Principles of Water Science and Technology

adopted for

ЧУВАШСКИЙ ГОСУДАРСТВЕННЫЙ
УНИВЕРСИТЕТ
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TRENT
UNIVERSITY

Our focus

- Water
- Environment
- Technology

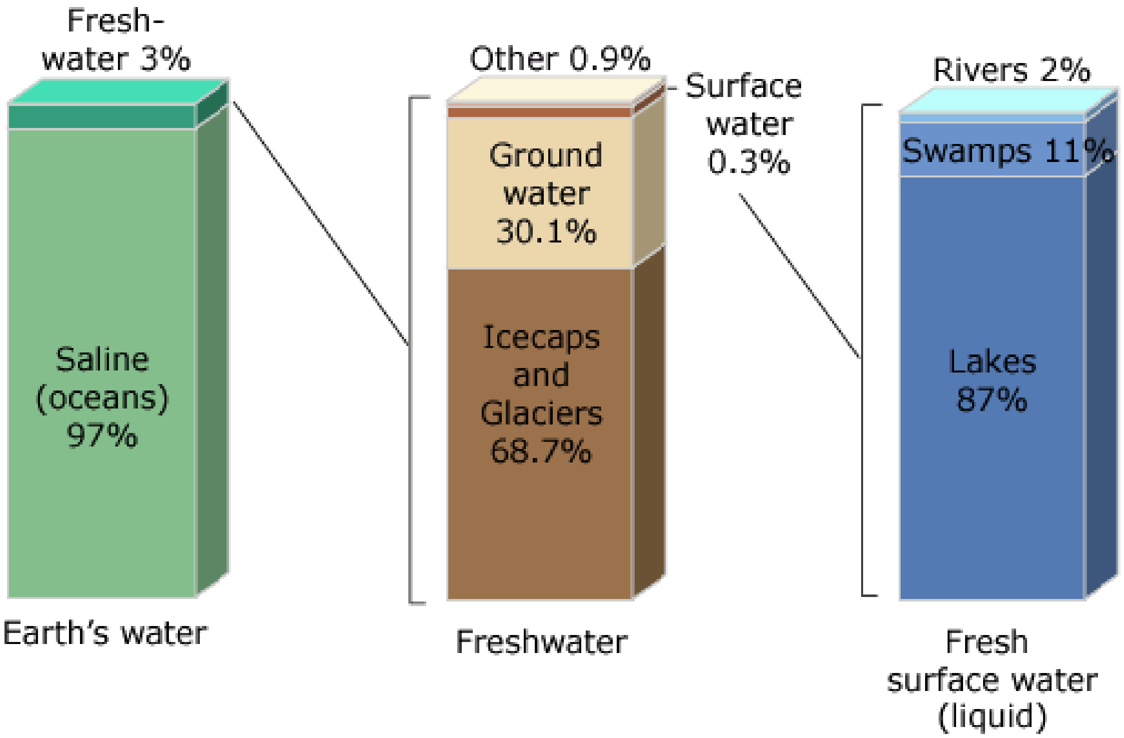
View from Trent University

View from Space

Importance of water

- Widespread distribution
- Medium for organic life
- Use in technology

Global water resources



Atmosphere (water vapor) 0.001%

Figure: Distribution of Earth's water [1]

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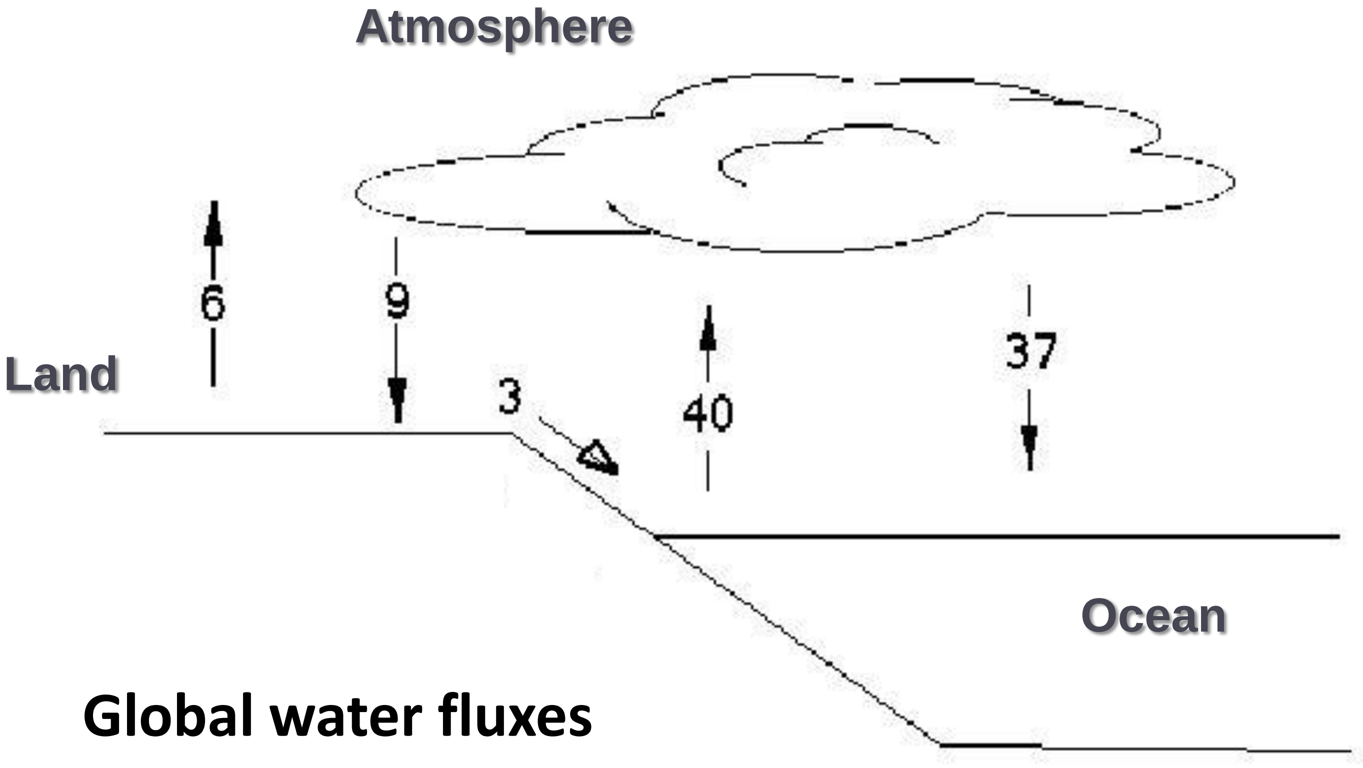
1. **http://www.ga.water.usgs.gov/edu/waterdistribution.html**

Global water cycle



Atmosphere

Land

Ocean

Global water fluxes

all values are in 10^{13} tons/year

Properties of Water

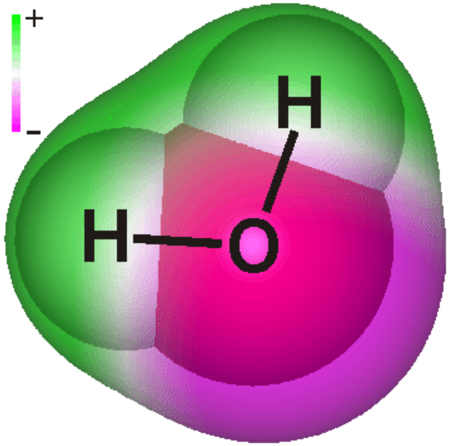
Unique properties of water.

Solutions. Hydrophobic effects .

Ionic hydration

Water molecule

- Small molecule, large dipole moment
- Easily polarizable
- sp^3 hybridization of valent electrons



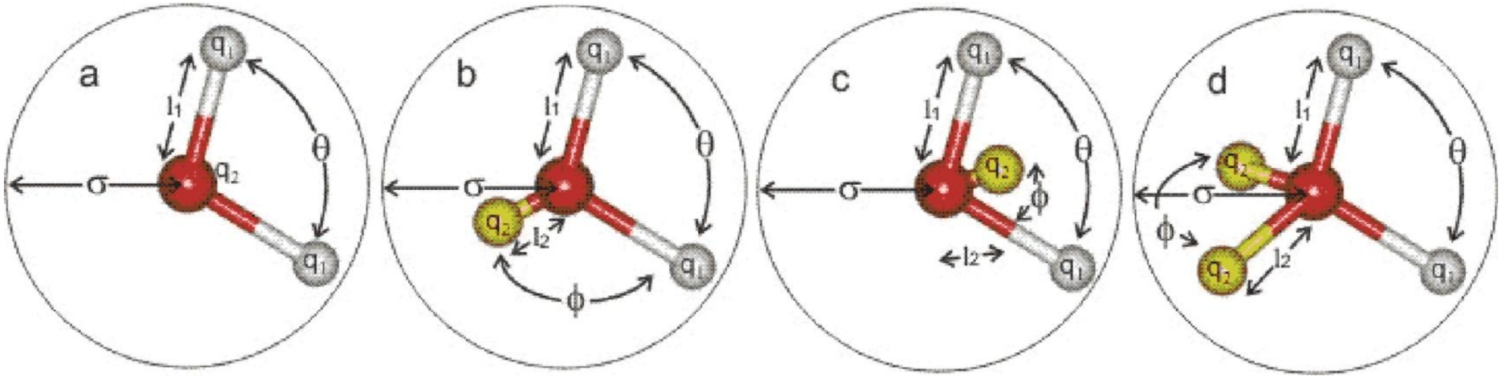
Shape and charge distribution

The experimental values for the geometry of gaseous water molecule are: O-H length 0.95718 Å, H-O-H angle 104.474°

2. http://www.lsbu.ac.uk/water (Dr. M. Chaplin)

Molecular models for water

SPC/E	Simple Point Charge Extended	Berendsen, 1987
TIP4P	Transferable Intermolecular Potential	Jorgensen, 1983
PPC	Polarizable Point Charge	Svishchev, 1995
TIP5P	Transferable Intermolecular Potential	Jorgensen, 2000



“Classical” water models: a) SPC/E, b) PPC, c) TIP4P and d) TIP5P

Did you know?

