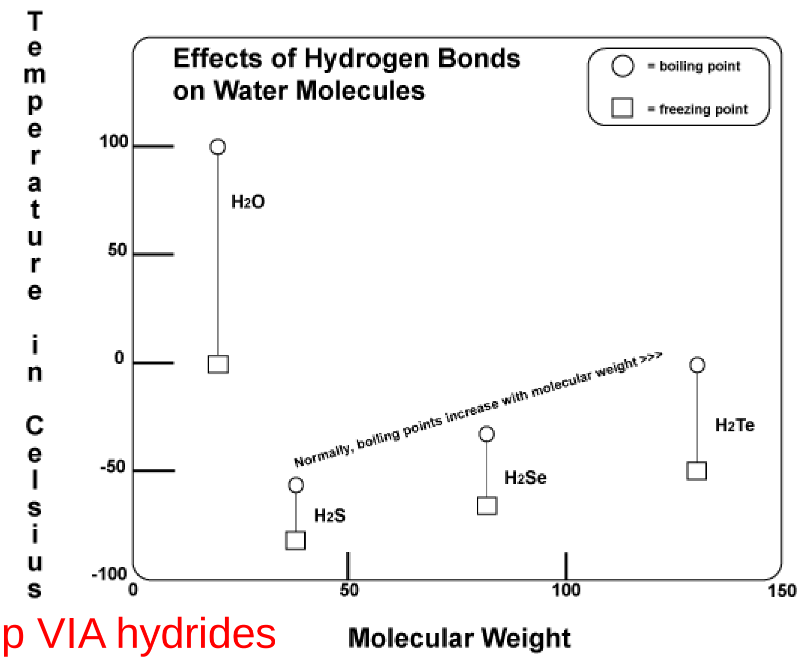
Each molecule can form UP TO 4 H-bonds;
(2 lone electron pairs; 2 H-atoms)

Some Properties of Water

The importance of hydrogen bonding

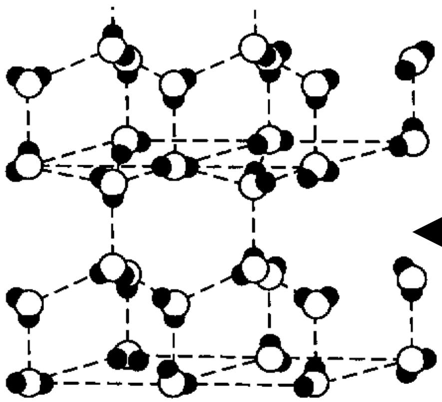
- Unusually high melting point (low entropy of liquid water / high organization)
- Unusually high boiling point (high cohesion between molecules; lower vapour pressure)
- Very high enthalpies of fusion and vaporization (highest heat of vaporization of any liquid)
- Very high polarity (readily dissolves ionic salts)→water is a very good solvent!
- Very high surface tension and high viscosity
- Very high specific heat (33 times that of mercury!) as H bonds need to be broken up during heating in addition to increasing vibration
- Shrinks on melting (expands on freezing)



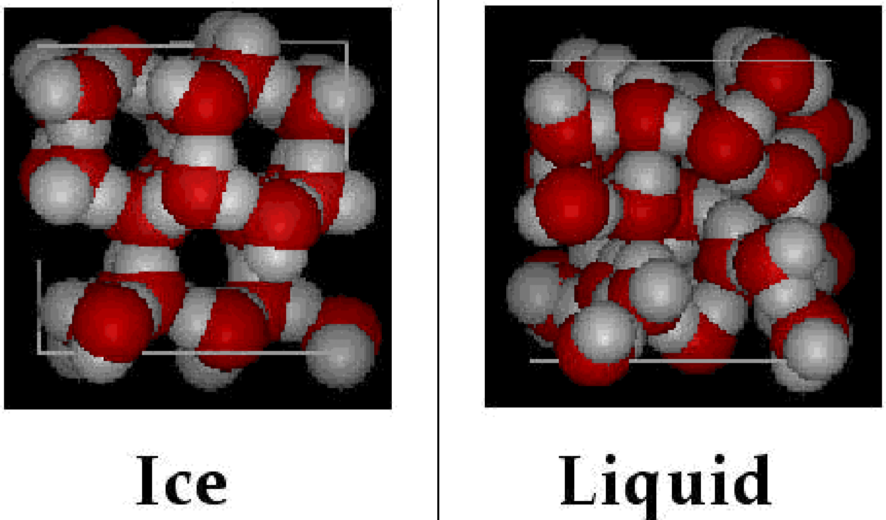


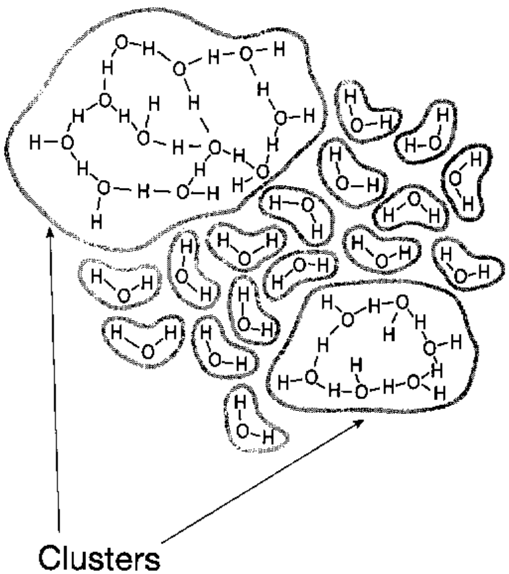
Group VIA hydrides

Water has 'structure'



