EPFL

FOOD CHEMISTRY

Chapter 2 : Water

2.1 IMPORTANCE OF WATER IN FOOD

Roles of water

→ Solvent	Dissolution of salts and polar compounds Transport medium
→ Reactant	Numerous biochemical reactions Hydrolysis Oxydation
→ Structuring agent	Maintains the tridimensional structure of proteins and macromolecules Maintains the rheological properties of emulsions and gels
→ Texturing agent	Maintains the structure of food (eg. bread)

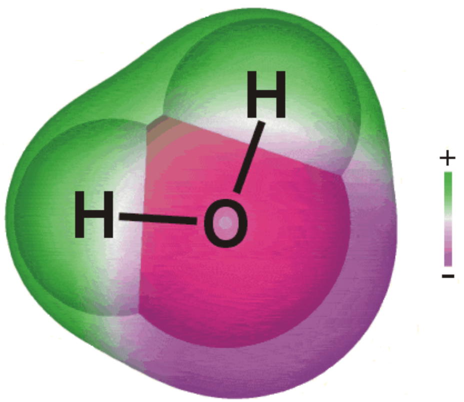
2.1 IMPORTANCE OF WATER IN FOOD

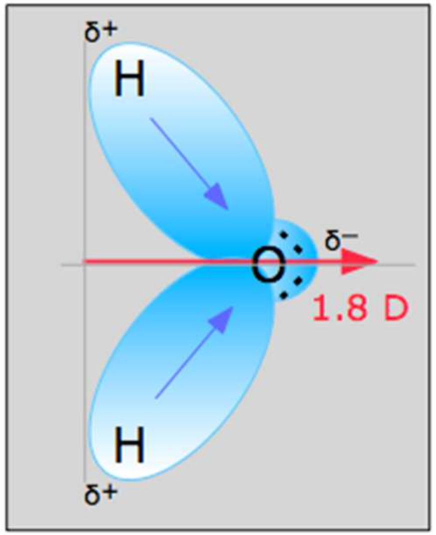
Amount of water in various foods

Drinking water	100%	Bread	35%
Tomatoes	94%	Honey	20%
Apple juice	88%	Rice	13%
Milk	87%	Wheat flour	12%
Eggs	75%	Corn flakes	6%
Beef steak	72%	Roasted coffee	4%
Emmenthal cheese	35%	Milk chocolate	2%

2.2 MOLECULAR STRUCTURE

Shape and electronic distribution of a water molecule





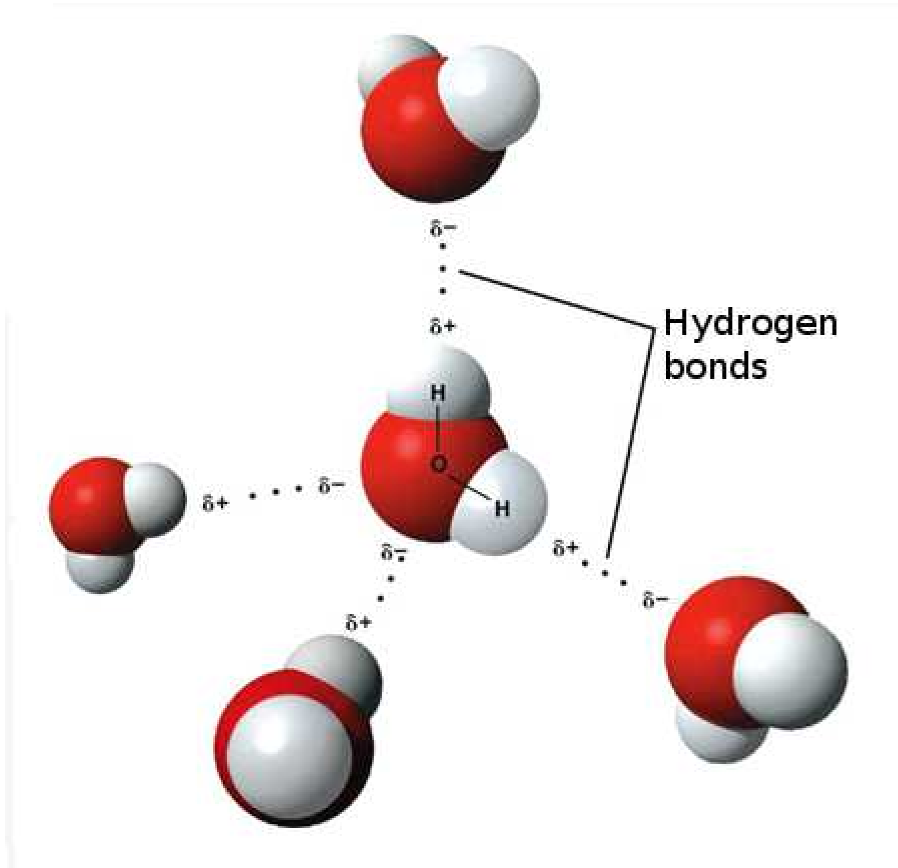
Ab initio calculations on isolated molecules do not confirm the presence of significant directed electron density where lone pairs are expected by the usual sp^3 hybridization model. The negative charge is more evenly concentrated along the line between where these lone pairs would have been expected, and lies closer to the center of the O-atom.

$$\vec{\mu} = q \cdot \vec{d}$$

$$\mu = 1{,}8 \text{ D}$$

$$1 \text{ D} = 3{,}34 \cdot 10^{-30} \text{ C m}$$

2.2 MOLECULAR STRUCTURE
Water and hydrogen bonding



O-H bond

Length = 96 pm

Energy = 460 kJ/mol

Hydrogen bond

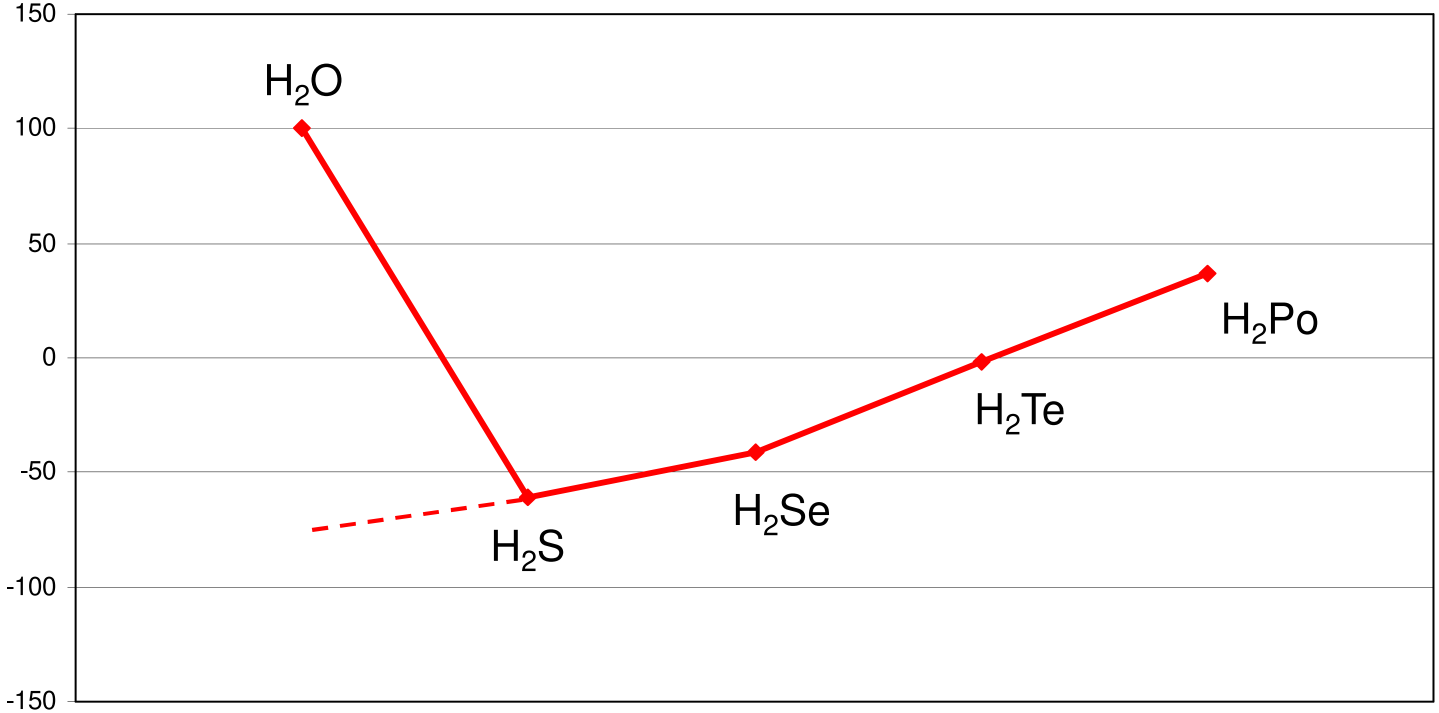
Length = ~180 pm

Energy = ~20 kJ/mol

Hydrogen bonding is in fact a dipole-dipole interaction, and is important only for O, N and F atoms.

2.2 MOLECULAR STRUCTURE

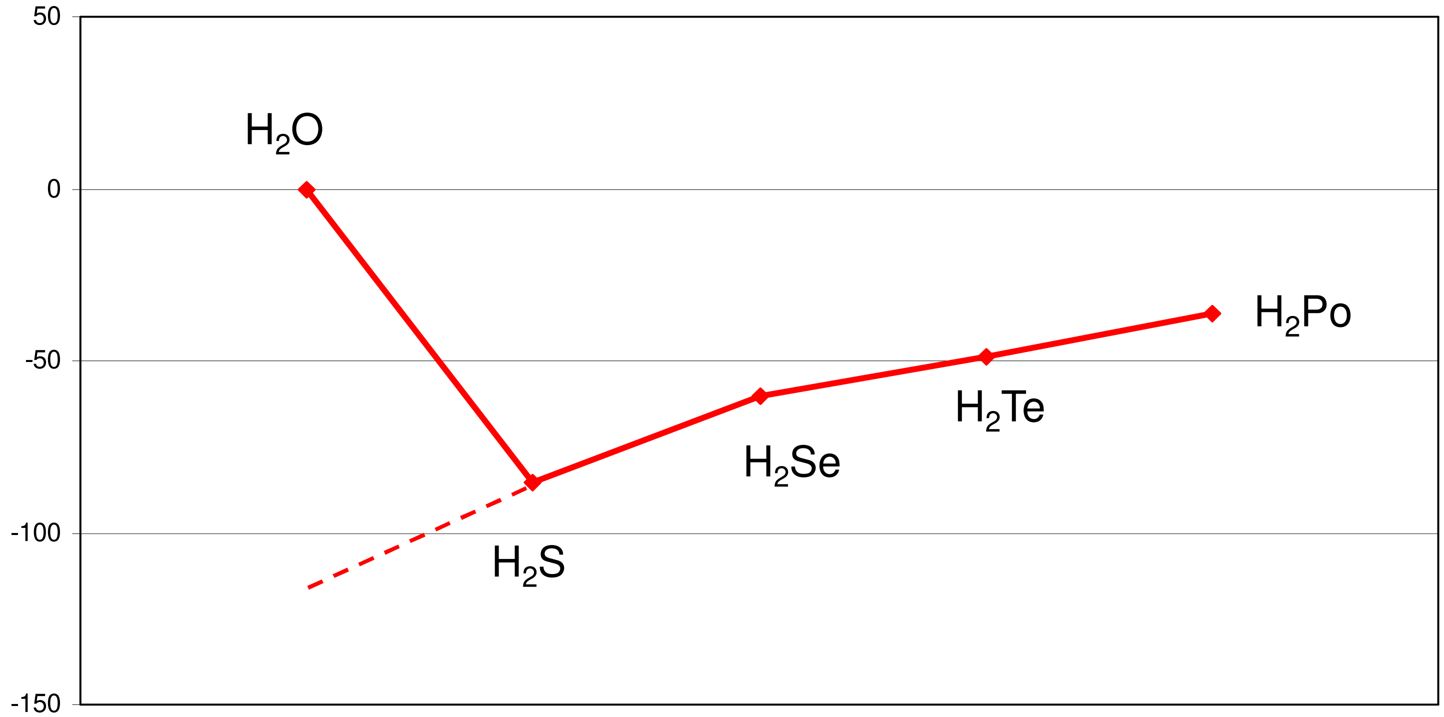
Boiling points of group VI A hydrides



Even at 100°C, the strong hydrogen bonding in H_2O requires more energy to vaporize the molecules than in other group VIA hydrides.