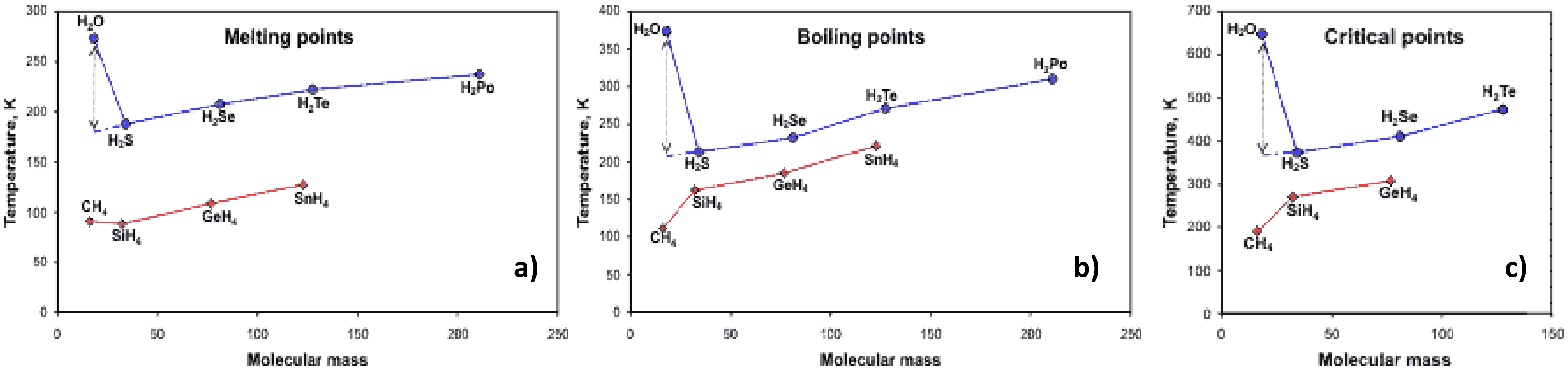
- Water is atypical liquid, ~ 63 anomalies [2]

- Phase changes (high density ices)
- Thermodynamics (heat capacity)
- Density maximum
- Low-temperature anomalies (2nd critical point)

2. http://www.lsbu.ac.uk/water (Dr. M. Chaplin)

Is there anything “normal” about water?

- High melting point (T_f = 0 °C)
- High boiling point (T_b = 100 °C)
- High critical point (T_c = 374 °C, P_c = 22.1 MPa)



Thermodynamic anomalies of water: a) melting temperature, b) boiling temperature and c) critical temperature

Is there anything “normal” about water?

“Life depends on anomalous properties of water” [4]

- ❑ High heat capacity (C_p = 4.187 J g^{-1} K^{-1} at SATP)
- ❑ High thermal conductivity (κ = 0.6 W m^{-1} K^{-1})
- ❑ High heats of fusion (H_f = 334 J g^{-1}) and vaporization (H_v = 2.258 kJ g^{-1})
- ❑ High dielectric constant (ε = 78 at SATP)

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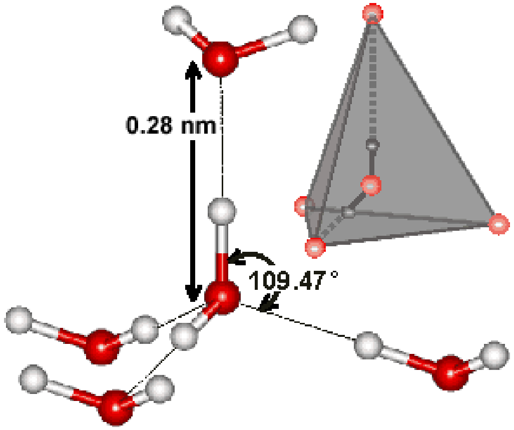
4. W. A. P. Luck, in *Water and Ions in Biological Systems*, eds. A. Pullman and L. Packer (Plenum, 1985) .

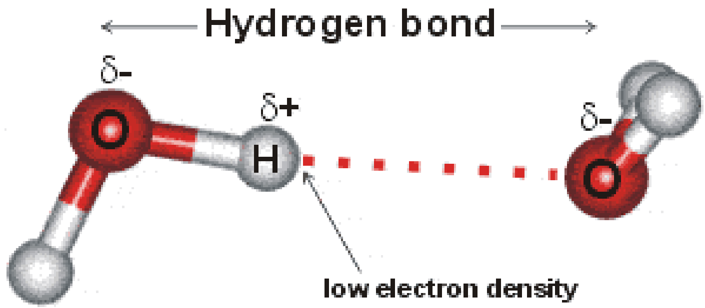
Is there anything “normal” about water?

- Did you know?
  - Water substance exists as a glass at very low temperatures (- 123 to -149 °C) and freezes on heating
  - Hot water may freeze faster than cold water; the Mpemba effect.
  - Water droplets remain far longer on a hotplate just above 200 ˚C than if the hotplate was just above 100 ˚C; the Leidenfrost effect.

Why does liquid water exhibit unique properties?

- Ability of water molecules to form hydrogen bonds
- Tendency of water molecules for tetrahedral coordination





Bond energies

van der Waals interaction:

- ~ 0.01 – 0.1 kcal/mol

Hydrogen bond:	Example:
weak, comparable to van der Waals interaction ~ 1 - 4 kcal/mol	N-H···O N-H···N
moderate, most common ~ 4 - 15 kcal/mol	O-H···O O-H···N
strong, almost covalent above 15 kcal/mol	F···H···F

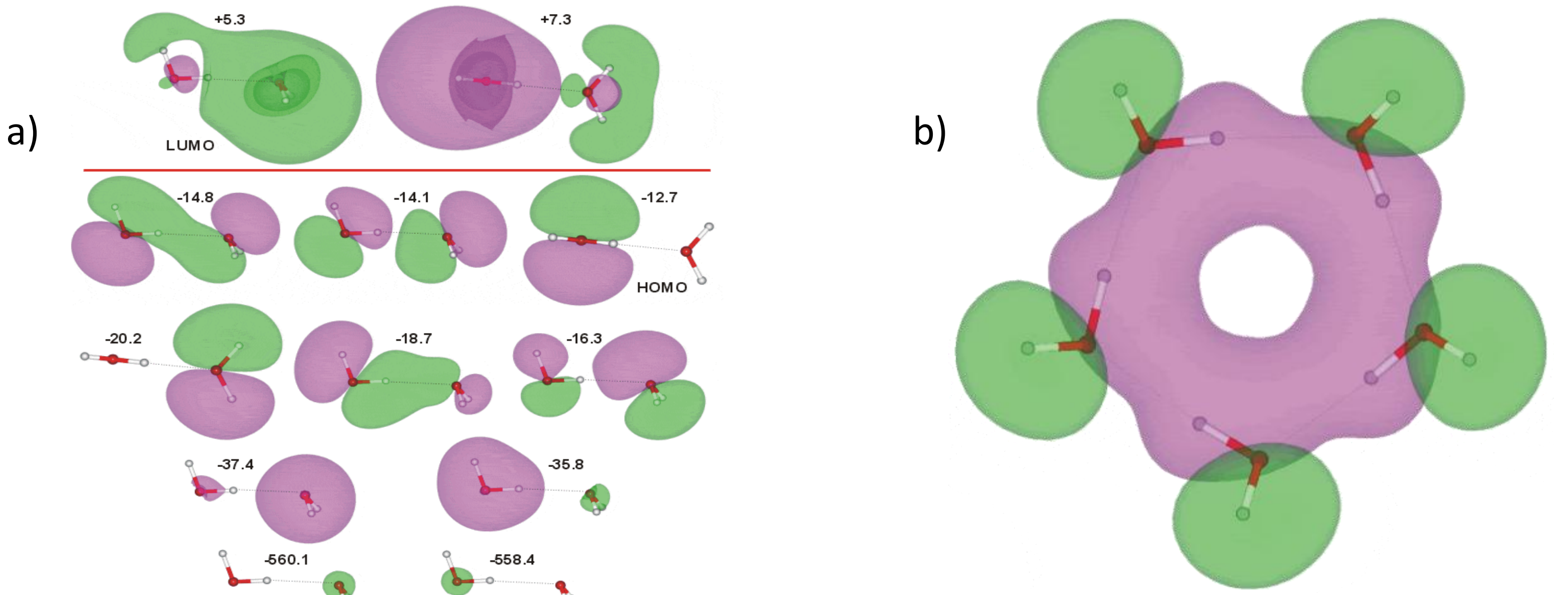
Covalent bond:

- ~ 100 kcal/mol

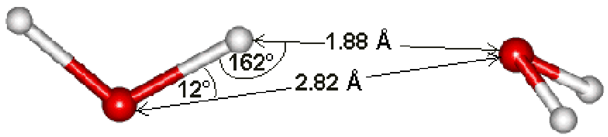
- S. J. Grabowski, Theoretical studies of strong hydrogen bonds, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, 2006, 102, 131-165

Hydrogen bonding: Examples

- **Dimers and larger water clusters (water vapor)**



Figures above: Molecular orbitals for a) water dimer and b) water pentamer (Ref. [2])



Hydrogen bonds prefer near linear geometry (orientation specific)
Bonding energy of water dimer is around 10 kJ/mol

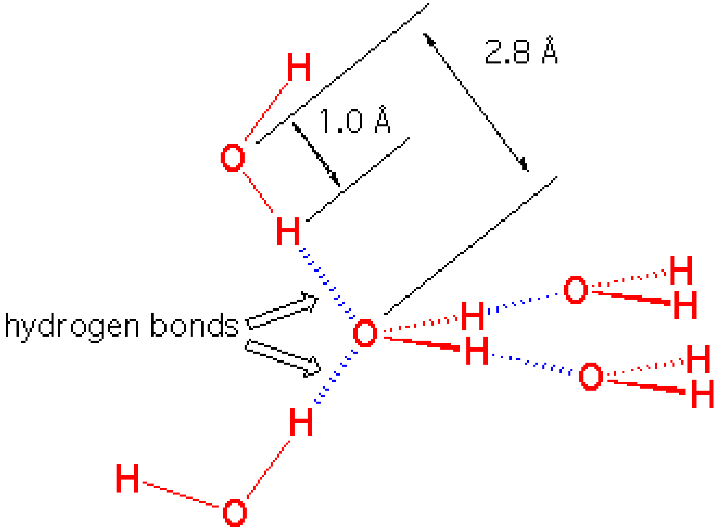
Hydrogen bonding: Examples

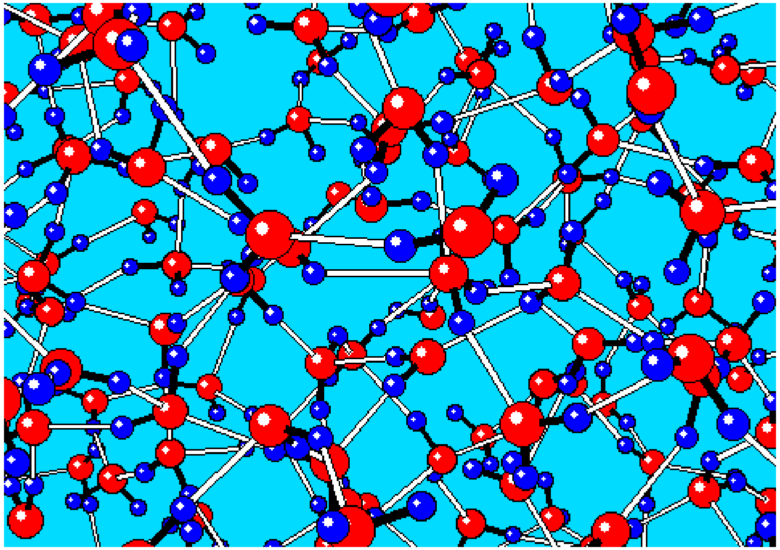
- **3D continuous tetrahedral network (liquid water and ices)**

Liquid water energy is about 40 kJ/mol (heat of vaporization)