Solid



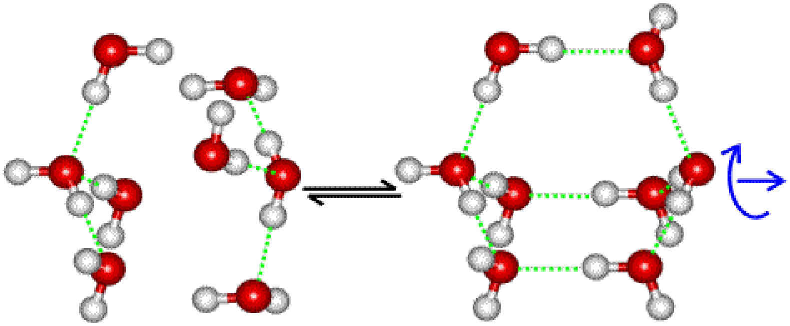


Liquid (with ‚flickering clusters')

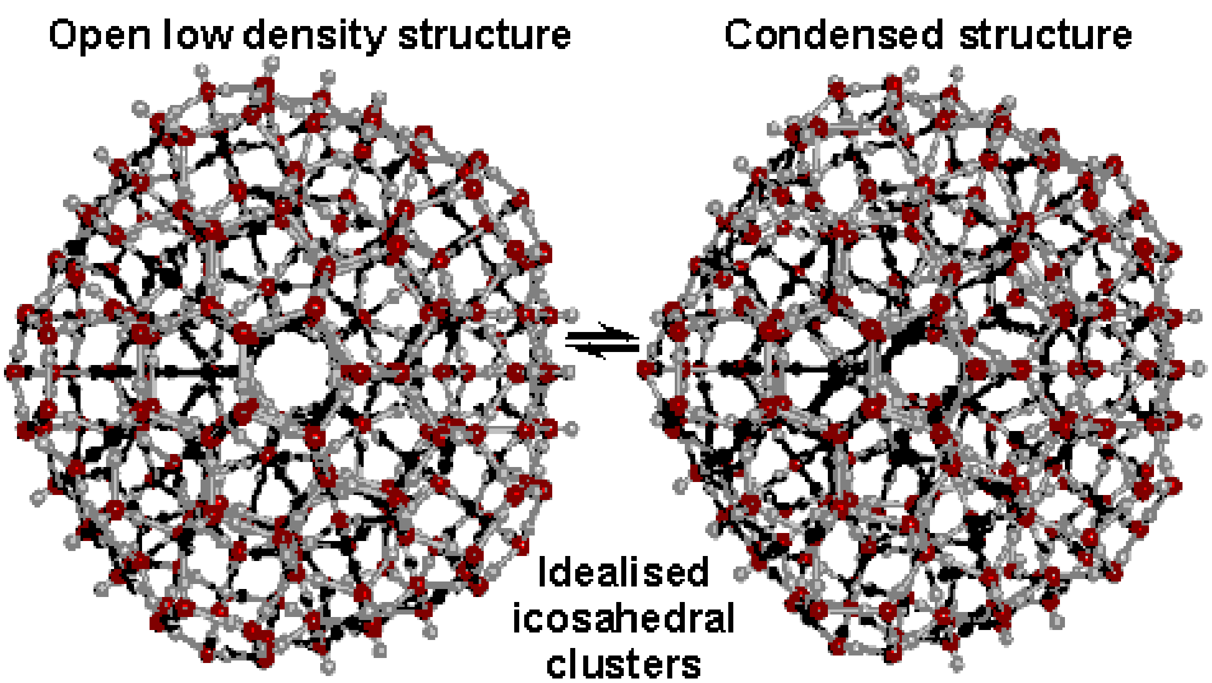
Water molecules further apart in structures

Structure causes lower density

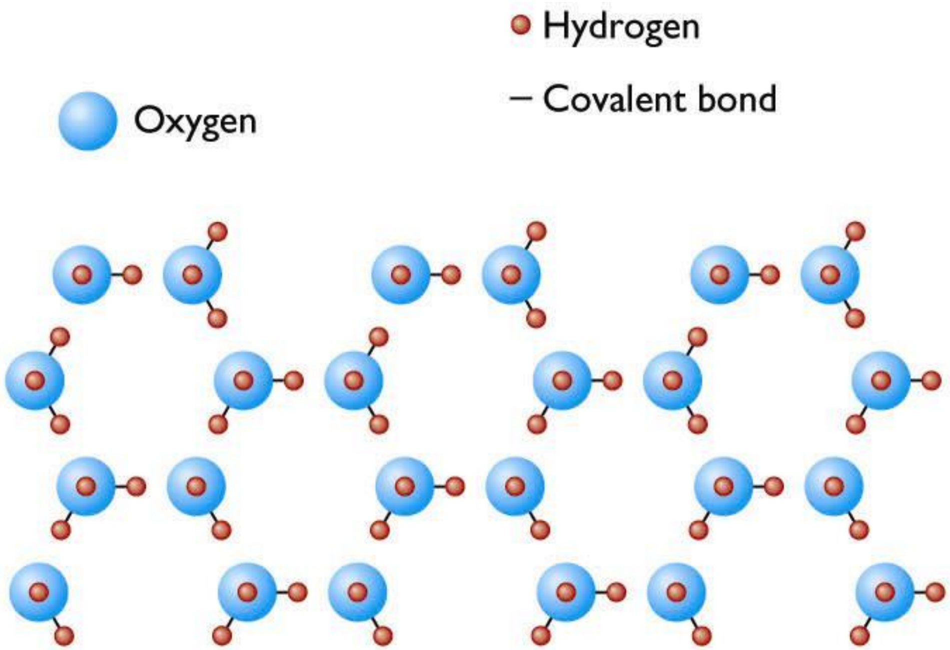
Tetramers associate to form bicyclo-octamers