2.2 MOLECULAR STRUCTURE

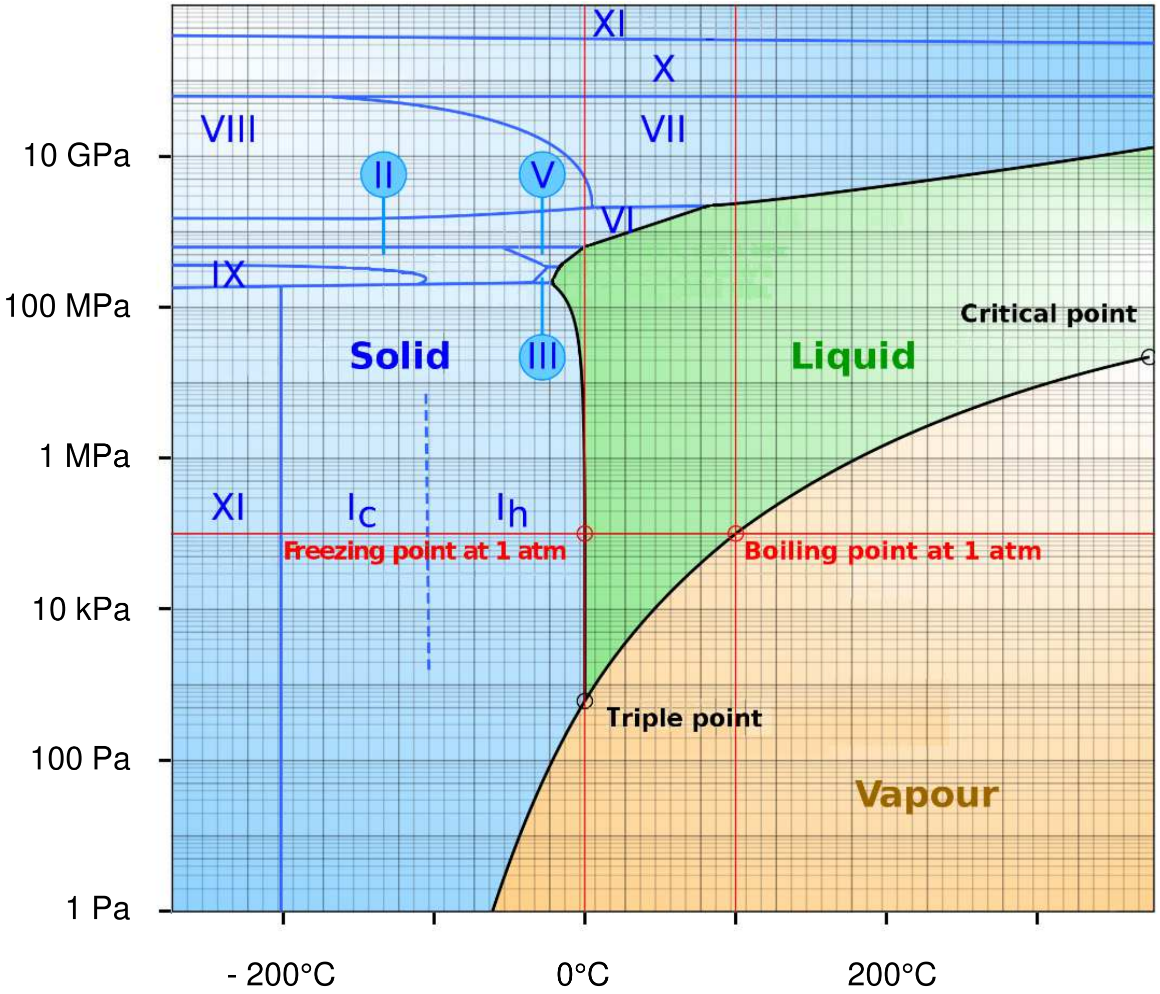
Melting points of group VI A hydrides



In normal ice, all water molecules participate in four hydrogen bonds (two as donor and two as acceptor) and are held relatively static. A large energy is required for breaking these bonds, which are much smaller (if any) in other VIA hydrides.

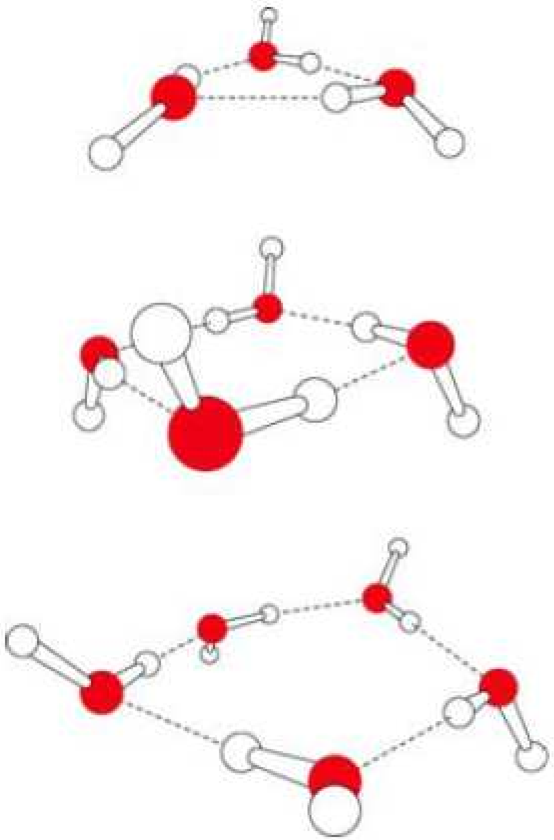
2.3 ICE AND LIQUID STRUCTURES

Phase diagram of water



2.3 ICE AND LIQUID STRUCTURES

Water molecules in the liquid state

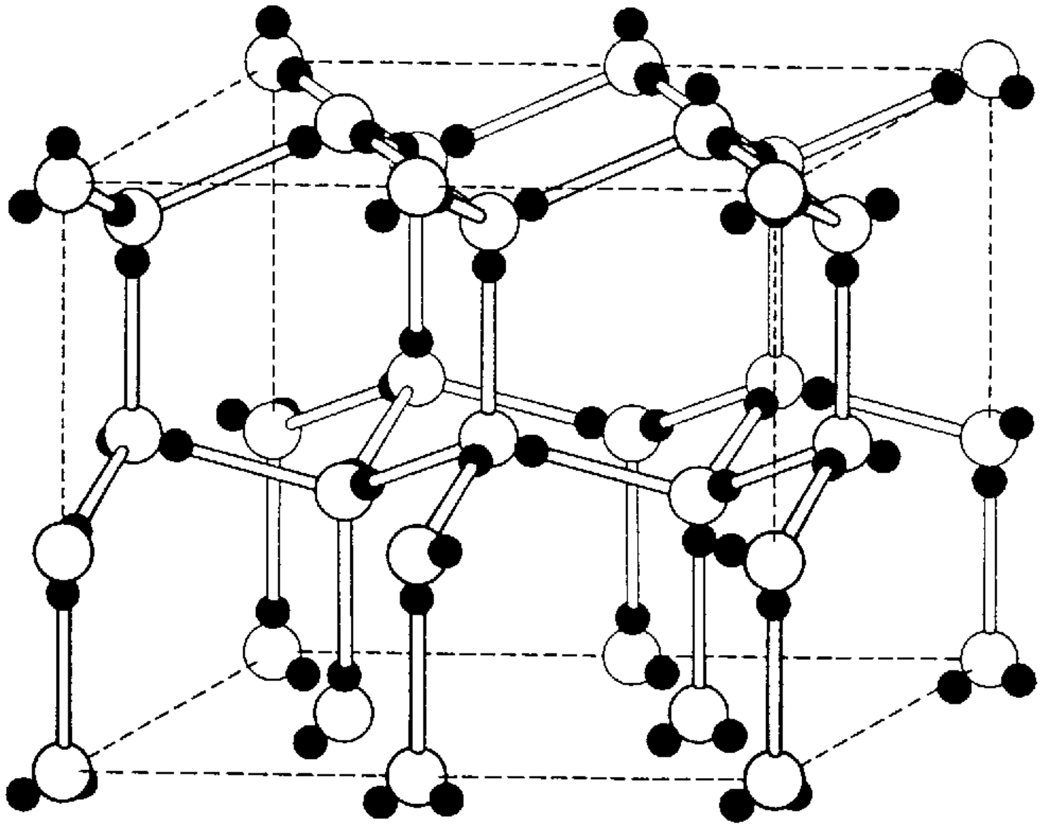


At room temperature, water molecules exist mainly as trimers, tetramers and pentamers.

The exchange rate of water molecules is very rapid (picosecond).

2.3 ICE AND LIQUID STRUCTURES

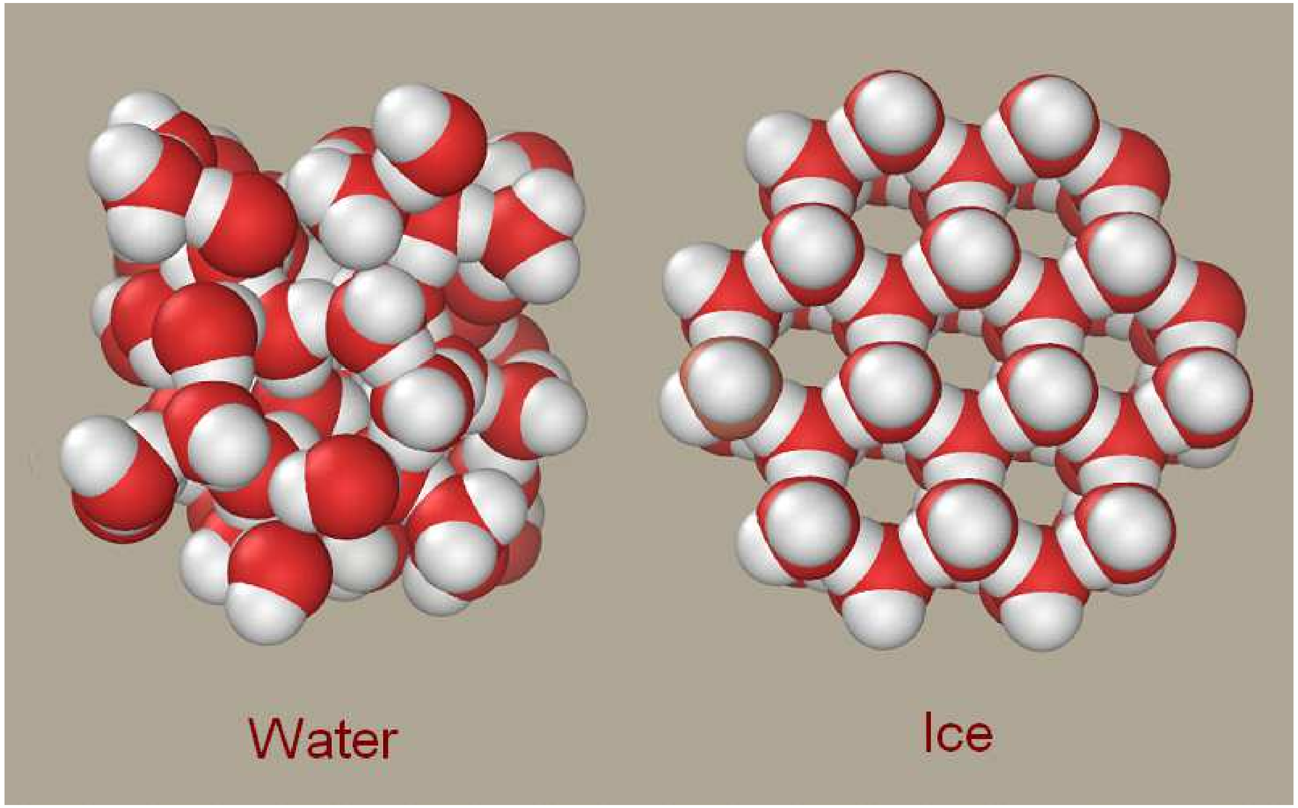
Water molecules in the solid state



Ordinary ice consists of a hexagonal close packed stacking arrangement. Each molecule is connected to four other ones.