4 H-bonds per molecule in a neat liquid

2 accepting and 2-donating

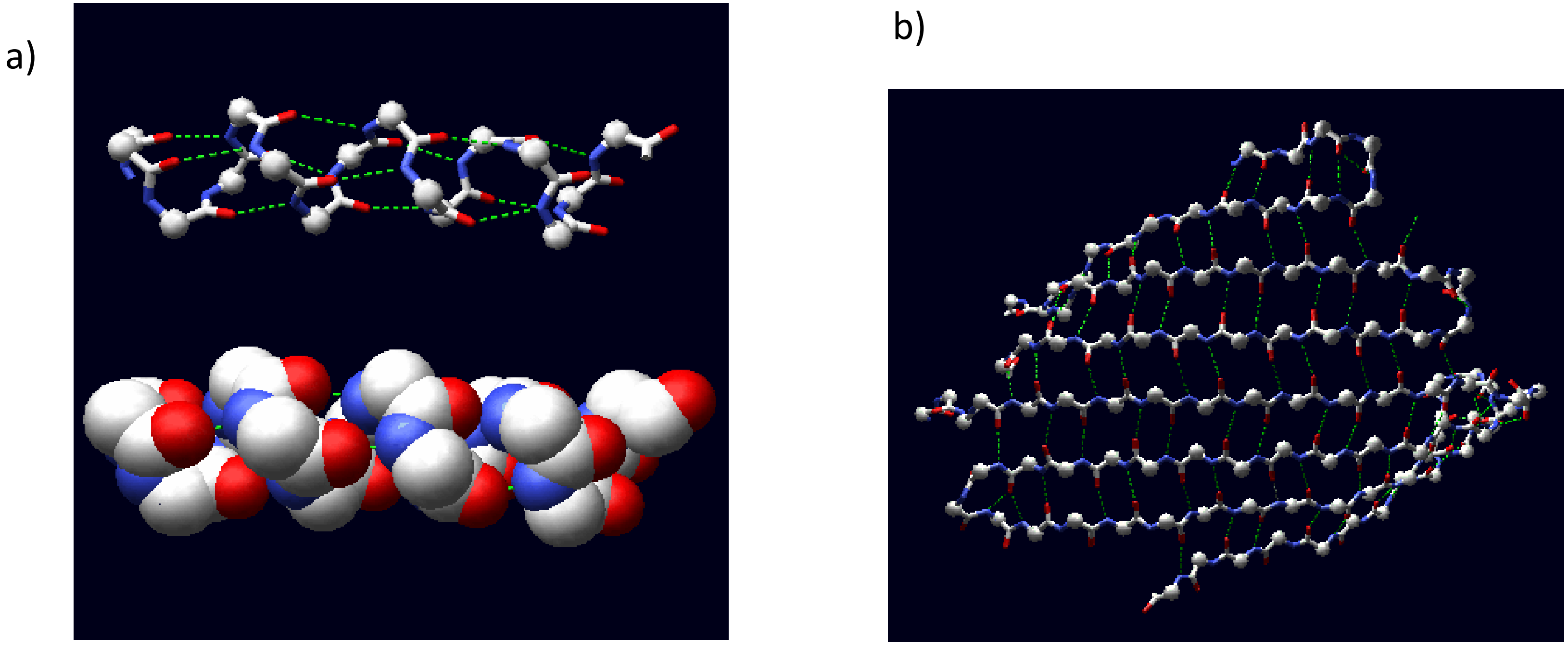




3D network

Hydrogen bonding: Examples

- **Intramolecular links in polypeptides**



Figures: 3D structures of polypeptides: a) α – helix and b) antiparallel β-sheet

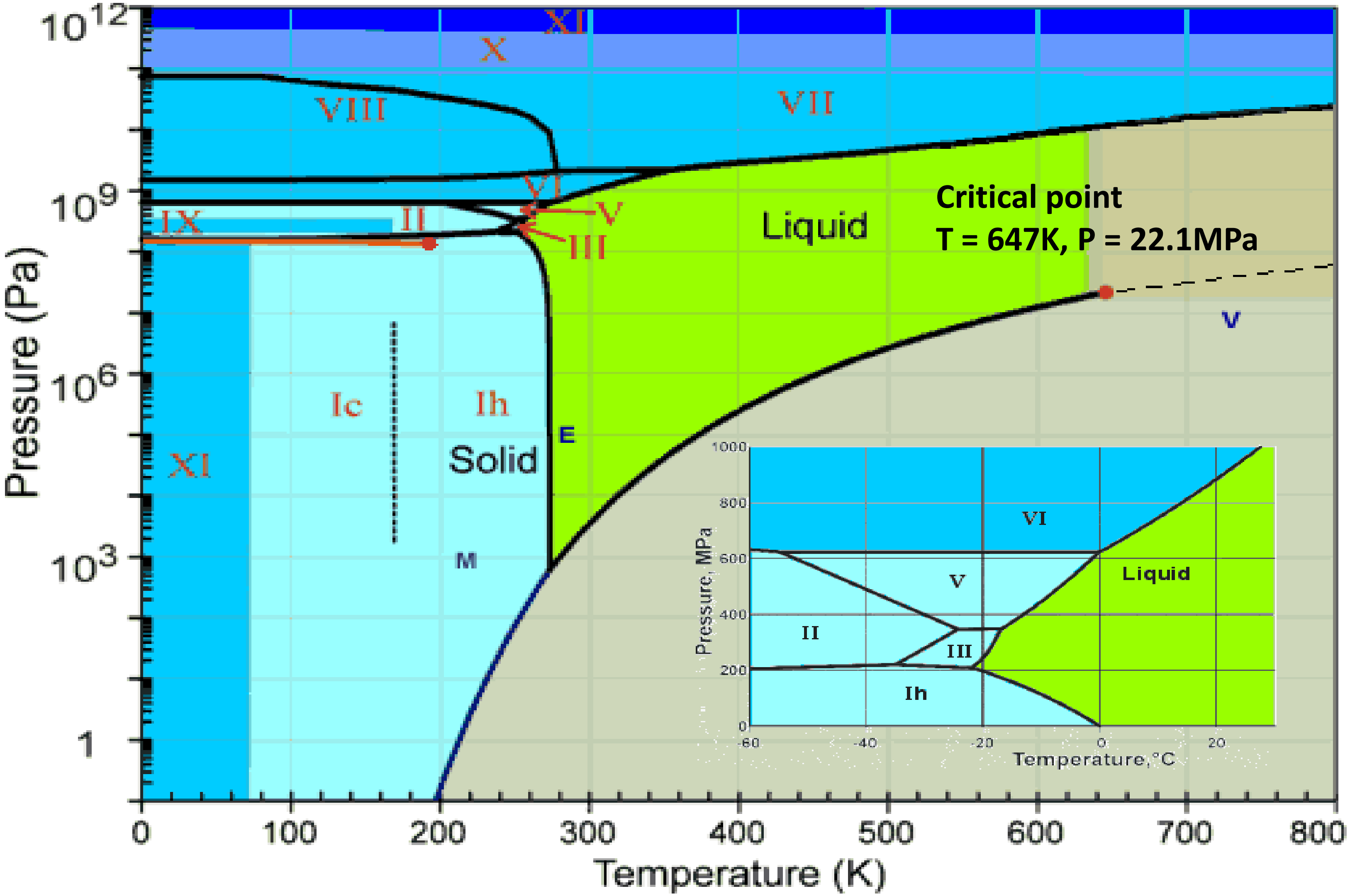
Hydrogen bonding in water

- How important is the strength of H-bond of water?

Table: Effects of change of H-bond strength of water (Ref. [2])

% Change in H-bond strength	Effect at 37°C
Decrease 29%	**Water boils**
Decrease 18%	**Most proteins heat denature**
Decrease 7%	**pK_w up 3**
Decrease 5%	**CO_2 is 70% and O_2 is 27% less soluble**
Decrease 2%	**No density maximum**
Increase 2%	**Significant metabolic effects**
Increase 5%	**CO_2 is 440% and O_2 is 270% more soluble**
Increase 7%	**pK_w down 1.7**
Increase 18%	**Water freezes**
Increase 51%	**Most proteins cold denature**

Phase diagram of water



Critical point
T = 647K, P = 22.1MPa

- **Phase diagram of water (Ref. [2])**

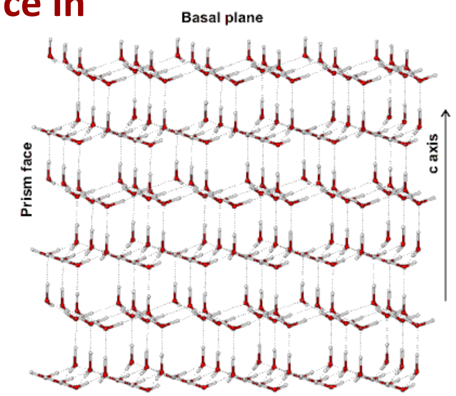
Ice polymorphism

- Hydrogen bonding and tendency for tetrahedral coordination result in a variety of crystalline and amorphous phases
- Ordinary ice I_h is formed only at low pressures (Earth environment)
- High density forms of ice can exist in nature (giant gas planets)

Ice polymorphism

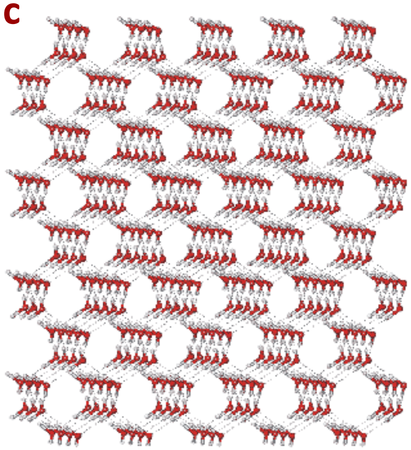
Ice Ih

P_{atm} , T < 0 ˚C



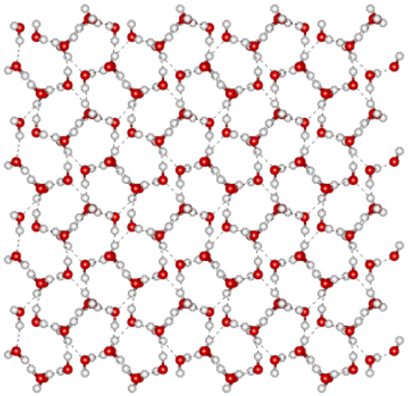
Ice Ic

P_{atm} , T < - 80 ˚C



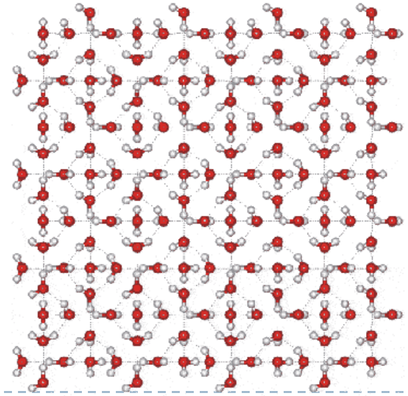
Ice III

P ~ 300 MPa, T ~ -23˚C



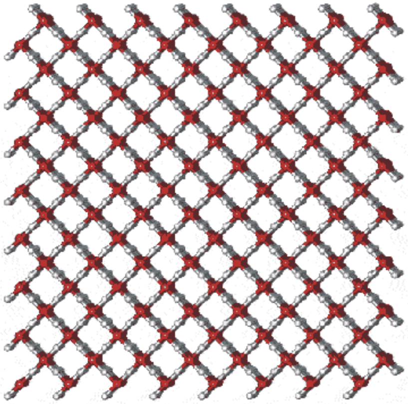
Ice VI

P ~ 1.1 GPa, T ~ -3˚C



Ice X

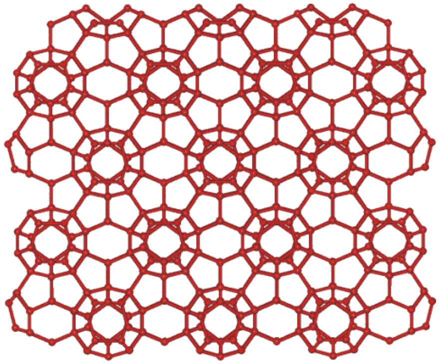
P ~ 62 GPa, T ~ 25˚C



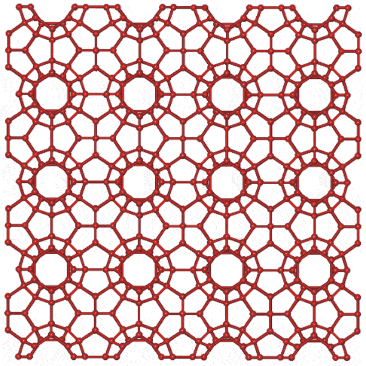
- Crystal structures of different forms of ice (Ref. [2])

Clathrates

Clathrate I (sI) ($5^{12}6^{2}$)
46 water molecules

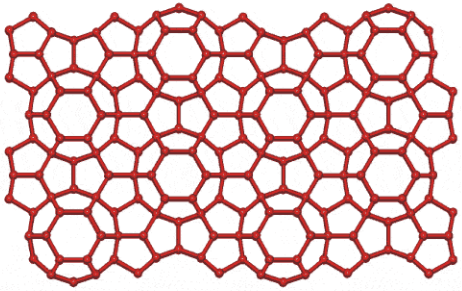


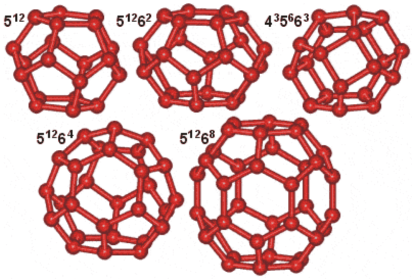
Clathrate II (sII) ($16 \bullet 5^{12} + 8 \bullet 5^{12}6^{4}$)
136 water molecules



- **Formed from water and non-stoichiometric amounts of small non-polar molecules at moderate pressures (several MPa) and temperatures close to 0 °C.**

Clathrate H (sH) ($3 \bullet 5^{12} + 2 \bullet 4^{3}5^{6}6^{3} + 1 \bullet 5^{12}6^{4}$)
34 water molecules





Clathrate cages

Clathrate hydrate structures (Ref. [2])

Clathrates

- About 6.4 x 10^{12} tones of methane lies at the bottom of the oceans in the form of clathrate hydrate sI.