These can cluster further with themselves to form highly symmetric larger clusters



- **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.**

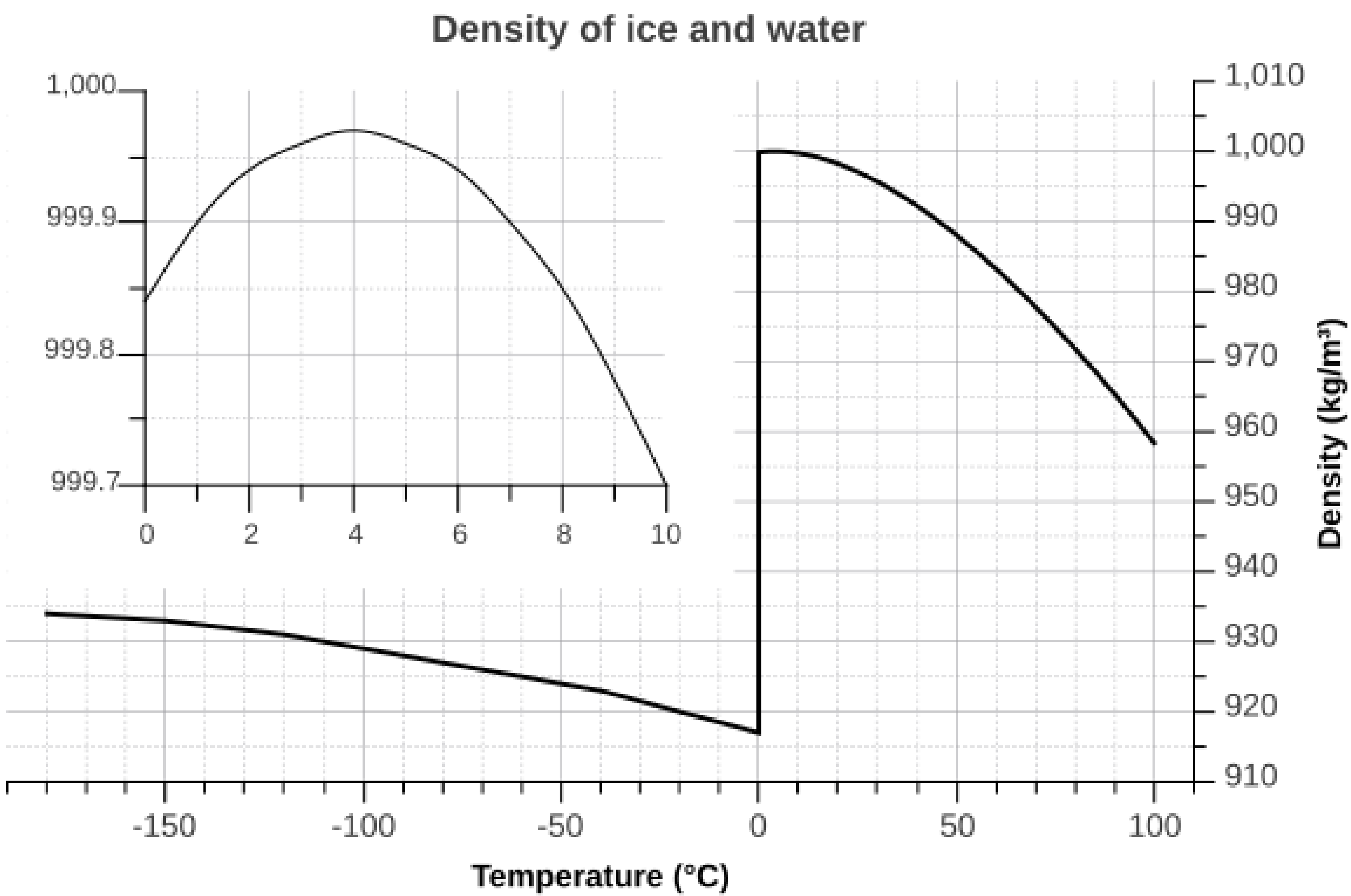


Hexagonal Crystal Structure of Ice

Temperature and Density: Freshwater

- **Water reaches its maximum density at 3.98°C.**
  - *Below this temperature increasing numbers of water molecules form hexagonal polymers and decrease the density of the water.*
  - *Above this temperature water molecules are increasingly energetic and move farther apart, thereby decreasing density.*
- **Hydrogen bonding is responsible for many of the unique properties of water because energy is required to break the hydrogen bonds and separate the water molecules.**