2.3 ICE AND LIQUID STRUCTURES

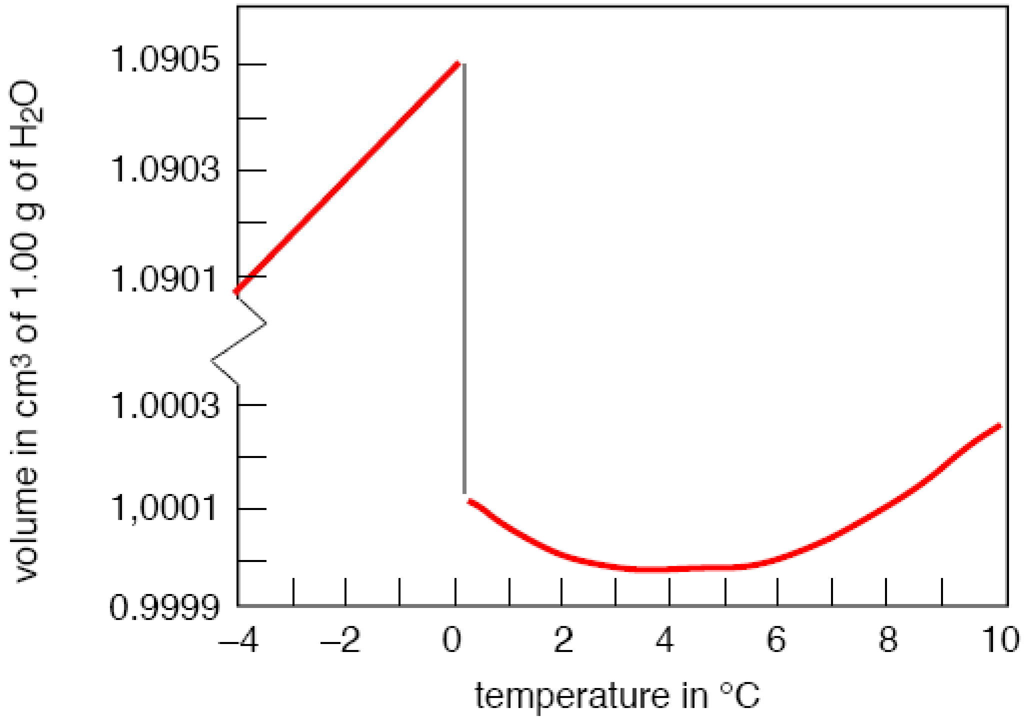
Models of ice and liquid water



Packing is closer in water than in ice !

2.3 ICE AND LIQUID STRUCTURES

Specific volume of water as a function of temperature



2.3 ICE AND LIQUID STRUCTURES

Density of water and ice

	Coordination number	O–H ······ O distance
Ice (0°C)	4.0	276 pm
Water (2°C)	4.4	290 pm
Water (83°C)	4.9	305 pm

Increase in CN and O······H distance have opposite influences. The maximum density is reached at 4°C. As a consequence, ice float at the surface of water.

➡ Another important consequence is the fact that on freezing, water occupies a larger volume than in the liquid state. This can cause a rupture of cell membranes (ie. thawed meat defects).

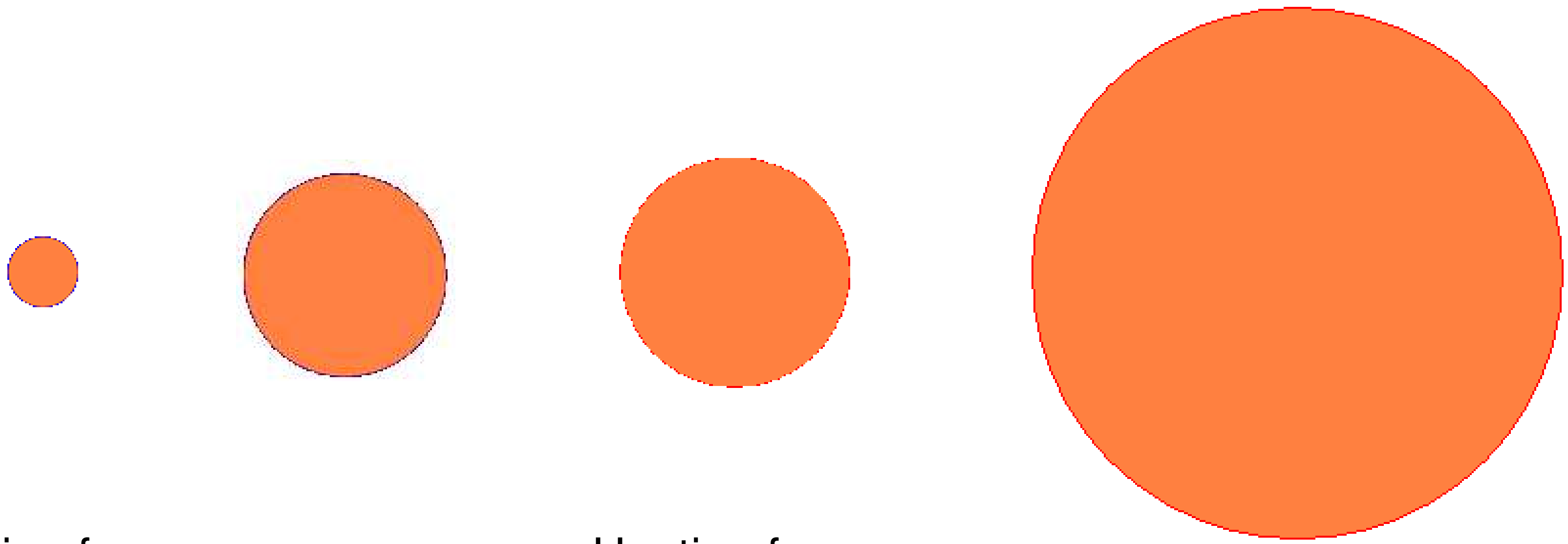
2.3 ICE AND LIQUID STRUCTURES
Phase transitions

Heat capacity (ice) : $C_p = 2.06$ J/g.K

Heat capacity (water) : $C_p = 4.18$ J/g.K

Heat of fusion : $\Delta H_{fus} = 334$ J/g

Heat of vaporisation : $\Delta H_{vap} = 2260$ J/g



Heating from -18°C to 0°C

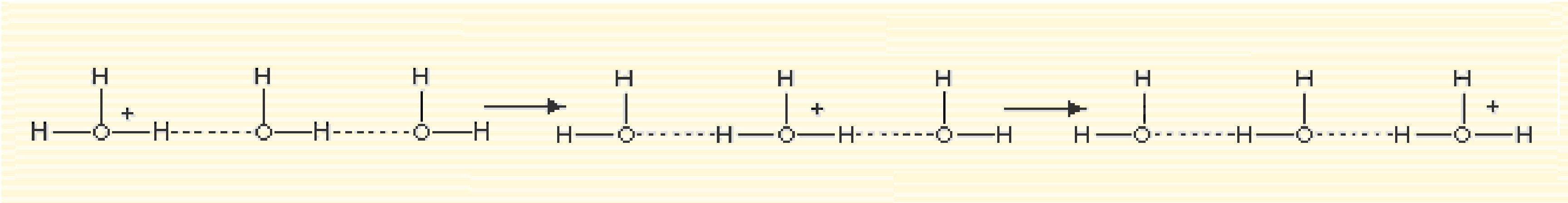
Melting

Heating from 0°C to 100°C

Vaporisation

2.4 REACTIVITY

The Grotthus mechanism

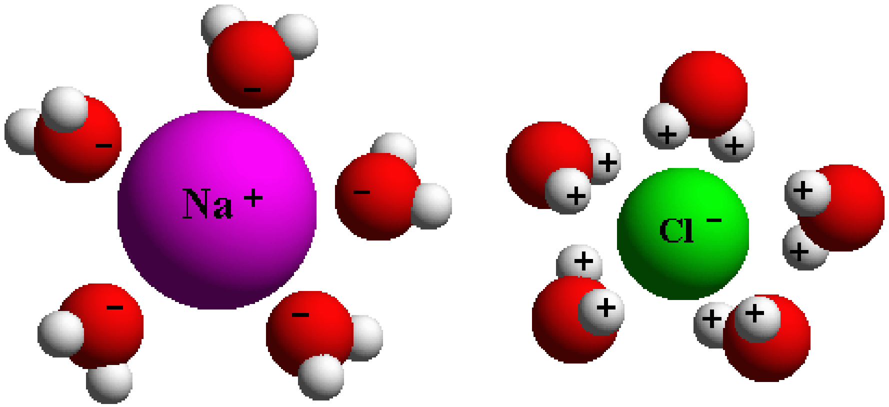


Exchange of protons occur extremely rapidly ($v > 10^{12}\ s^{-1}$), surpassing all other ions mobilities by a factor of 4 – 5.

Exchange of OH- occurs via the same mechanism, which is only ~40% slower.

➡ Water is an excellent medium (and often plays a catalytic role) for acid/base and oxydo-reduction reactions.

2.5 WATER - SOLUTE INTERACTIONS
Ionic and polar compounds



Ionic and polar compounds greatly hinder mobility of water molecules, the strength of a water-ion bond being much greater than a hydrogen bond. Even in dilute solutions, ions have structure breaking effect (solution can be more or less fluid than pure water).

→ Conformation of proteins and stability of colloïds can be greatly influenced by the ions in solution (salting-in / salting-out effects).

2.5 WATER - SOLUTE INTERACTIONS
Diffusion in water

Diffusion coefficient of water at 25°C : $D = 2.6 \cdot 10^{-9}\ m^2/s$

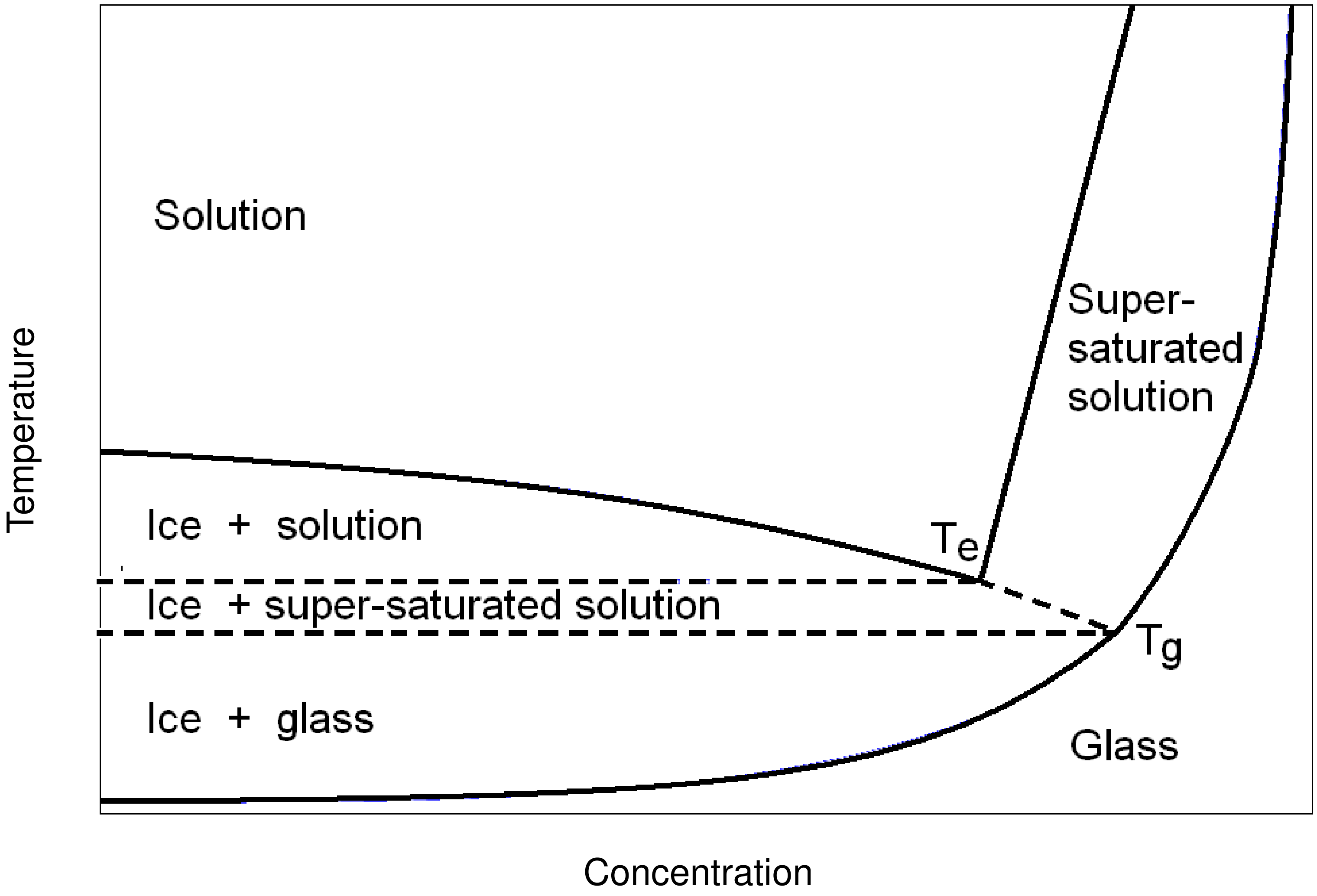
$$L = \sqrt{D \cdot t}$$

➡ For a molecule in water, in 11 h, $L = 1$ cm.