- Each kilogram of fully occupied hydrate (~ 96 % occupancy) hold about 187 liters of methane (at atmospheric pressure).

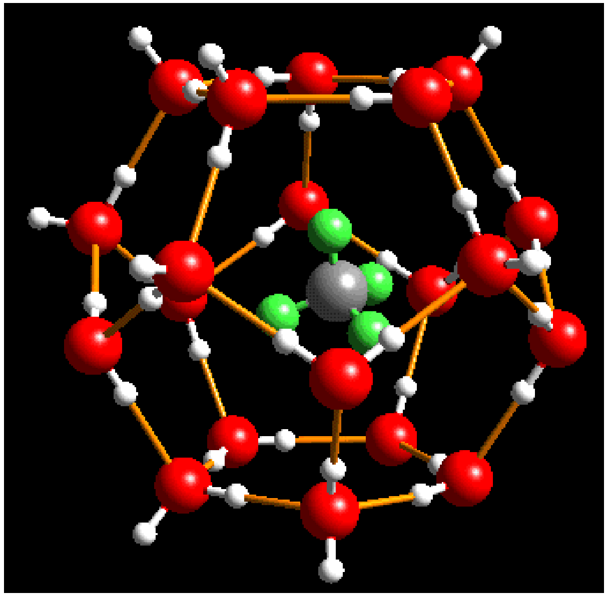
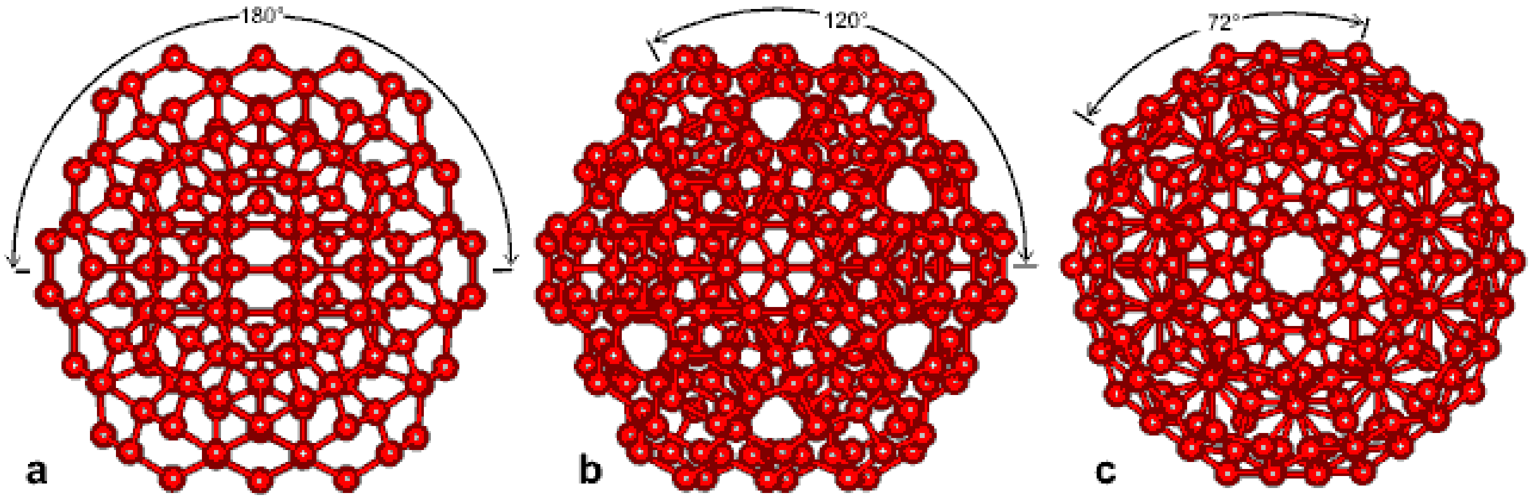


Figure: Clathrate hydrate sI with "guest" methane molecule.

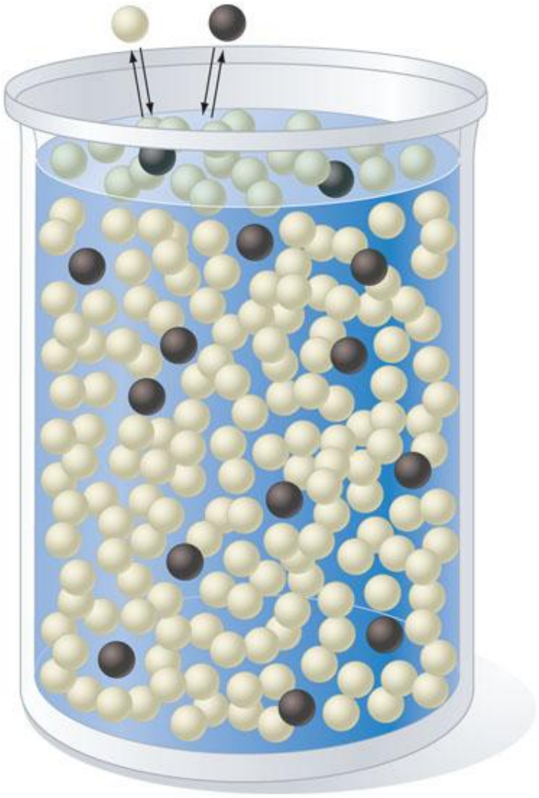
Icosahedral water clusters

Superstructure of frozen liquid water nanodroplets



The structure of $(H_2O)_{280}$ cluster (*Ih* symmetry), a) 15 two-fold rotation axes (C_2), b) 10 three-fold rotation axes (C_3) and c) 5 five-fold rotation axes (C_5).

Essentials of Solution Thermodynamics



Ideal dilute solutions

An ***ideal dilute solution*** is a solution in which the solvent is described using Raoult's Law and the solute is described using Henry's Law.

Real solutions at very low concentrations, typically, a dissolved gas (O_2) in a solvent (H_2O), obey Henry's Law

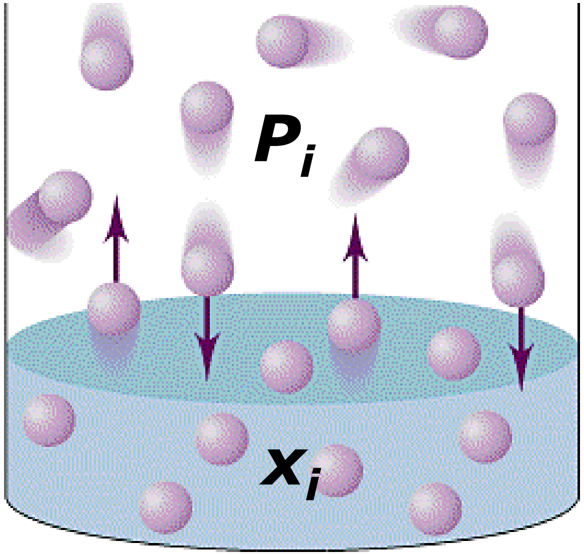
Henry's Law:

$$x_i = \frac{1}{K_i} P_i = K_i^{'} P_i$$

Solubility of gas
(in water)

Partial Pressure
(in atmosphere)

K_i = Henry's Law constant



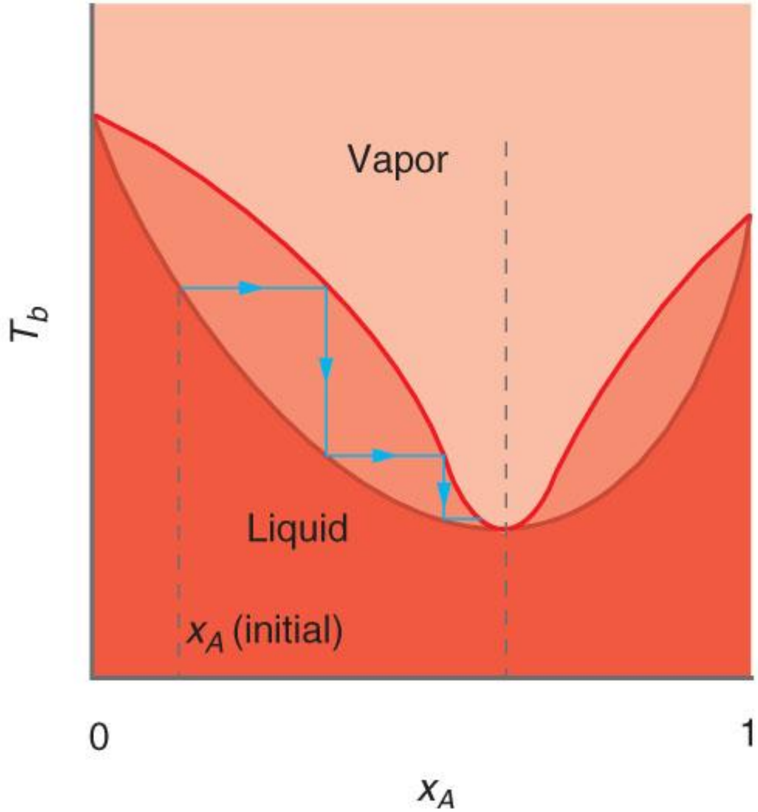
Azeotropes

If the A-B interactions are less attractive than the A-A and B-B interactions, the result is a **minimum boiling azeotrope**.