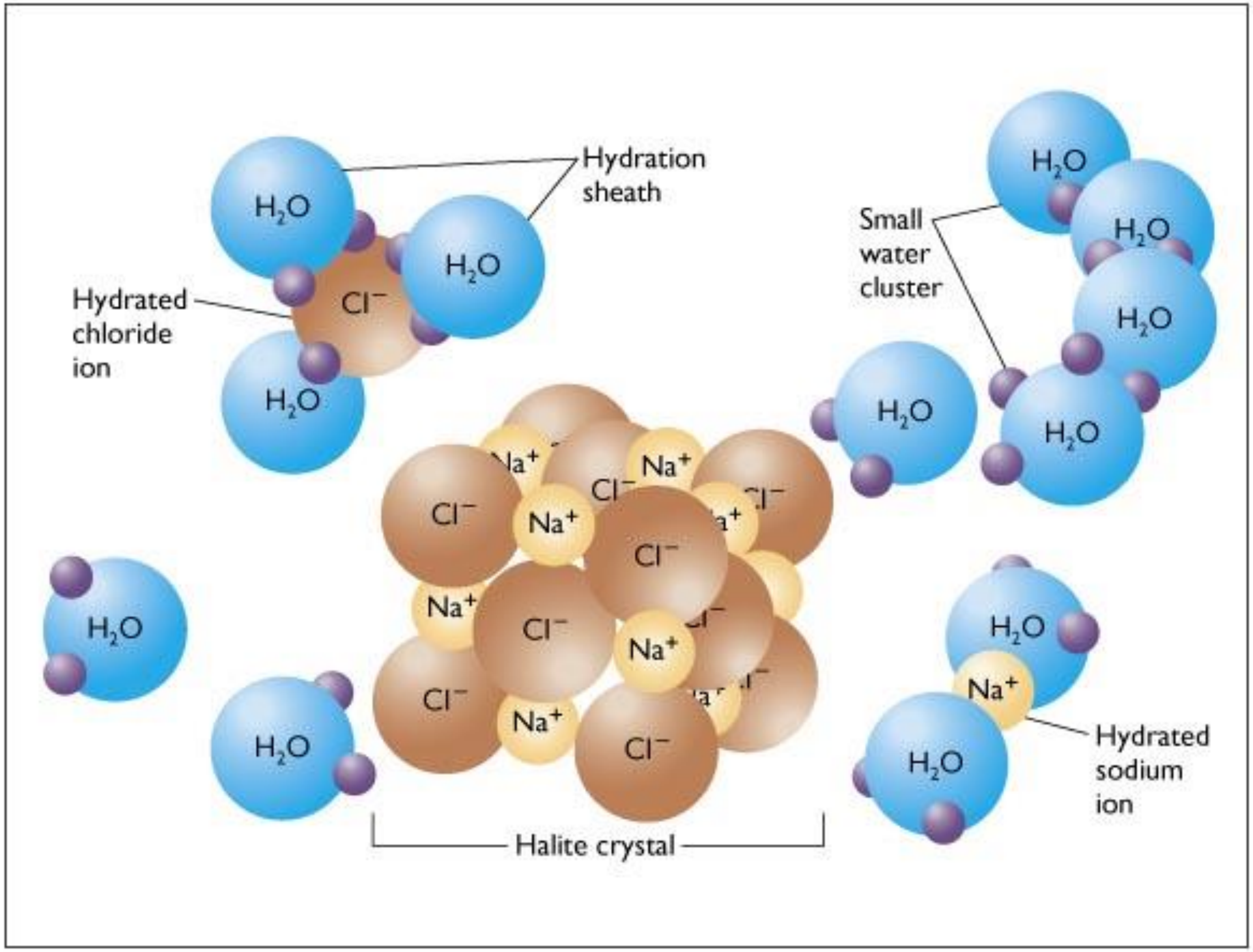
Temperature and Density: Freshwater



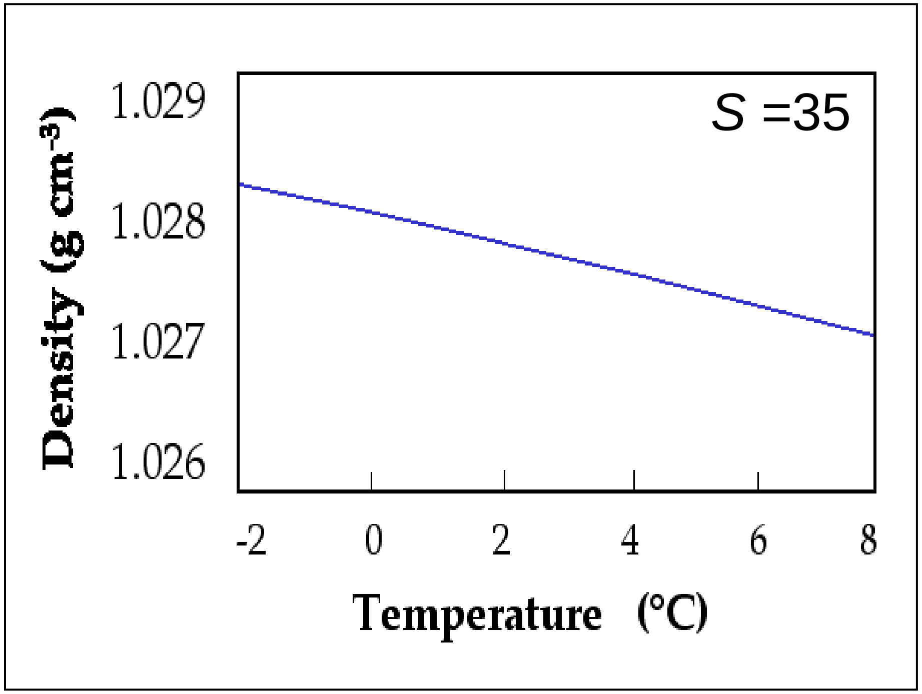
Salt is a ‚structure-breaker‘

Halite (rock salt).