➡ It requires ~ 10 days for NaCl to penetrate inside a cured ham.

2.5 WATER - SOLUTE INTERACTIONS

Phase diagram of a sucrose solution



2.5 WATER - SOLUTE INTERACTIONS
The effect of freezing

As a solution cools, ice is produced and the solution becomes more and more concentrated. The effect on the unfrozen phase can be very important, especially inside the animal or vegetal cells :

- ► Properties such as pH, redox potential or viscosity are modified
- ► Supersaturated oxygen and carbon dioxyde may be expelled
- ► Reaction rates can be increased (!)

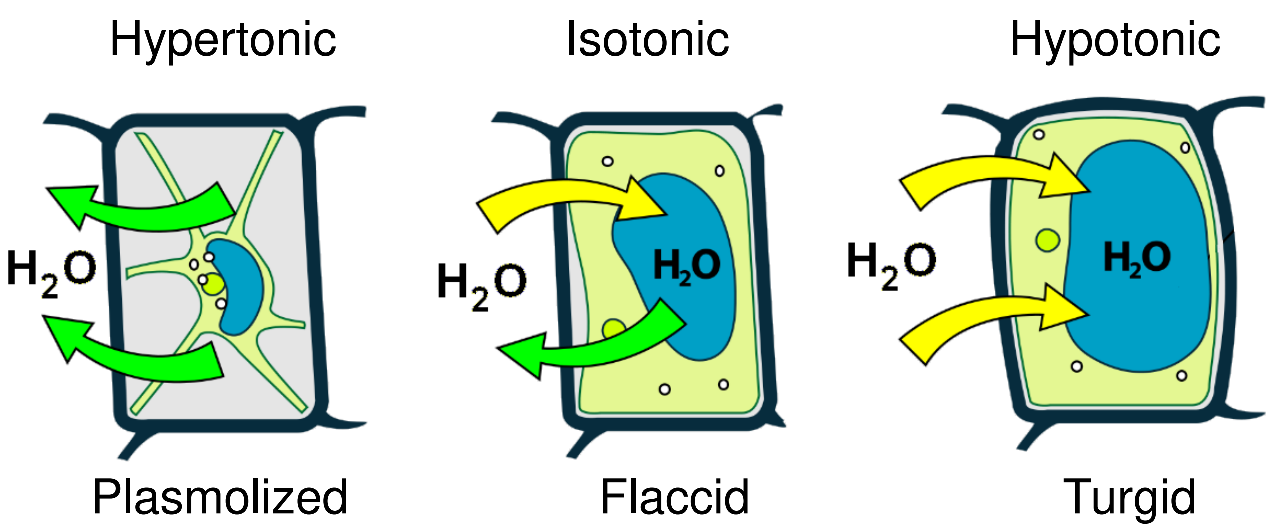
A favourable example is the production of sweet wines, either by cryoconcentration or using the so called « Ice wine technique ».

2.5 WATER - SOLUTE INTERACTIONS
The osmotic effect on vegetal cells

Semi-permeable membranes can separate water from dissolved solutes. The driving force for this separation is the osmotic pressure gradient.

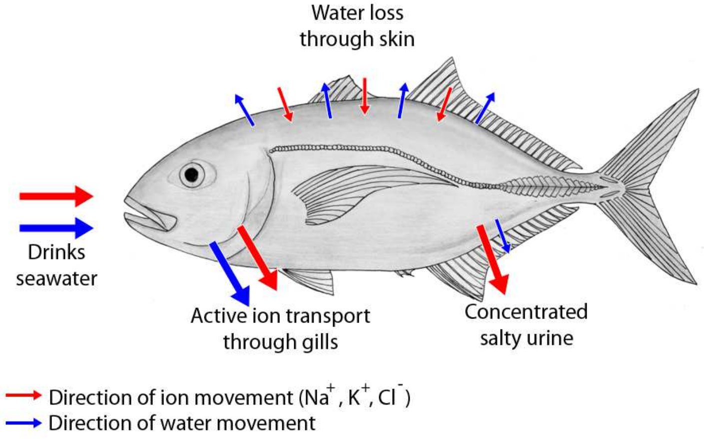
$$J_w = A\,(\Delta\pi - \Delta P)$$

J_w : water flux
A : hydraulic permeability of the membrane
$\Delta\pi$: difference in osmotic pressures on both sides
ΔP : difference in hydrostatic pressure

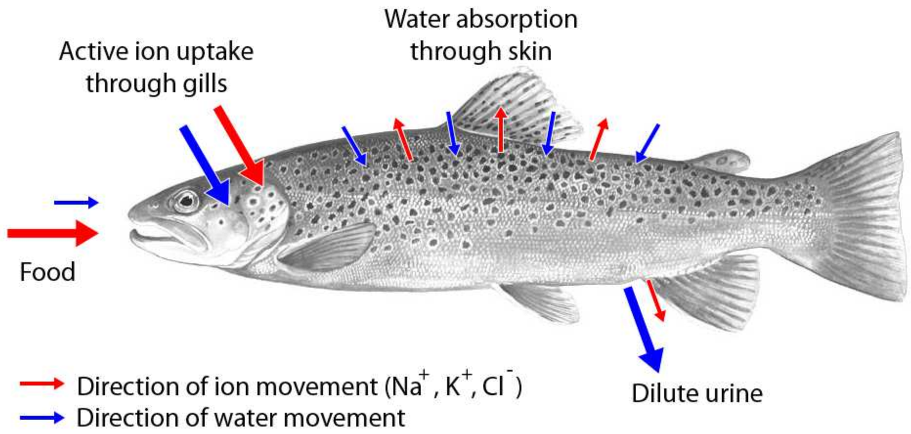


2.5 WATER - SOLUTE INTERACTIONS
Osmoregulation in fishes

Sea water fish



Fresh water fish



Osmoregulation is the active regulation of the osmotic pressure of an organism's fluids to maintain the adequate water content.

2.5 WATER - SOLUTE INTERACTIONS
Osmoregulation in humans : Fluid balance

In the normal state, input and output are balanced : the water equilibrium is zero and its balance is neutral

Water input comes from :

- beverage intake (recommended diet : 1400 ml)
- water contained in food (850 ml)
- water produced by oxidation (350 ml)

Water output is excreted :

- as urine (1500 ml)
- with the stool (200 ml)
- in sweat (500 ml)
- by respiration (400 ml).

Under normal circumstances, only diuresis changes to compensate for variations in inputs, which may be important one day to another.

2.5 WATER - SOLUTE INTERACTIONS

Osmoregulation in humans : water pool

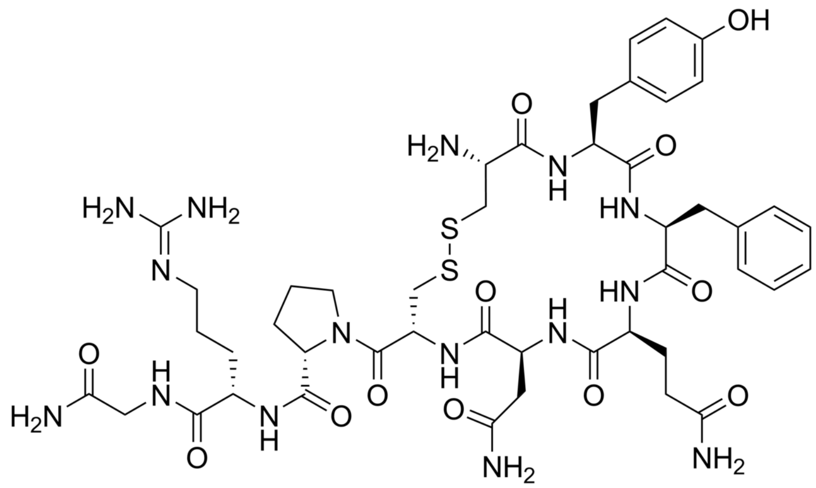
Water capital (or pool): amount of water which the body holds. Thus, the water pool is usually 40 liters for a person weighting 60 kg.

When someone becomes dehydrated, an alarm system set off in the brain, causing a stimulation of the thirst center. Water intake, and its reabsorption via the kidney, restores the balance.

In the elderly, the alarm system is easily disrupted and the thirst center less stimulated.

2.5 WATER - SOLUTE INTERACTIONS
Osmoregulation in humans : the role of vasopressin

Vasopressin increases the water permeability of distal tubule and collecting duct cells in the kidney, thus allowing water reabsorption and excretion of more concentrated urine, i.e., antidiuresis.



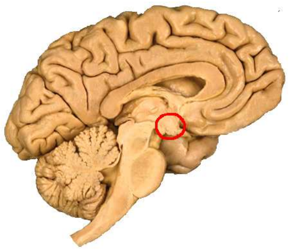
Vasopressin is secreted from the posterior pituitary gland in response to reductions in plasma volume, and to increases in the plasma osmolality :

Cys-Tyr-Phe-Gln-Asn-Cys-Pro-Arg-Gly

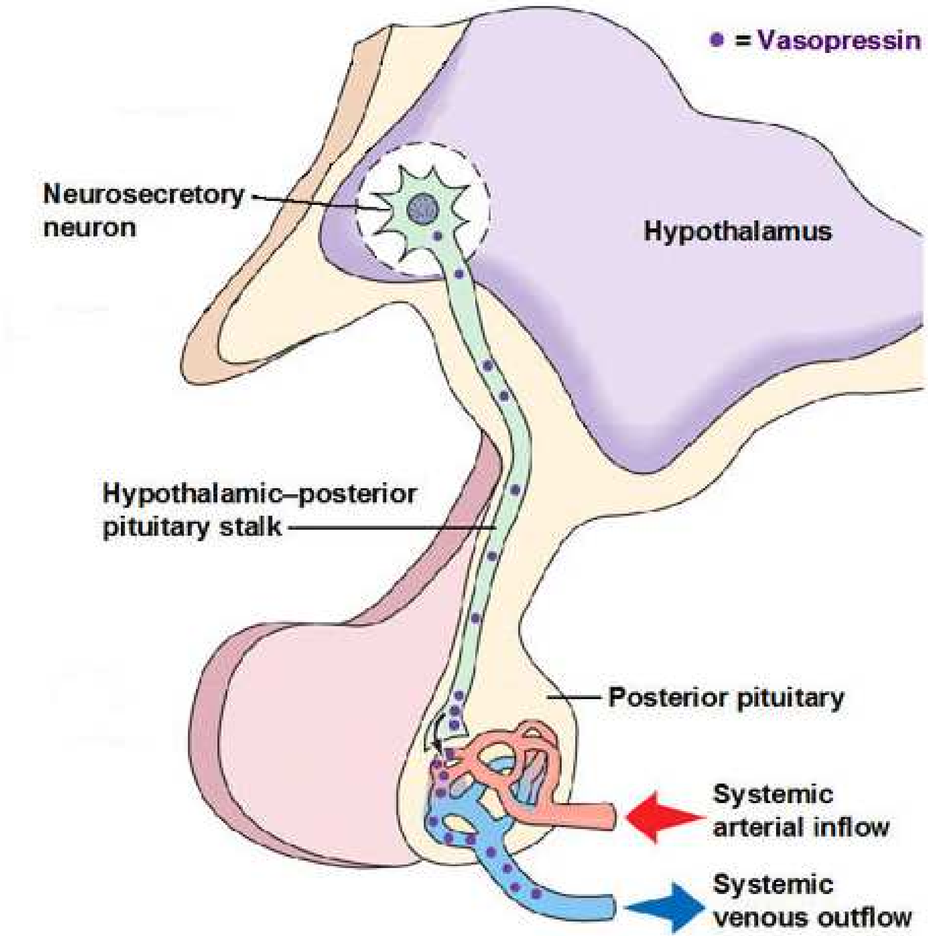
- Secretion in response to reduced plasma volume is activated by pressure receptors in the veins, and carotids.
- Secretion in response to increases in plasma osmotic pressure is mediated by osmoreceptors in the hypothalamus