Azeotrope: boiling mixture with identical compositions of vapour and liquid phases

Figure : Boiling point diagram is shown for a **minimum boiling point azeotrope**.

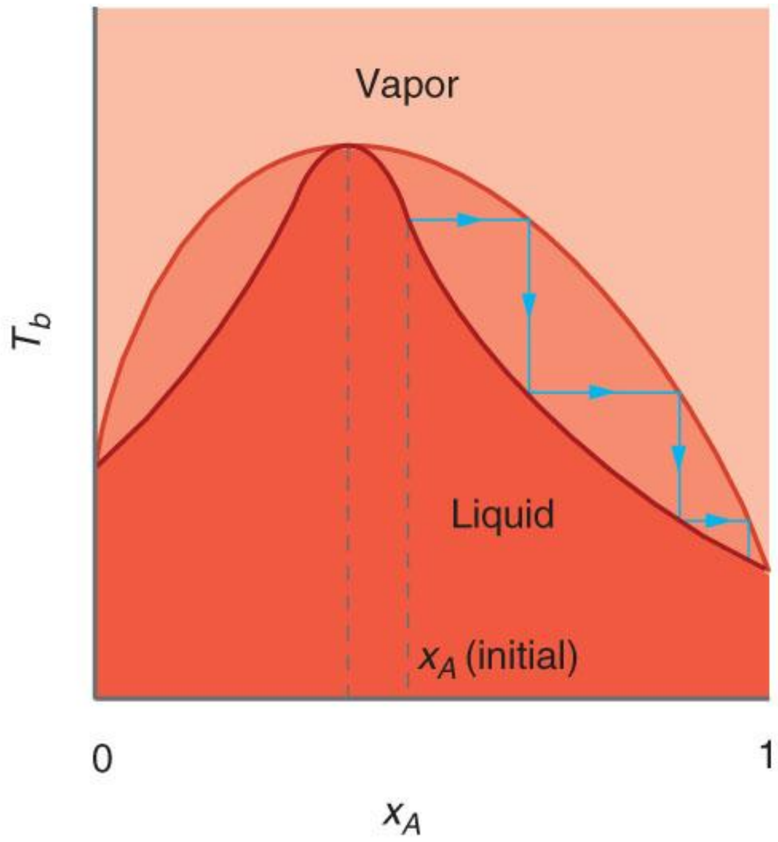
Example: water/ethanol



Azeotropes

Figure : Boiling point diagram is shown for a **maximum boiling point azeotrope**. The dashed lines represent the initial composition of the solution and the composition of the azeotrope. The sequence of horizontal segments corresponds to successively higher (cooler) portions of the fractional distillation column.

Example: water/nitric acid



Partial molar properties

Thermodynamic properties of solutions are usually described using Partial Molar quantities

For a binary mixture, the volume of the mixture would be:

$$V = n_1\overline{V}_1(P, T, n_1, n_2) + n_2\overline{V}_2(P, T, n_1, n_2)$$

where partial molar volume :

$$\overline{V}_1(P, T, n_1, n_2) = \left(\frac{\partial V}{\partial n_1}\right)_{P, T, n_2}$$

For an ideal mixture: $V = V_1 n_1 + V_2 n_2$

Volumetric properties of nonelectrolyte solutions

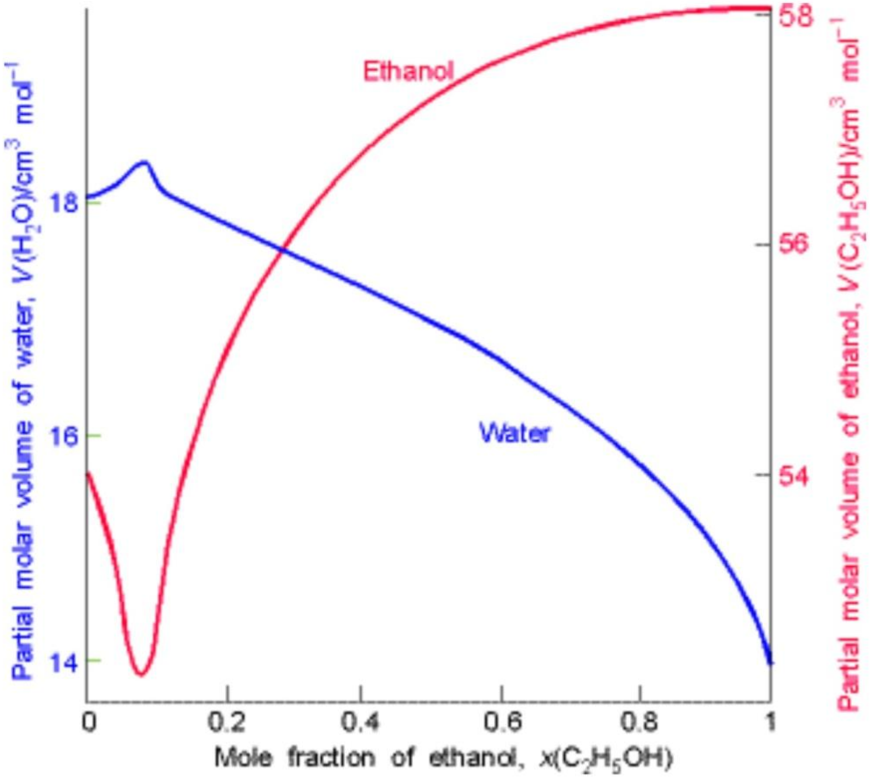
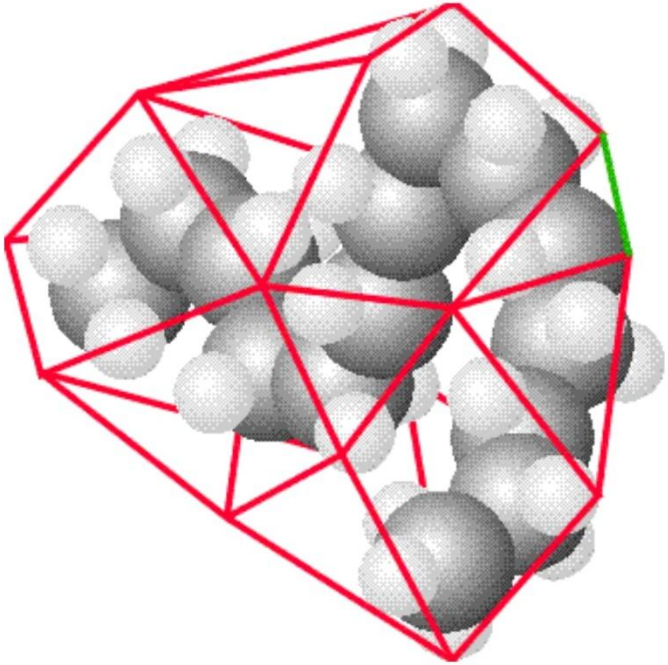


Fig .2. The partial molar volumes of water and ethanol at 25°C.

Note: expansion of molar volume of water upon addition of nonelectrolyte – effect of *hydrophobic hydration*