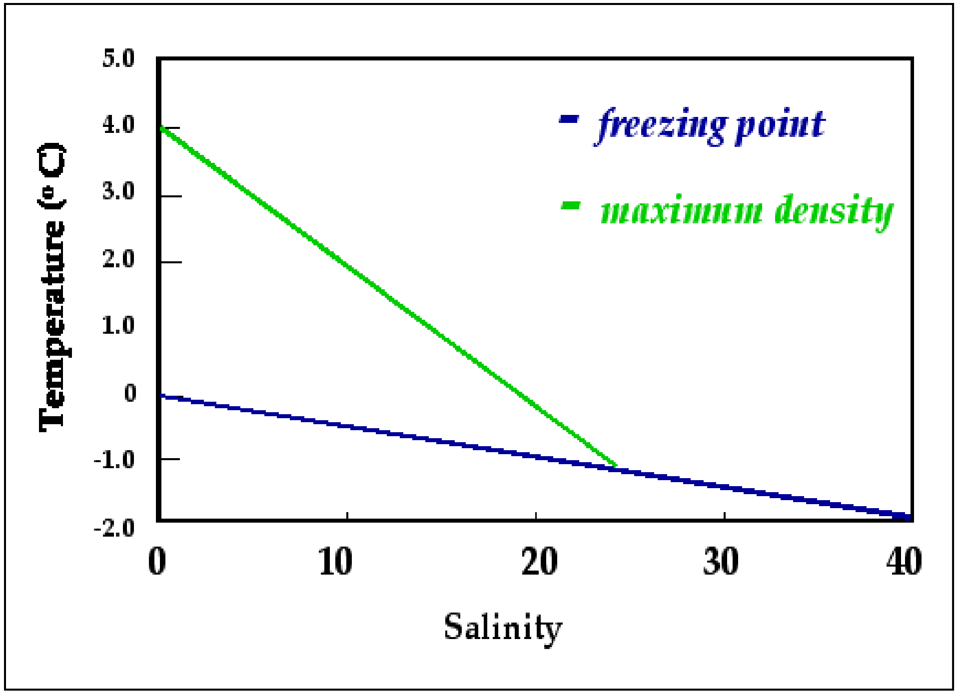
Figure 5.4



Salt is a ‚structure-breaker‘

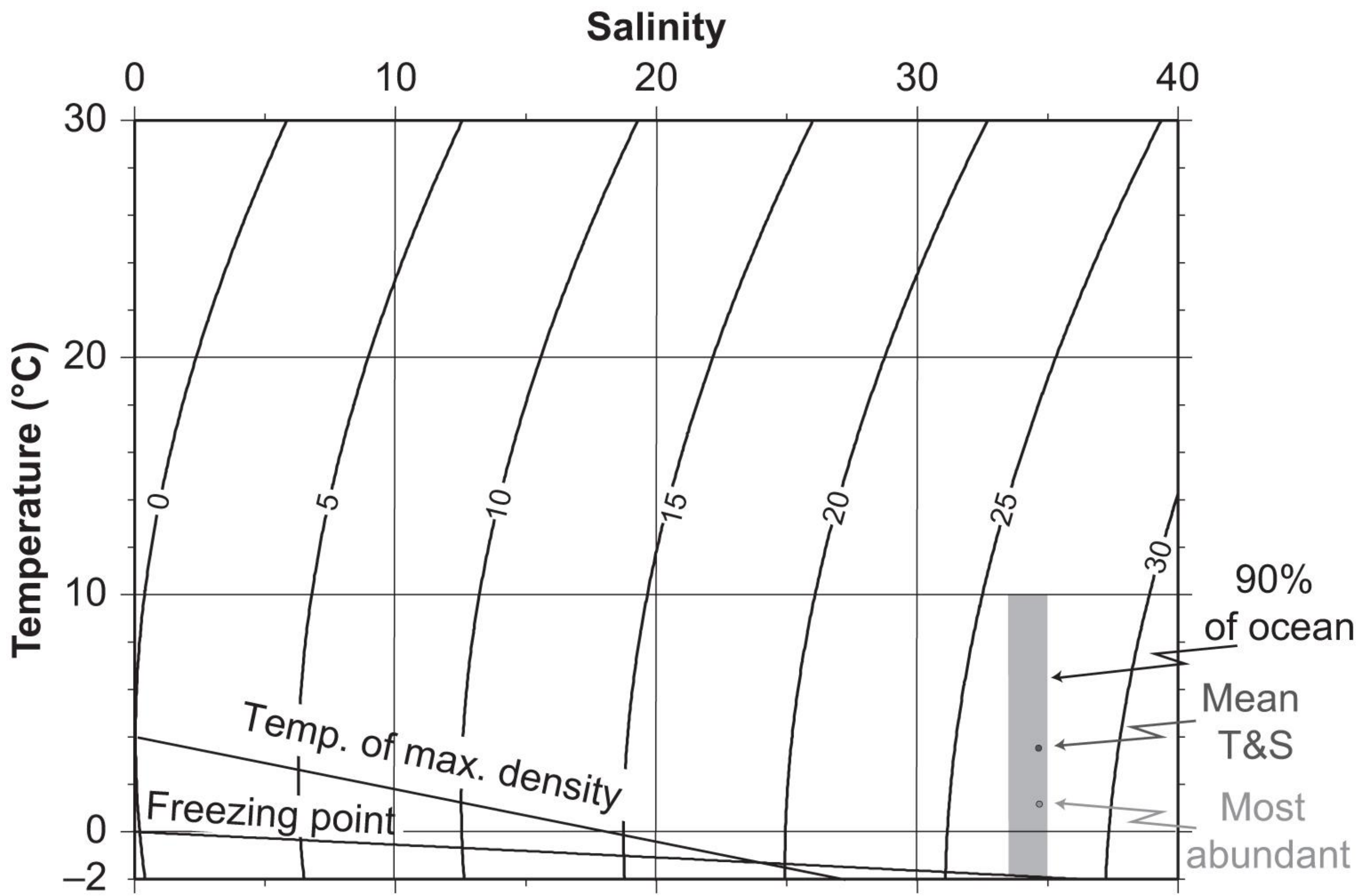


Seawater Density as a Function of Temperature



Maximum Density and Freezing Point

Salt is a ‚structure-breaker‘

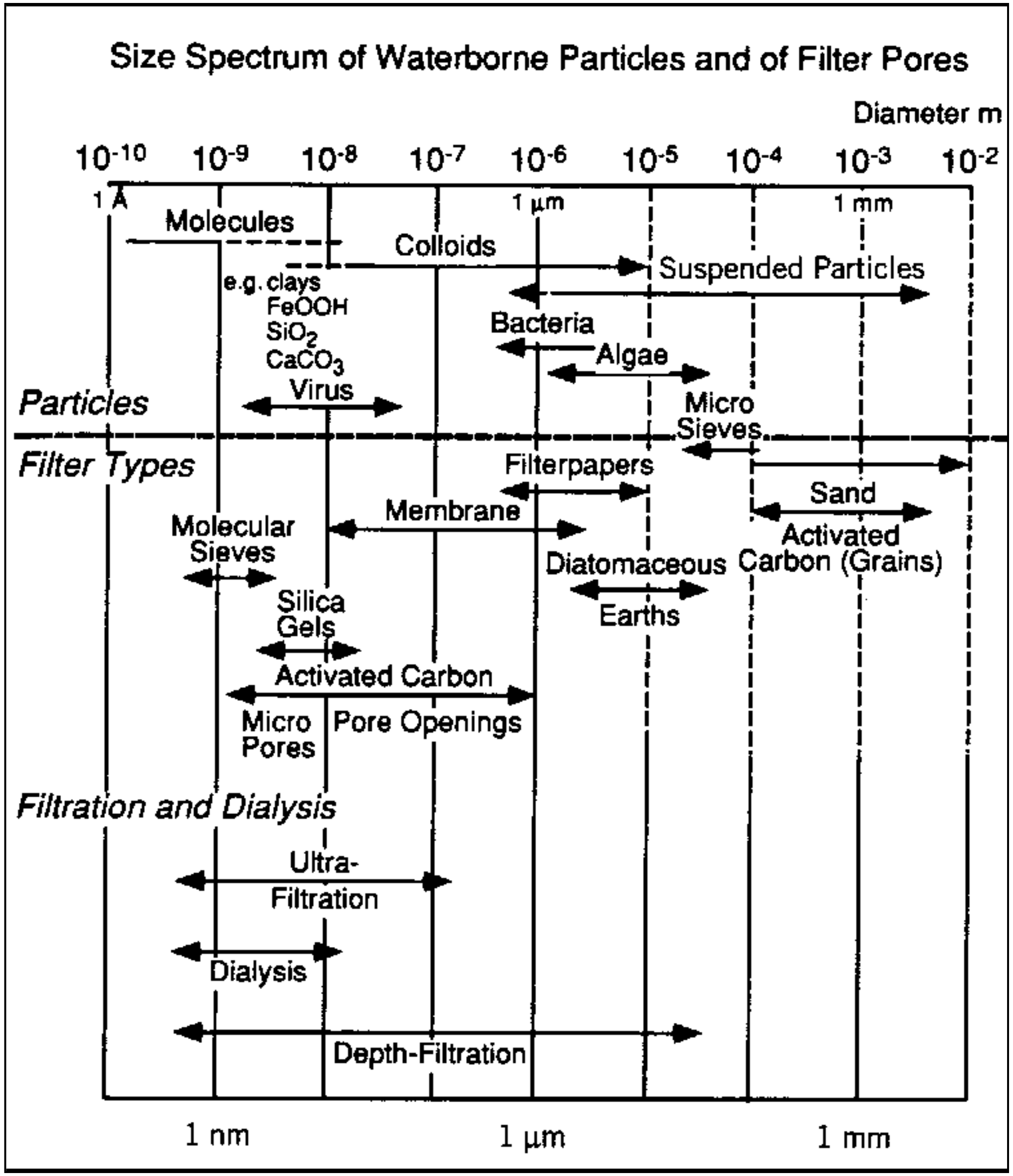


Materials in Seawater

Some materials are 'dissolved', others are 'particulate' in marine science the distinction was/is ,operational'.

• Anything that goes through a 0.2 or 0.4 µm pore-size filter is 'dissolved'.

• Everything that is retained by the filter is 'particulate'.



For Concentrations: Use Moles !

Mass

1. Chemical Mass: By definition, 1 mole of the number 12 isotope of carbon (^{12}C) has a mass of 12.000 g.
2. Masses of all other elements and isotopes are defined relative to this.

The Mole

1. A mole is: the amount of substance of a system that contains as many ‚elementary entities' (e.g., atoms, molecules) as there are atoms in 12 g of ^{12}C .
2. The current best-measure of the number of atoms in 12.000 g of ^{12}C is $6.02214129 \times 10^{23}$ (Avagadro's number).

3. When the mole is used, the ‘elementary entities‘ must be specified (they may be atoms, molecules, ions, electrons, charge, etc.).