2.5 WATER - SOLUTE INTERACTIONS

The role of vasopressin

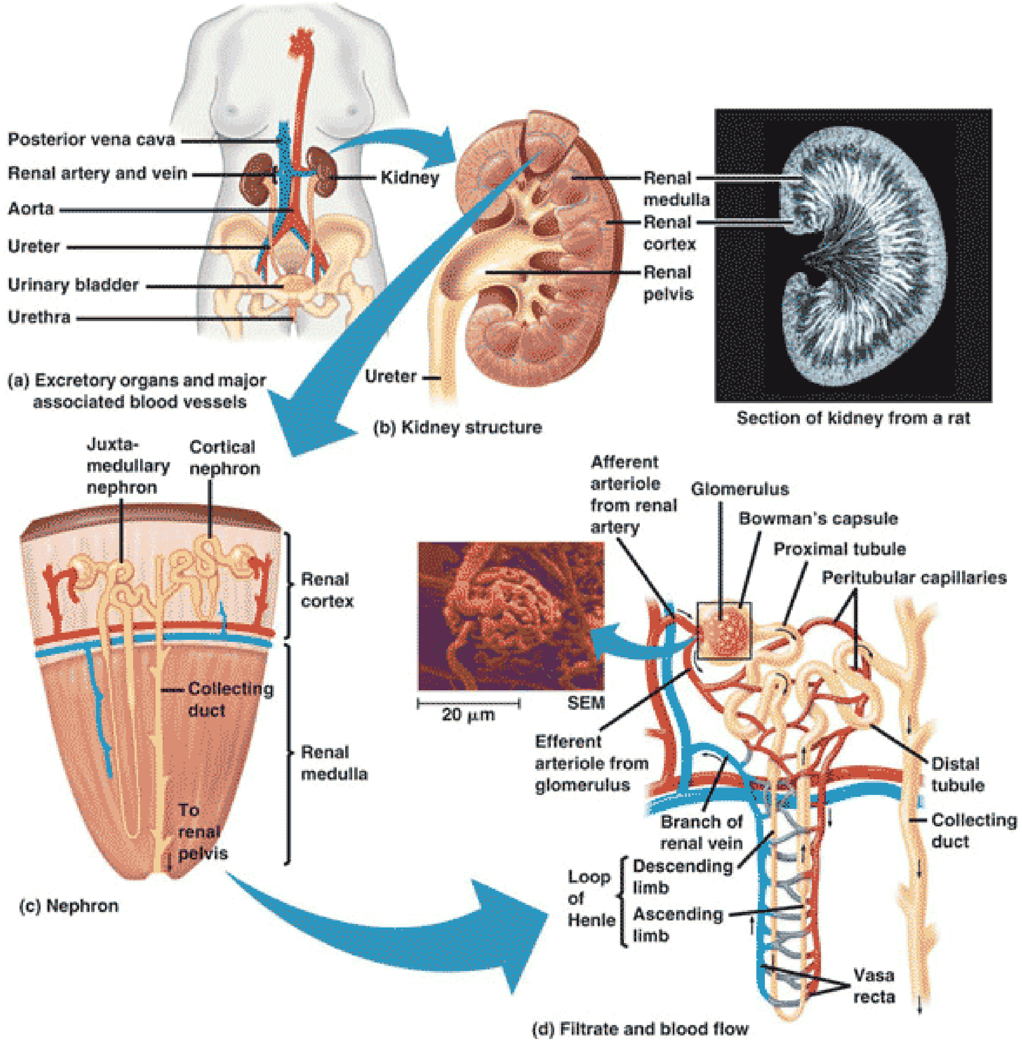


Hypothalamus and pituitary



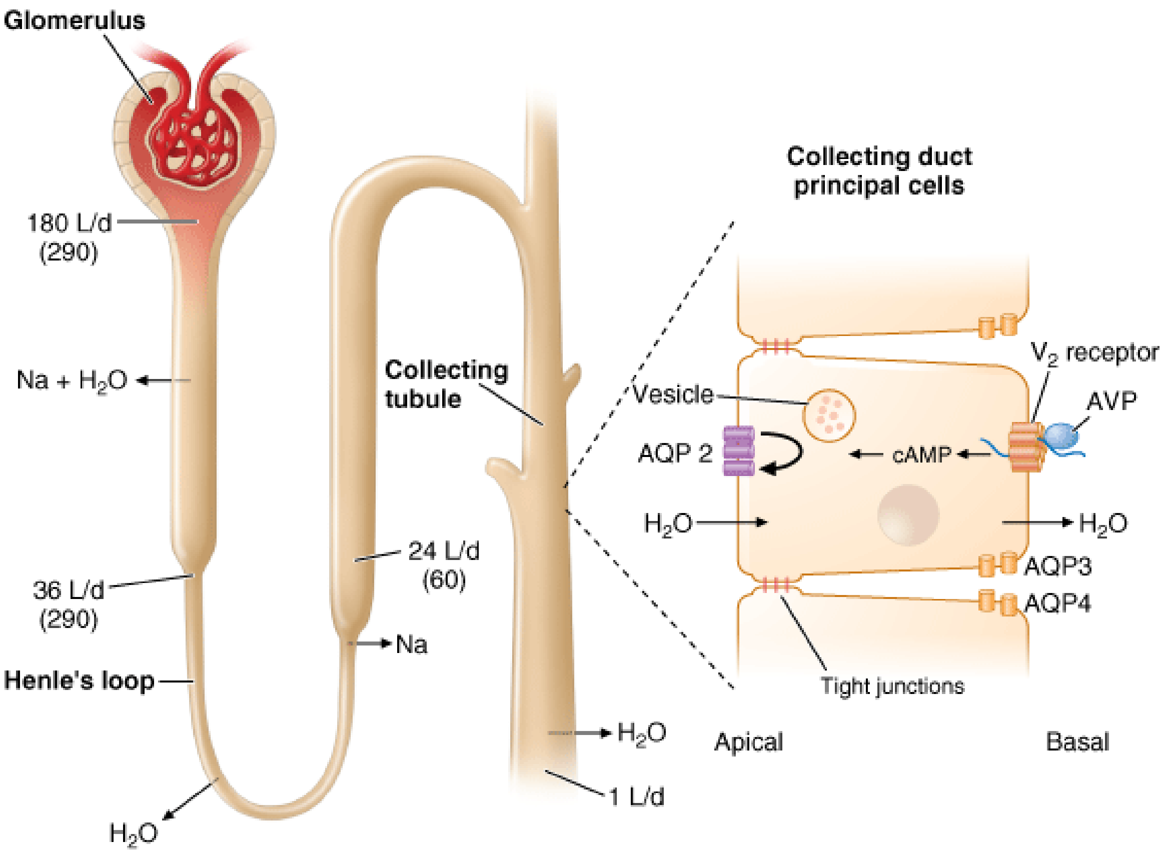
2.5 WATER - SOLUTE INTERACTIONS

human-excretory_system



2.5 WATER - SOLUTE INTERACTIONS

The role of vasopressin



Source: Fauci AS, Kasper DL, Braunwald E, Hauser SL, Longo DL, Jameson JL, Loscalzo J: *Harrison's Principles of Internal Medicine*, 17th Edition: http://www.accessmedicine.com

2.6 WATER ADSORPTION
Definition of water activity

Water activity is a measure of the energy status of the water in a system (free vs. bound water). Water activity is influenced by the following factors :

⇨ Interaction with dissolved species (e.g. salt or sugar) due to dipole-dipole, ionic, and hydrogen bonds.

⇨ Capillary effect (the vapor pressure of water above a curved liquid meniscus is less than that of pure water because of changes in the hydrogen bonding between water molecules).

⇨ Surface interactions in which water interacts directly with chemical groups on undissolved ingredients (e.g. starches and proteins) through dipole-dipole forces, ionic -, hydrophobic -, and hydrogen bonds.

2.6 WATER ADSORPTION

Activity of water

$$\mu = \mu_o + RT \ln \frac{P}{P_o}$$

$$\boxed{a_w = \frac{P}{P_o} = e\left(-\frac{\Delta\mu}{RT}\right)}$$

μ : chemical potential of water

μ_o : standard chemical potential of pure water

R : perfect gas constant

T : temperature

p : partial pressure of water

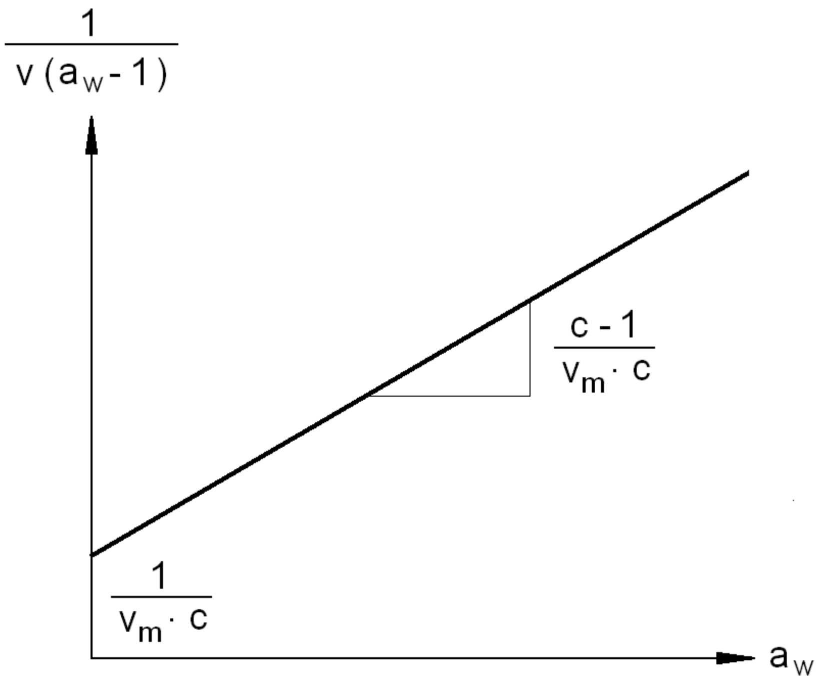
p_o : saturated vapor pressure

a_w : activity of water

2.6 WATER ADSORPTION

Brunauer, Emmet and Teller theory (BET)

BET equation : $$\frac{1}{v\,(a_w - 1)} = a_w\,\frac{c-1}{v_m \cdot c} + \frac{1}{v_m \cdot c}$$



C : constant

V_m : mass of water monolayer

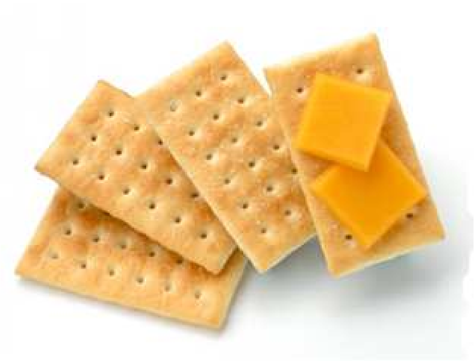
V : added mass of water

A_w : water activity

2.6 WATER ADSORPTION

Effect of water activity

Cheese and crackers



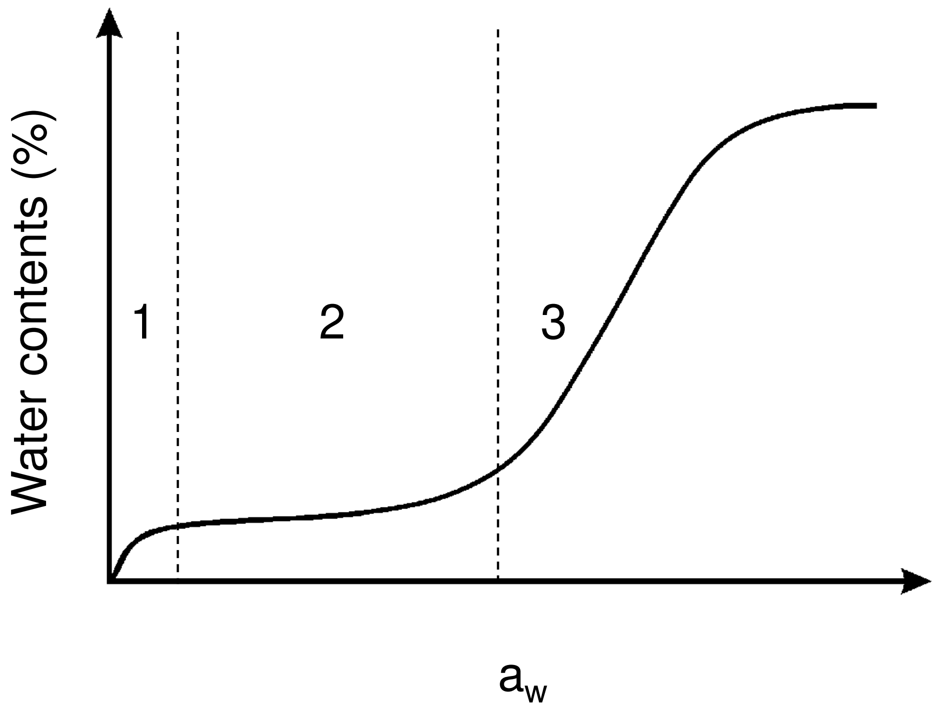
a_w	Moisture
0.97	38%
0.27	4%

↓ Equlibration
In closed wrapping

a_w	Moisture
0.84	32%
0.84	20%

Water flows from high to low a_w : Soggy cracker and dry cheese !