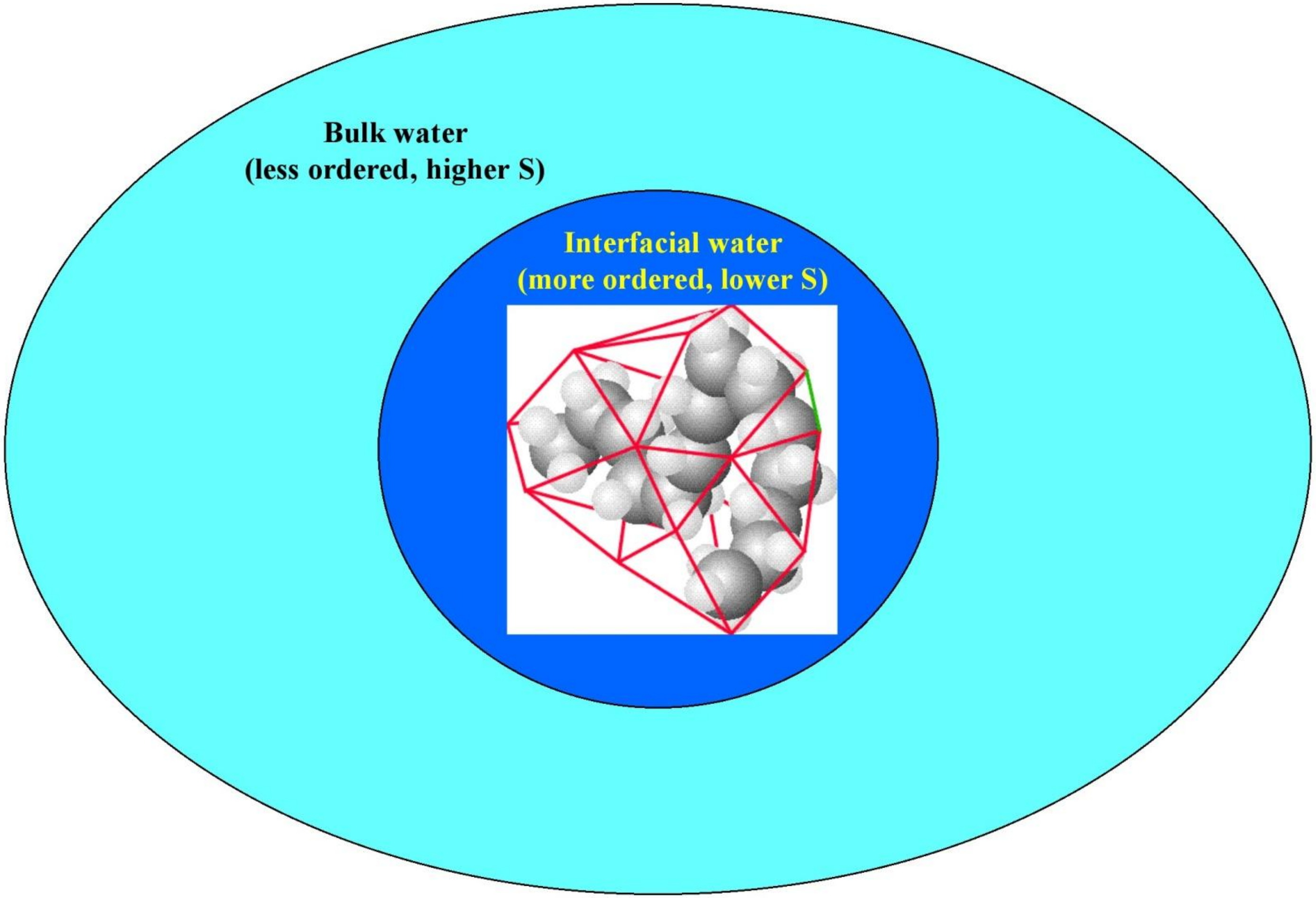
What is hydrophobic hydration?

Formation of quasi-clathrate hydration cage around “hydrophobic” molecule



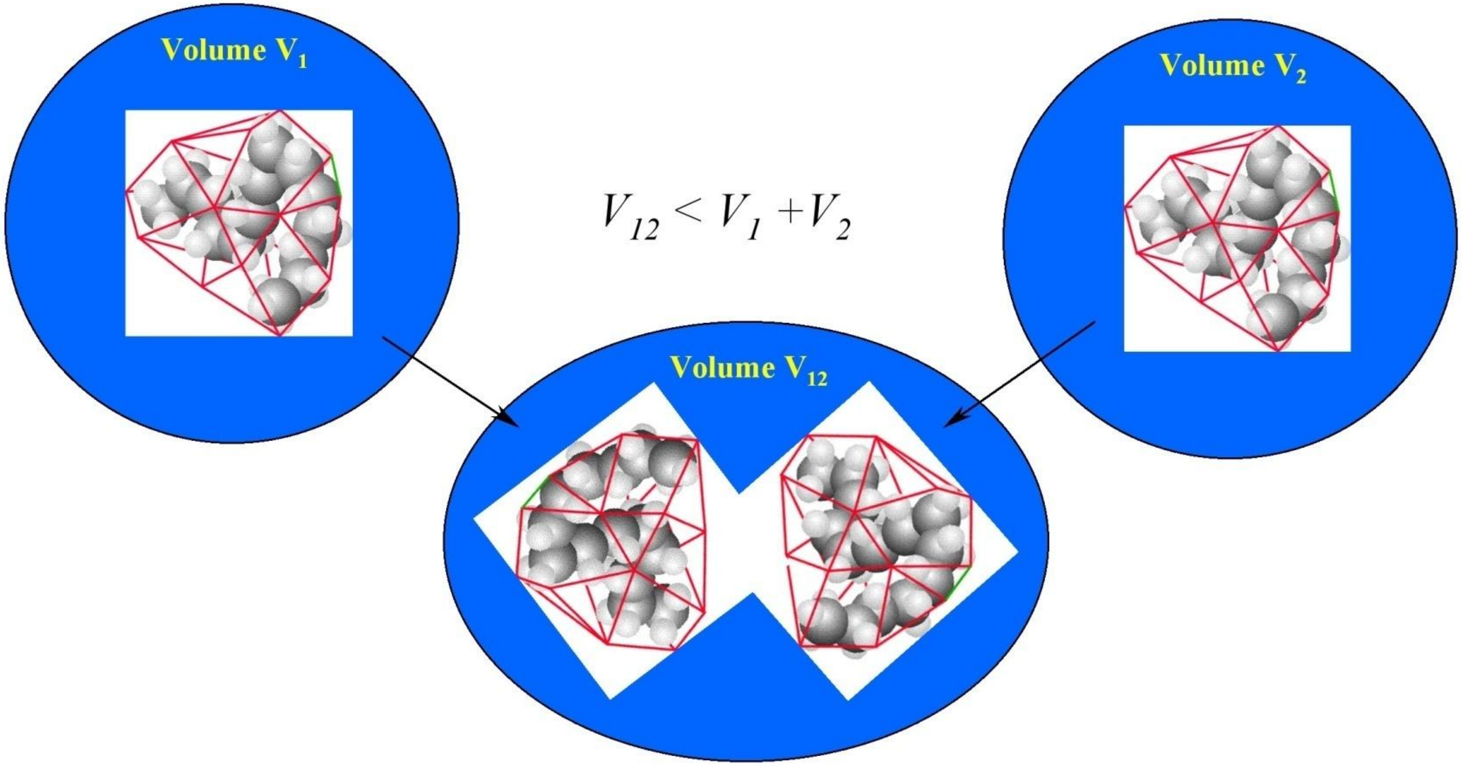
Leads to an increase in
molar volume of water

Hydrophobic hydration: entropic picture



S(total) = S(solute) + S(solvent)= S(solute) + S(bulk solvent) + S(interfacial solvent)

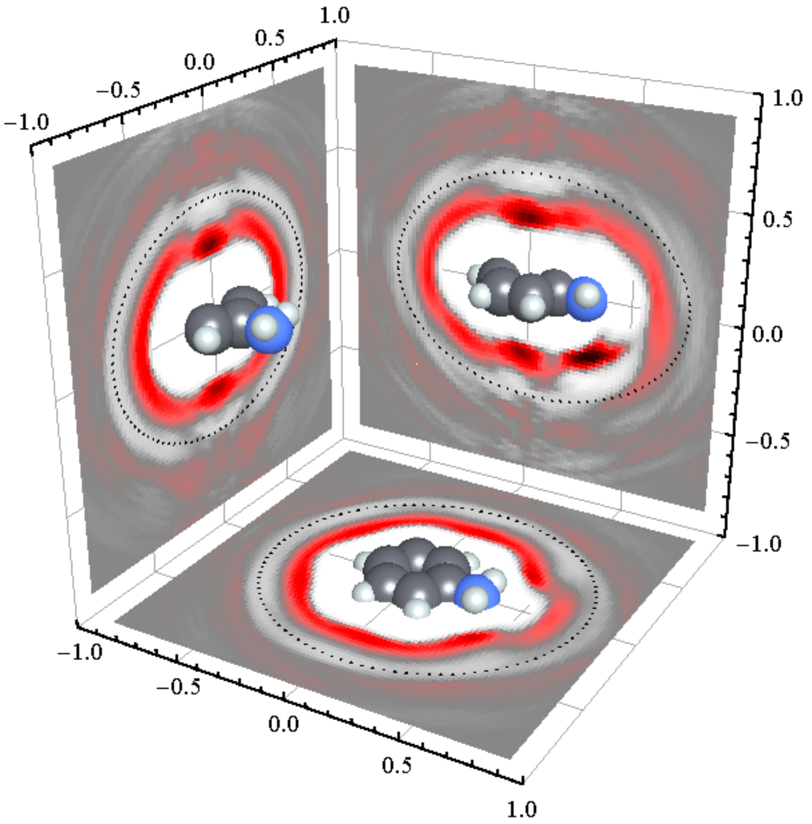
Hydrophobic association: driving force



Total volume of interfacial water with lower entropy decreases when molecules aggregate. As a result, the total entropy of aqueous solution increases upon aggregation.