4. The number of moles of a chemical substance is therefore defined as:

$$moles = \frac{\text{mass of a substance (g)}}{\text{molar weight (g/moles)}}$$

For example: 1 g of ^{12}C represents (1/12) or 0.08333 moles or 5 x 10^{22} atoms of ^{12}C

Concentration Scales

Name	Definition	Unit Symbol	Notes
Molarity	moles per liter of seawater	M mol L^{-1}	Requires density of the solution to be specified
'Molinity'	moles per kg of seawater	mol kg^{-1} mol $(kg\text{-}sw)^{-1}$	Recommended unit. Conservative with changes in pressure and temperature.(But name is not well recognized).
Molality	moles per kg of H_2O	mol $(kg\text{-}H_2O)^{-1}$	Used mainly by physical chemists (often confused with 'molinity').
Weight Ratio	mass of solute per unit mass of solvent	Various. e.g. ppb = parts per billion, $\mu g\ kg^{-1}$ ppm = parts per million, mg kg^{-1}	Used mainly by engineers and pollution chemists. Not useful for chemical calculations. Definitions often vague. Potentially confusing.

Major Constituents of Seawater

- Almost all elements in the Periodic Table that are found on Earth are found in the ocean (about 92 elements).

- 2 are exclusively human-derived (Pu and Am). They are now present!

- Francium (Fr) probably does not exist in the ocean. $t_{0.5}$ of only 22 minutes. Total amount on Earth < 30g.

- ‚Major‘ constituents are defined as those with concentrations in *normal seawater* that are > 1 mg $(kg\text{-}sw)^{-1}$ (> ~50 μmol kg^{-1})

<u>Remember:</u> (kg-sw) refers to a kilogram of seawater and 1 liter of *typical seawater* weighs about 1.025 kg at 20°C).

Concentrations of the Major Constituents in surface seawater

		At salinity (PSS 1978): $S = 35.000$		
	mg kg^{-1} S^{-1}	*g/kg*	*mmol/kg*	*mM*
Na^+	308.0	10.781	468.96	480.57
K^+	11.40	0.399	10.21	10.46
Mg^{++}	36.69	1.284	52.83	54.14
*Ca^{++}	11.77	0.4119	10.28	10.53
*Sr^{++}	0.227	0.00794	0.0906	0.0928
Cl^-	552.94	19.353	545.88	559.40
$SO_4^=$	77.49	2.712	28.23	28.93
*HCO_3^-	3.60	0.126	2.06	2.11
Br^-	1.923	0.0673	0.844	0.865
$B(OH)_3$	0.735	0.0257	0.416	0.426
F^-	0.037	0.00130	0.068	0.070
Totals	1004.81	35.169	1119.87	1147.59
*Alkalinity	—.—	—.—	2.32	2.38
Everything else	—.—	~0.03	—.—	—.—
Water	—.—	~964.80	~53,555.	~54,881.

* = non-conservative

Constancy of Composition

- Salinity is a measure of the dissolved salt content of seawater.

  Originally expressed as *(g salt)/(kg-sw)* or ppm (parts-per-thousand) or ‰ (per mille), the quantity is now defined as being dimensionless (no units).

  (We speak only of a ‚salinity of 35')

  Exact definitions and measurement techniques have varied over time.

- Mean salinity of the ocean is ~35

- Variation of salinity through most of the ocean is < ±7%

Conservative Behaviour

Salinity varies from place to place BUT:

Most, *but not all*, of the major constituents of seawater are

→ ***‚conservative‘*.**

i.e. they are found in constant proportions to salinity throughout the open ocean from surface to bottom.

Constituents that are NOT found in constant proportion to salinity are:

‚non-conservative‘

Big Questions: *Why is the sea salty?*

How is seawater composition regulated?

Why Conservative and Non-Conservative?

- Conservative elements have to have relatively long residence times:

  (Residence time >>> oceanic mixing time of ~1000 years)

- Strong non-conservative behaviour occurs when

  residence time ~ or < ocean mixing-time.

  or

  there are strong localized sources and sinks in different parts of the ocean (e.g. biologically-utilised elements)

Steady-state vs. Equilibrium

Steady-state:

- production and removal rates are the same
- absence of change over time
- input = output