2.6 WATER ADSORPTION
Adsorption isotherms



1 Bound Water

a_w up to 0.3 (monomolecular layer)
Hydrogen bonded to compounds
Non freezable
Not available as solvent or reactant
Not available as transport medium

2 Water with restricted mobility

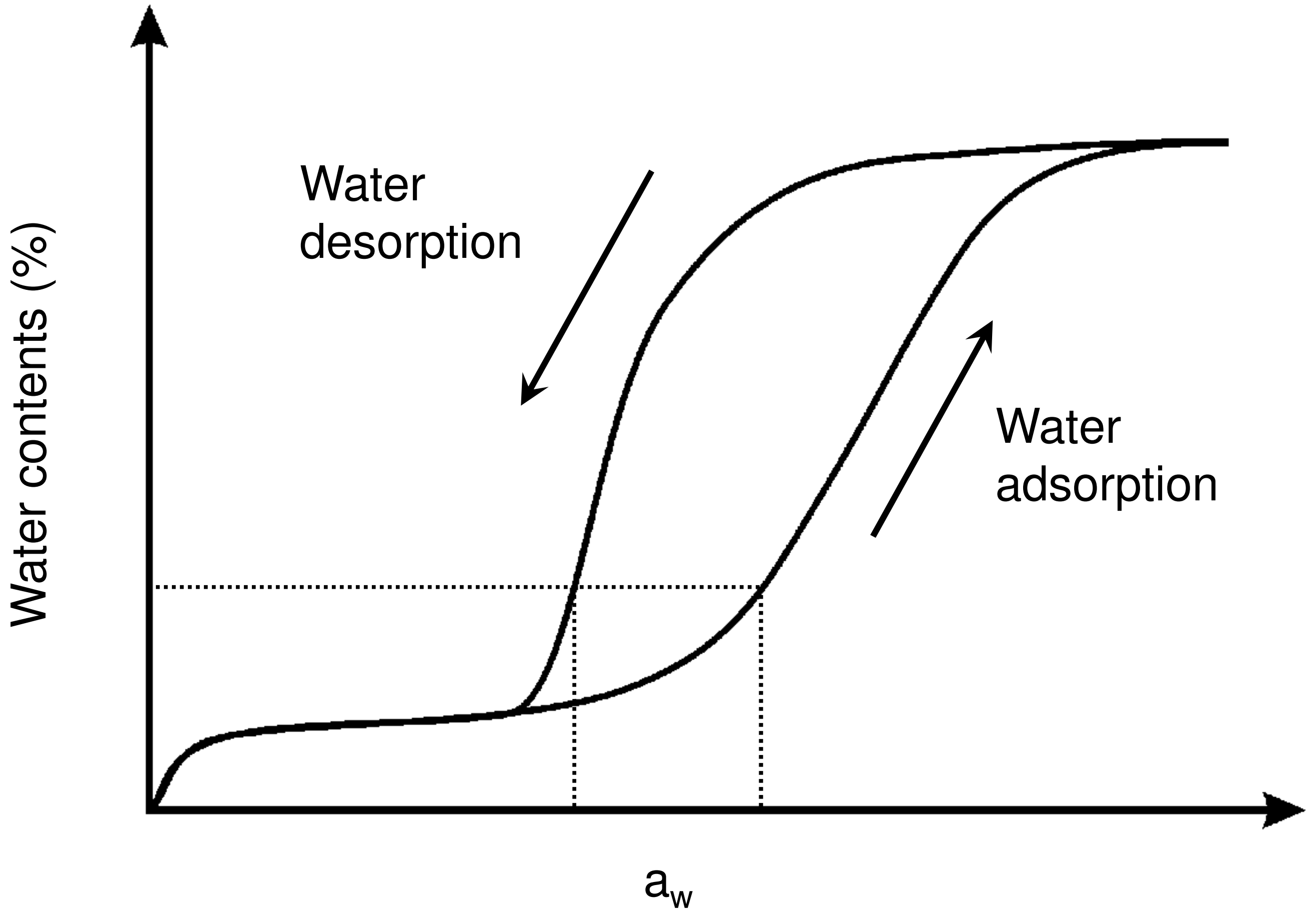
2nd and higher layers
Freezable
Available as solvent or reactant
Not available as transport medium

3 Free water

Mobile water
Freezable
Available as solvent or reactant
Available as transport medium

2.6 WATER ADSORPTION

Hysteresis of adsorption isotherms



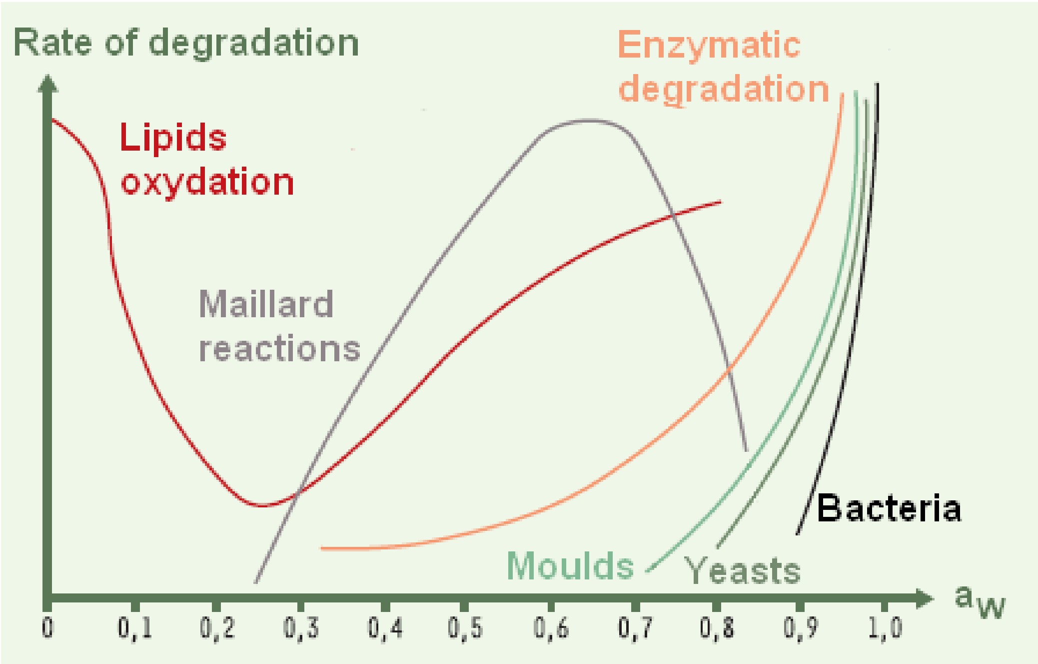
2.6 WATER ADSORPTION

Adsorption data

a_w	Cellulose	Whey protein	Sugar crystals	Oat bran	Breakfast cereals
0.10	2.1	4.5	0.01	3.7	3.0
0.30	3.7	8.0	0.3	7.5	4.0
0.45	5.0	9.4	0.6	8.8	5.5
0.55	5.1	11.0	1.6	10.4	7.0
0.75	8.9	14.6	2.4	14.6	15.0
0.85	19.8	16.8	44.5	17.5	33.0

2.7 WATER AND FOOD DEGRADATION

Effect of water activity on various spoilage mechanisms



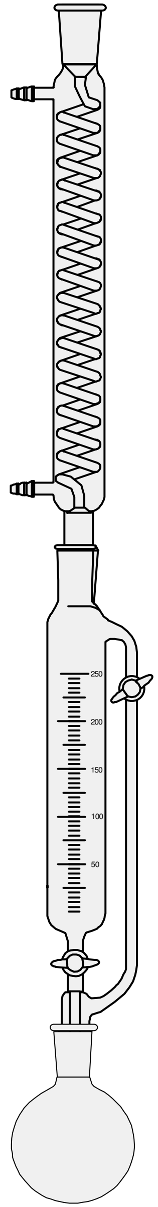
2.7 WATER AND FOOD DEGRADATION

Water activity and microorganisms growth

Food	***Water contents (%)***	***Water activity***	***Microbial growth***
Drinking water	100	1.00	
Vegetables, fruits, meat	95 – 60	0.99	Bacteria, moulds, yeasts
Bread, cheese	50 – 40	0.95	Bacteria, moulds, yeasts
Ham, cooked foods	40 – 20	0.90	Bacteria, moulds, yeasts
Marmelade	30 – 20	0.80	Moulds, yeasts
Cured meat	30 - 20	0.70	Moulds, yeasts
Honey, dried pasta	20 - 10	0.60	Moulds
Dehydrated foods	8 - 2	< 0.30	No growth

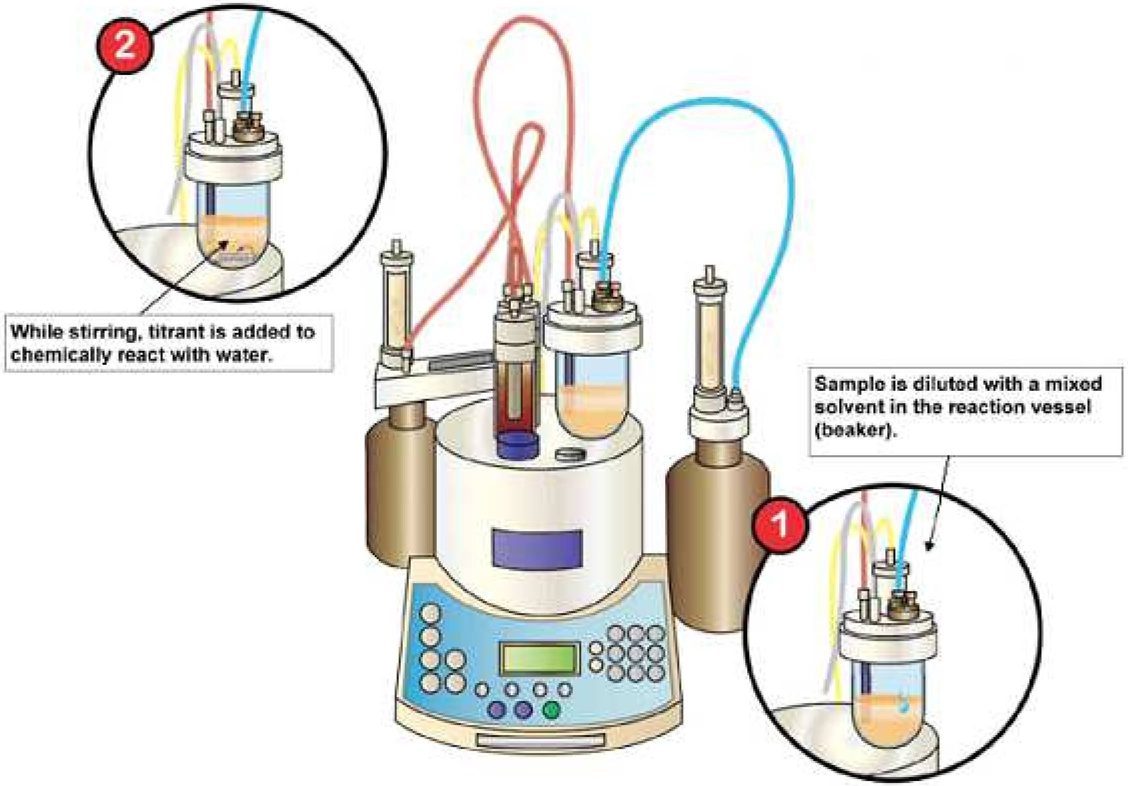
2.8 WATER ANALYSIS
Principles

- Dessication (heat, reduced pressure)
- Solvent extraction (toluene, xylene)
- Karl Fisher titration



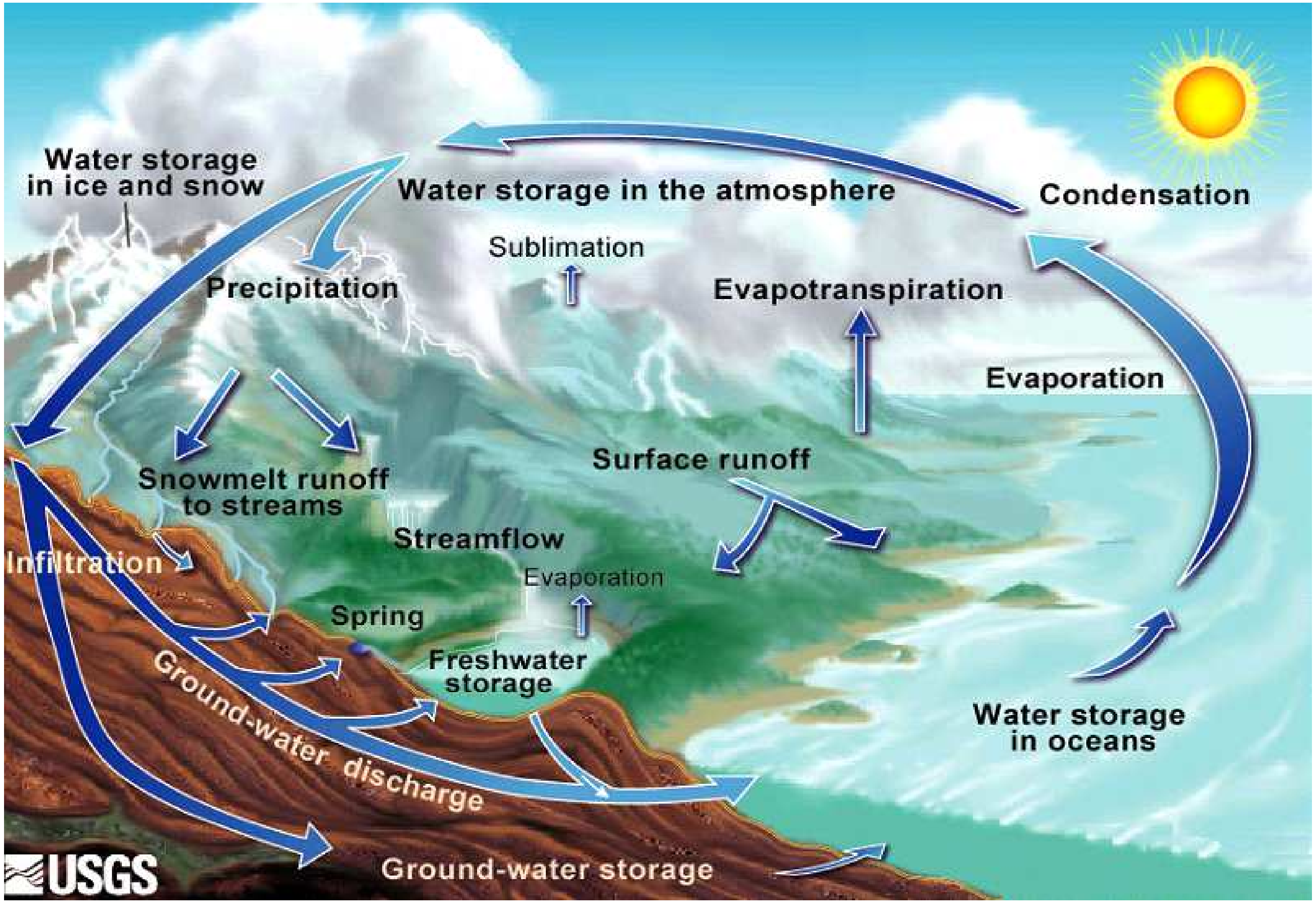
2.8 WATER ANALYSIS
Karl Fisher titration