Not the same as

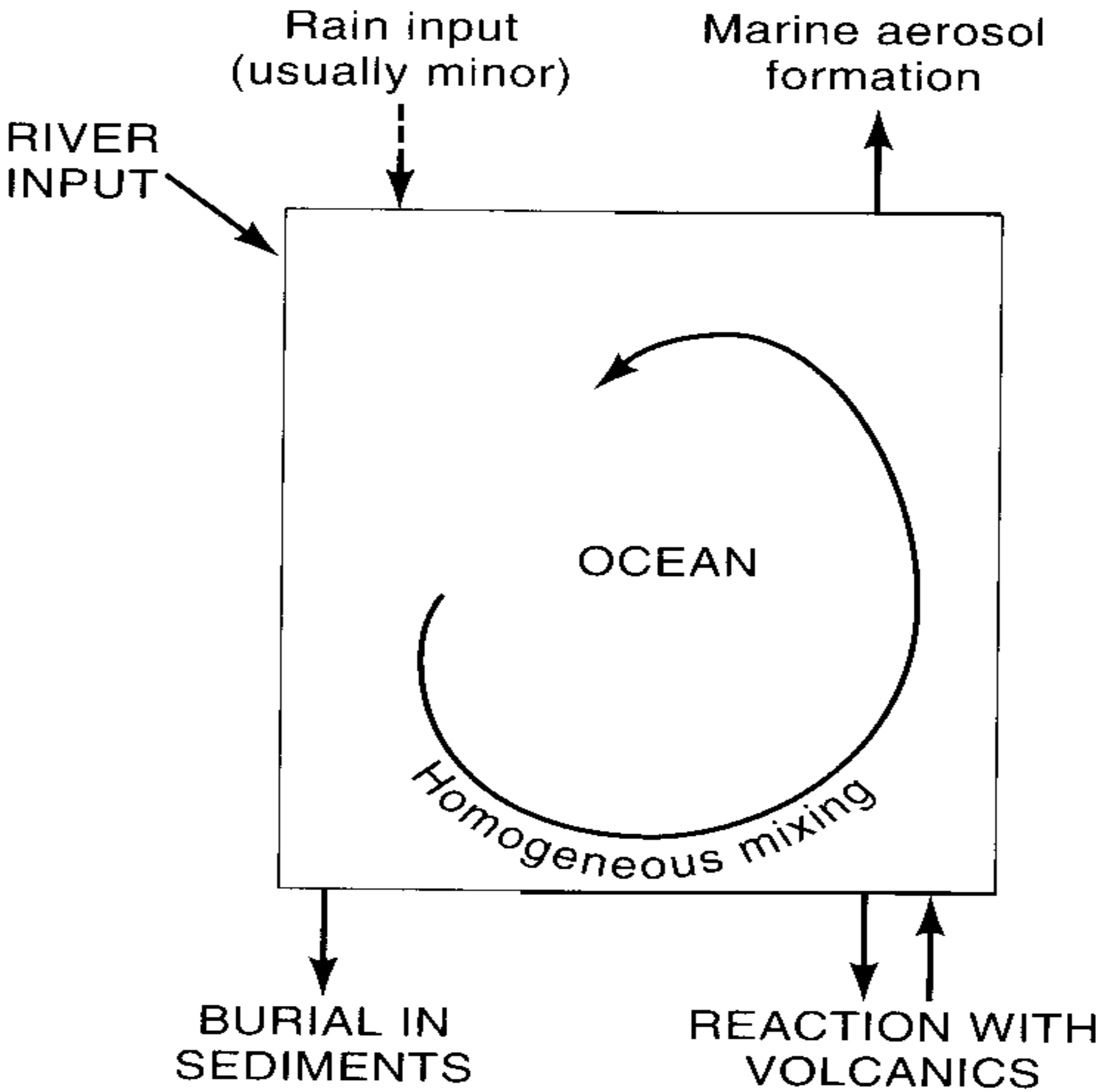
Equilibrium:

- in chemistry, when concentrations of reactants and products are in a state of minimum Gibbs energy for a reaction.

Seawater composition is NOT in equilibrium (e.g. with the solid earth and atmosphere) but IS for most major constituents (not all) in steady-state

For example: CO_2 and (HCO_3^-) are NOT in steady-state

One-Box Model



Residence time calculations

Flux: amount, per unit time, added
Reservoir: amount present

$$F_{in} \longrightarrow \boxed{R} \dashrightarrow F_{out}$$

$$t = \frac{R}{F}$$

$F_{in} \equiv F_{out}$ (assumed)

R = constant (steady-state)

Residence time of Water in the Ocean

$$R\ (\text{volume}) = 1370 \times 10^6\ \text{km}^3$$
$$= 1.4 \times 10^9\ \text{km}^3$$

$$F\ (\text{river influx}) = 37 \times 10^3\ \text{km}^3/\text{yr}$$
$$= 3.7 \times 10^4\ \text{km}^3/\text{yr}$$

$$t = \frac{R}{F}$$

$$= \frac{1.4 \times 10^9\ \text{km}^3}{3.7 \times 10^4\ \text{km}^3/\text{yr}}$$

$$\approx \boxed{4 \times 10^4\ \text{years}}$$

Residence time of Chloride in the Ocean

$$R\ (\text{amount}) = [\text{Cl}]_{sw} \times \text{Ocean Volume}$$

$$[\text{Cl}]_{sw} = 19\ \text{g/kg}$$

$$F\ (\text{river influx}) = [\text{Cl}]_{rw} \times \text{Global River Discharge}$$

$$[\text{Cl}]_{rw} \approx 6\ \text{mg/kg}$$

$$t = \frac{R}{F}$$

$$= \frac{[\text{Cl}]_{sw}}{[\text{Cl}]_{rw}} \times \frac{\text{Ocean Volume}}{\text{Global River Discharge}}$$

$$= \frac{19}{6 \times 10^{-3}} \times 4 \times 10^4$$

$$= 3 \times 10^3 \times 4 \times 10^4$$

$$= \boxed{1.2 \times 10^8 = 120\ \text{million years}}$$

Constituent	River water	Seawater	Enrichment factor (ocean vs. river)	Mean residence time (ocean)
	(mmol kg^{-1})	(mmol kg^{-1})		(10^6 years)
Na^+	0.22	468.96	2093	75
Mg^{2+}	0.14	52.83	383	14
Ca^{2+}	0.33	10.28	31	1.1
K^+	0.03	10.21	307	11
Sr^{2+}	0.0003	0.09	265	12
Cl^-	0.16	545.88	3366	120
SO_4^{2-}	0.09	28.23	329	12
HCO_3^-	0.85	2.06	2	0.1
Br^-	0.0003	0.84	3372	100
$B(OH)_3$	0.0002	0.42	2572	10
F^-	0.005	0.07	13	0.5

Non-conservative substances:

- Vary independently from salinity
- Often chemically or biologically-reactive substances
- Radioisotopes and decay products
- Or have short oceanic residence times (e.g. particle-reactive)