$$CH_3OH + I_2 + SO_2 + H_2O \rightarrow 3\,H^+ + 2\,I^- + CH_3OSO_3^-$$



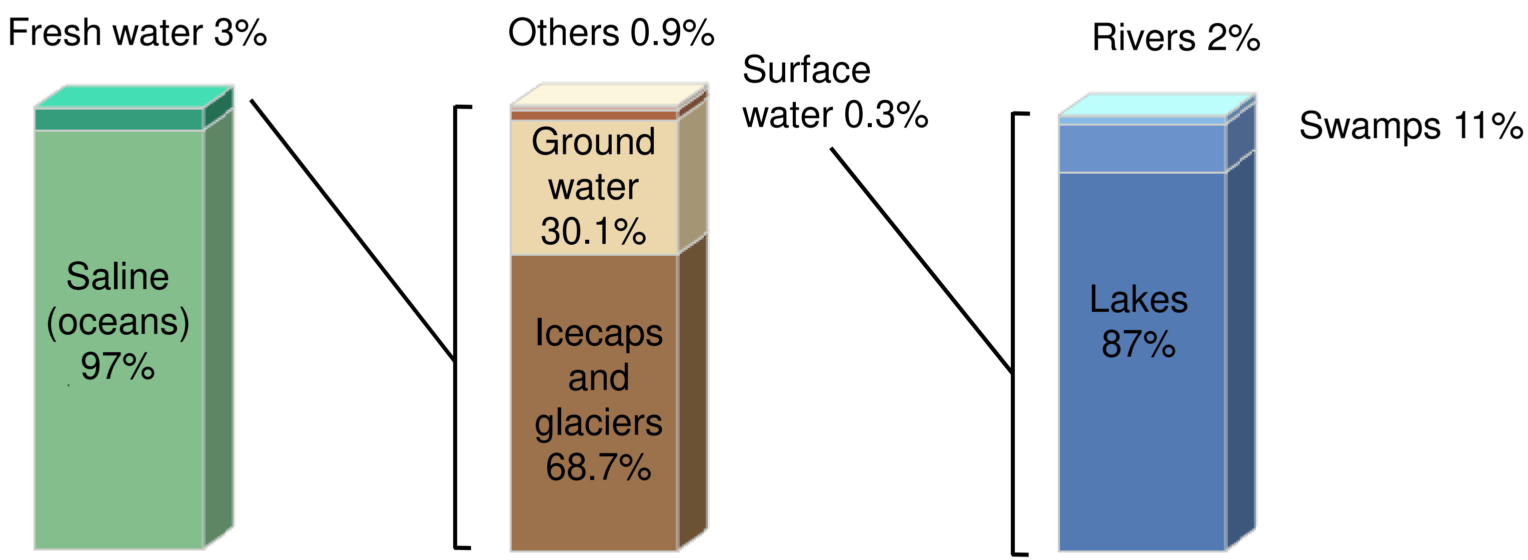
2.9 DRINKING WATER

The water cycle



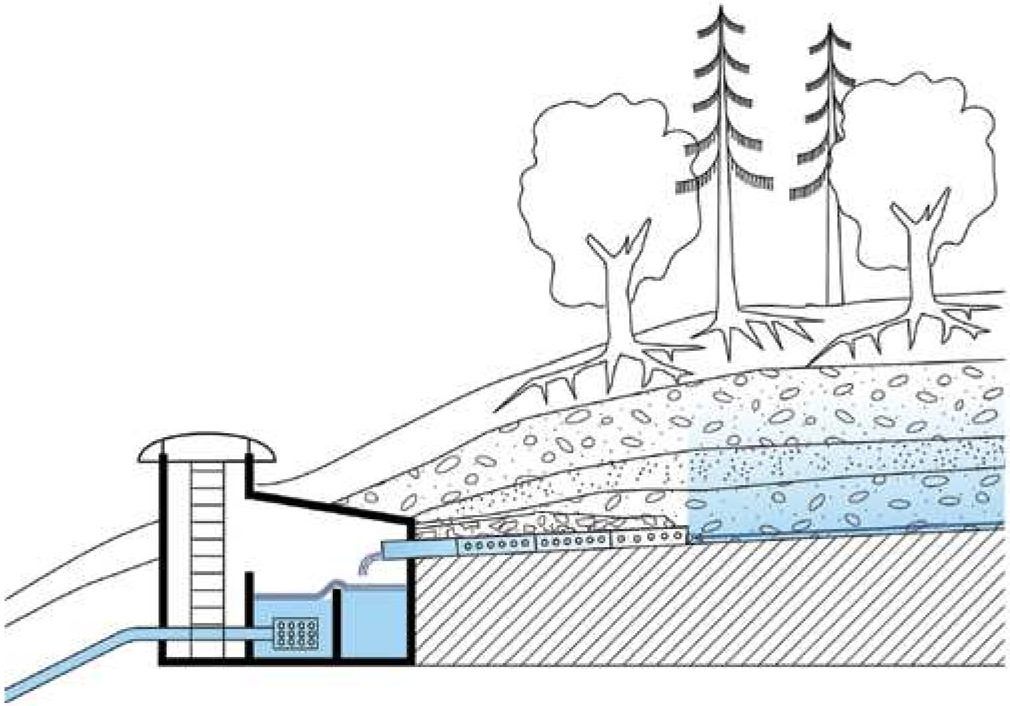
2.9 DRINKING WATER

Distribution of earth's water



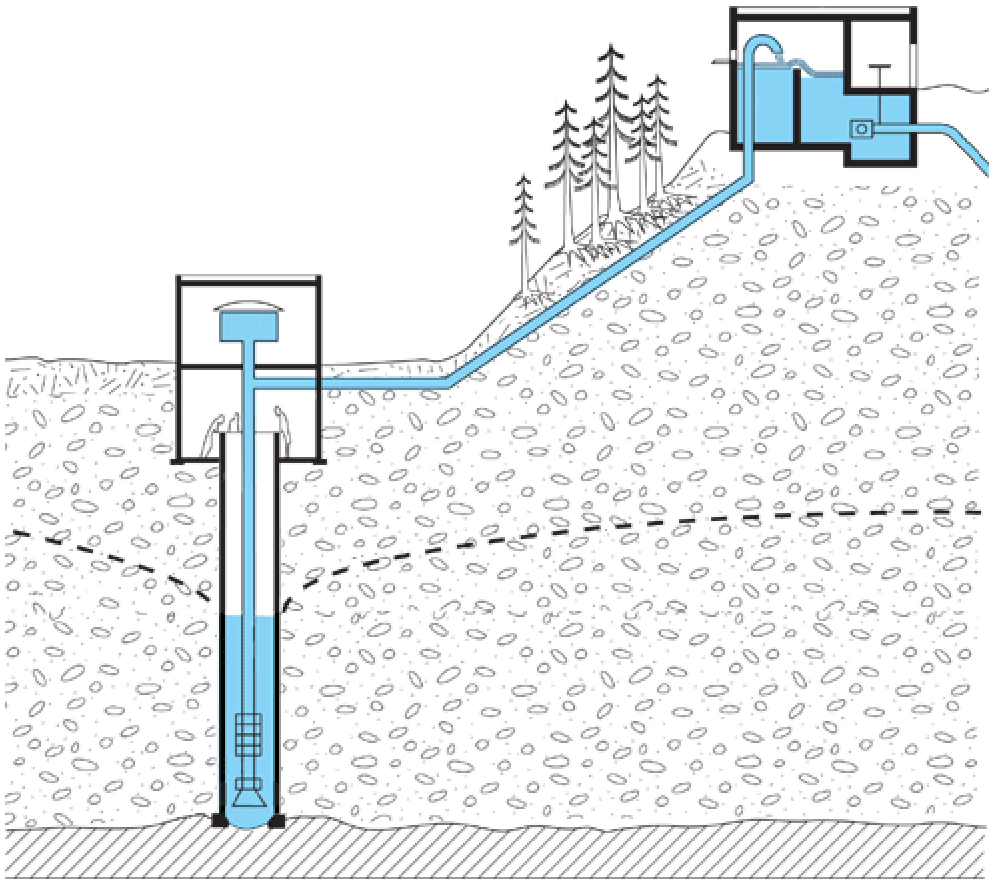
2.9 DRINKING WATER

Water supply : groundwater spring



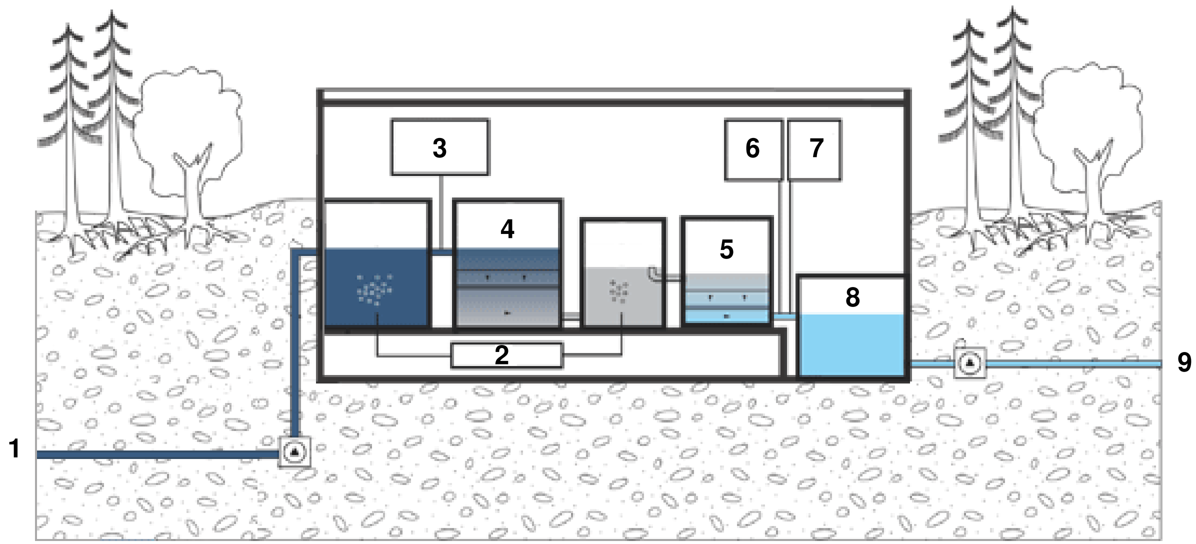
2.9 DRINKING WATER

Water supply : groundwater well



2.9 DRINKING WATER

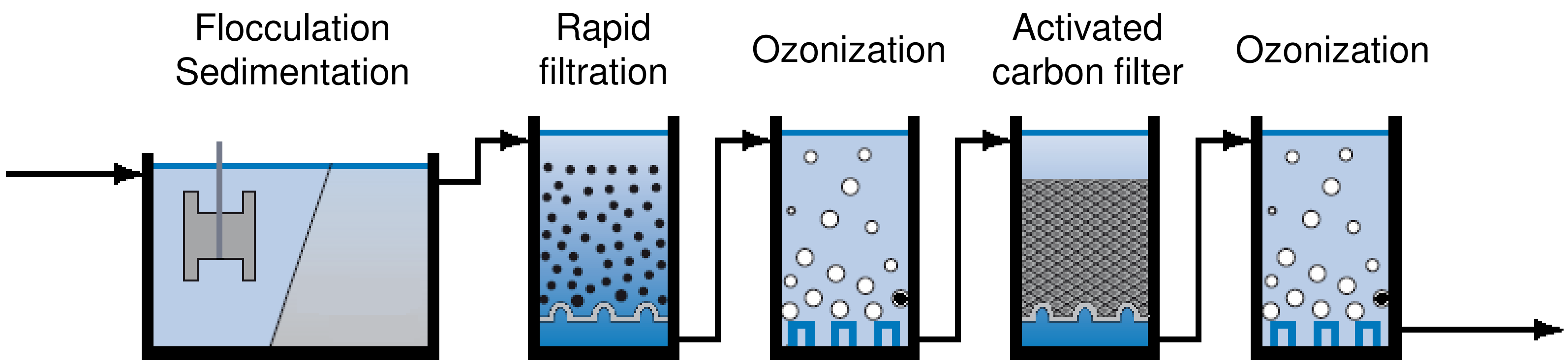
General water treatment

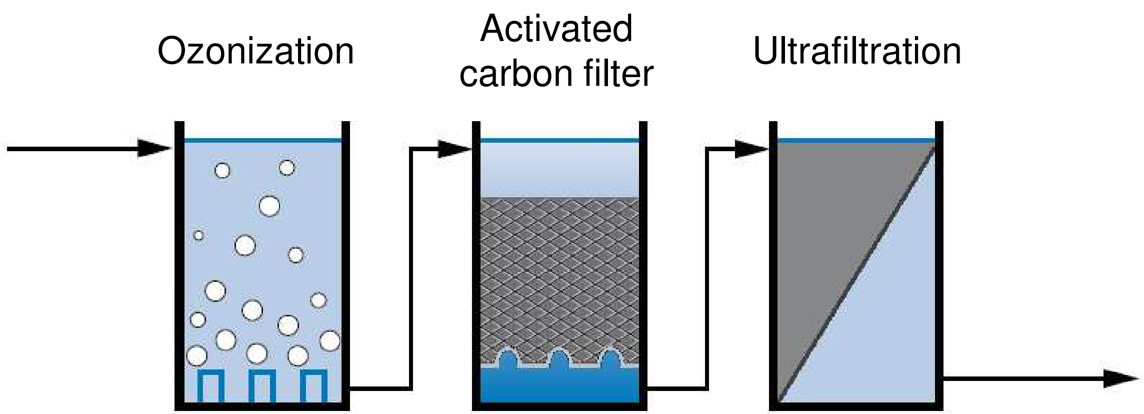


1	Raw water	4	Sand filter	7	Chlorination
2	Ozonization	5	Activated carbon filter	8	Drinking water
3	Flocculation	6	pH correction	9	Distribution

2.9 DRINKING WATER

Treatments of karstic and lake water





2.9 DRINKING WATER
Water chlorination

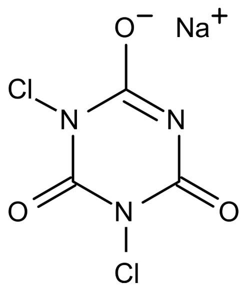
Javel water : NaClO in solution

Chlorine : Cl_2

Chlorine dioxyde : ClO_2

Calcium hypochlorite : $Ca(ClO)_2$

Dichloroisocyanurate $C_3Cl_2N_3O_3Na + 2\ H_2O \rightarrow C_3H_3N_3O_3 + HClO + Na^+ + ClO^-$



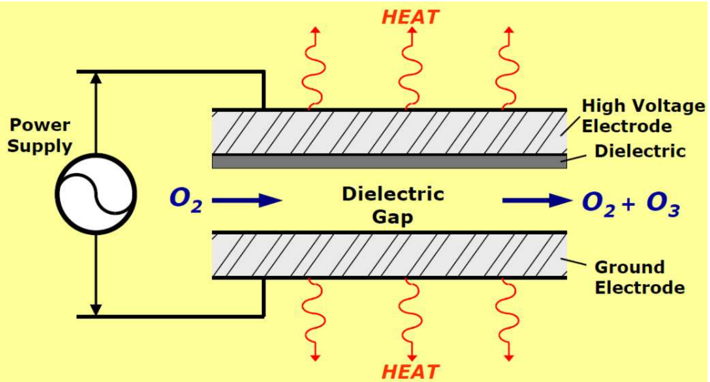
Chlorine and hypochlorous acid can diffuse through the cell walls and react with intracellular enzymes and proteins, making them nonfunctional. Microorganisms then either die or are no longer able to multiply.

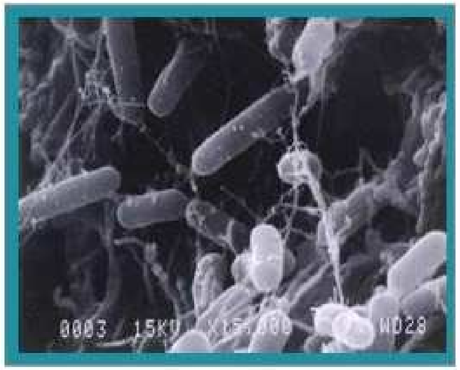
2.9 DRINKING WATER

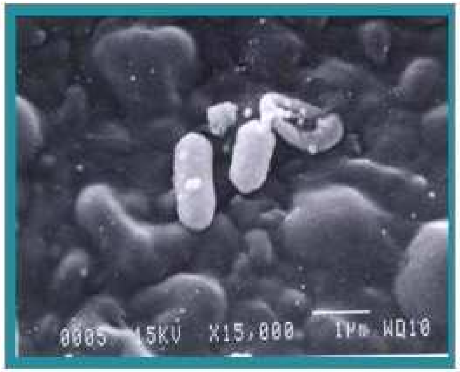
Ozone disinfection

	Lethality Coefficient [(mg/liter)-1(min.)-1]			
Agent	**Enteric Bacteria**	**Amoebic cysts**	**Viruses**	**Spores**
Ozone	500	.5	<5	2
HOCl as Chlorine	20	0.05	>1	0.05
OCl- as Chlorine	0.2	0.0005	<0.02	<0.0005

Ozone oxydises cell membranes, causing osmotic bursting







2.9 DRINKING WATER

Ultra-violet disinfection

Pathogens	UV dose mJ/cm² 4log inactivation (99.99)
Cryptosporidium parvum oocysts	<10
Giardia lamblia cysts	<10
Vibrio cholerae	2.9
Salmonella typhi	8.2
Shigella sonnei	8.2
Hepatitis A virus	30
Poliovirus Type 1	30
Rotavirus SA11	36

Purines and pyrimidines strongly absorb UV light, inducing permanent damages in nucleic acids which cause microorganisms inactivation.

2.9 DRINKING WATER

Solar water disinfection (SODIS)

UV-A (λ = 320–400 nm) interferes directly with the metabolism and destroys cell structures of bacteria.

UV-A reacts with oxygen dissolved in the water and produces oxygen free radicals and hydrogen peroxides that damage pathogens

If the water temperatures rises above 50 °C, the disinfection process is three times faster.

A threshold solar irradiance of at least 500 W/m^2 is required for about 5 hours for SODIS to be efficient.

The most favorable regions for SODIS are located between latitude 15°N and 35°N, and 15°S and 35°S.

2.9 DRINKING WATER
Water quality

Chemical guidelines

Heavy metals

Hydrocarbons

Halogenated hydrocarbons

Phenols

Pesticides

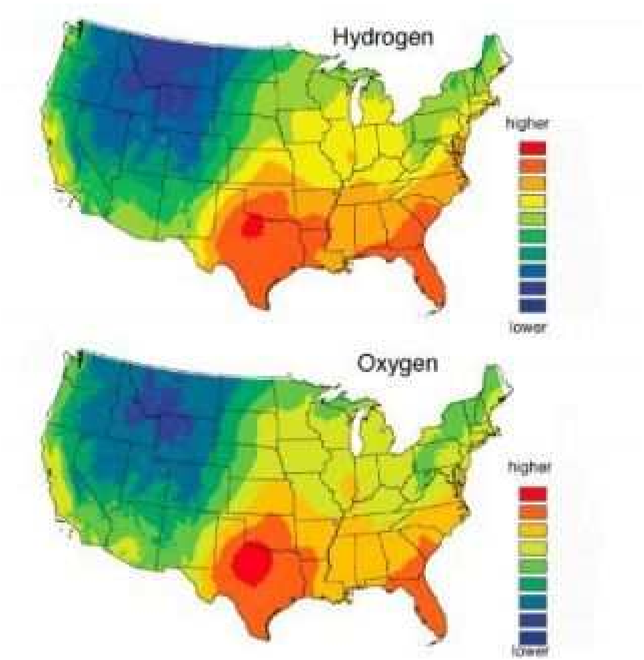
Radionuclei

Microbiological guidelines

Aerobic mesophile germs	< 300 CFU/ml
Escherichia coli	n.d. /ml
Enterococci	n.d. /ml

2.9 WATER - composition

Mapping Isotope Concentrations in Hair and Drinking Water



Hair Reveals Where Murder Victims Drank Water

2.9 DRINKING WATER

Water hardness definition

Water hardness is defined as the sum of multivalent cations

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2\,HCO_3^-$$

Same reaction for dolomite $CaMg(CO_3)_2$

It is usually reported in °f, which are equivalent to 10 mg/liter of $CaCO_3$

Hardness (°f)	0 - 7	7 - 15	15 - 25	25 - 42	> 42
Water	Very soft	Soft	Moderately hard	Hard	Very hard

2.9 DRINKING WATER

Water hardness map