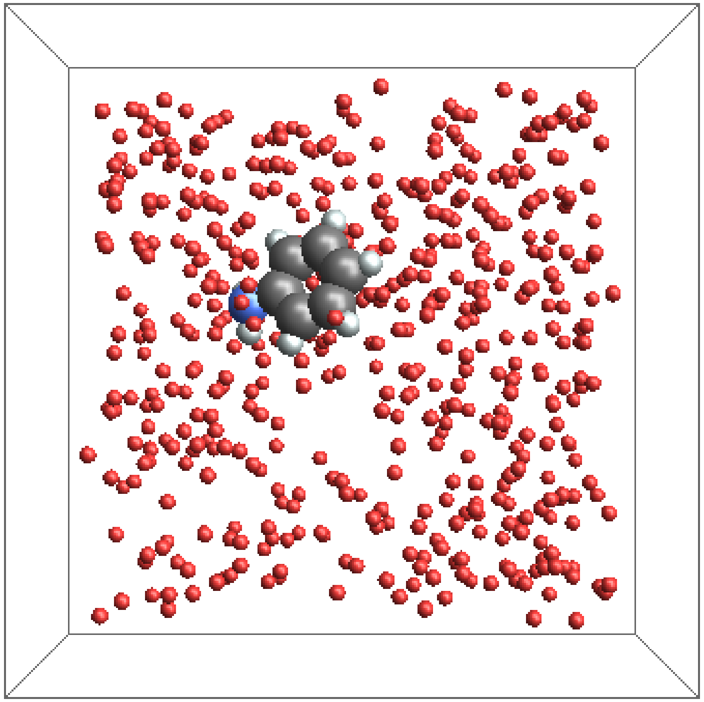
Driving force for aggregation of hydrophobic substances arises from increase in entropy of aqueous phase. It does not arise from intrinsic attraction between hydrophobic solute molecules.

Molecular Dynamics simulation of hydrophobic hydration



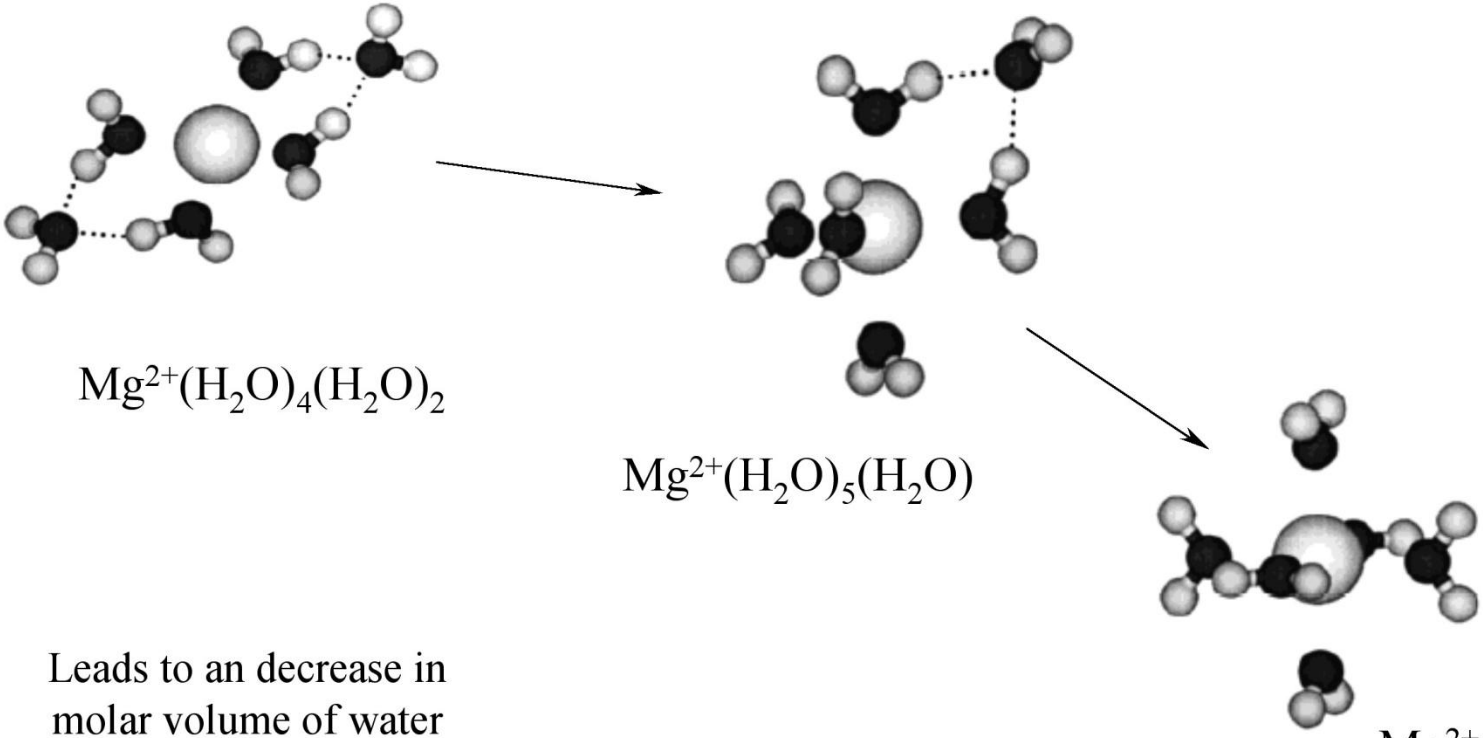
Hydration cage structure around aniline in an aqueous solution (atomic density map)

Animation of molecular dynamics



What is ionic hydration?

Formation of compact ion-water coordination complexes



$Mg^{2+}(H_2O)_4(H_2O)_2$

$Mg^{2+}(H_2O)_5(H_2O)$

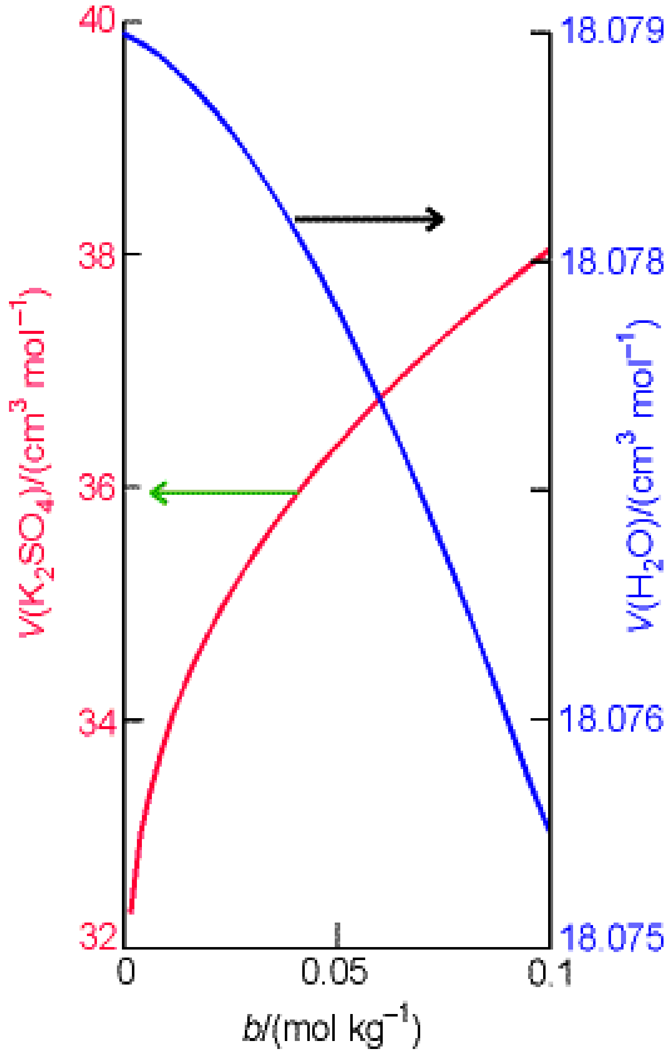
$Mg^{2+}(H_2O)_6$

Leads to an decrease in
molar volume of water

S. E. Rodriguez-Cruz, R. A. Jockusch and E. R. Williams, Hydration Energies and Structures of Alkaline Earth Metal Ions, $M^{2+}(H_2O)_n$, n = 5-7, M = Mg, Ca, Sr, and Ba, *J. Am. Chem. Soc.* 1999, *121,* 8898-8906

Volumetric properties

Figure : The partial molar volumes of an electrolyte solution (water-K_2SO_4)



Ionic solubilities:

Solution of salt AB in water (1:1 electrolyte)

$$AB(s) \longleftrightarrow A^{+}(aq) + B^{-}(aq)$$

Solubility constant, K_s

$$K_s = a_A a_B \qquad (48)$$

Since $a = \dfrac{\gamma b}{b^{\varnothing}}$, then

$$K_s = \gamma_A \gamma_B S^2 = \gamma_{\pm} S^2, \qquad (49)$$

Mean activity coefficient of 1:1 electrolyte, $\gamma_{\pm}$

$$\gamma_{\pm} = \sqrt{\gamma_{+}\gamma_{-}} \qquad (50)$$

Solubility, S – molality (molarity) of saturated solution

$$S = \frac{\sqrt{K_s}}{\gamma_{\pm}} \qquad (51)$$

Note:

$\gamma_{\pm}(A_n B_m) = \left(\gamma_{+}^{n} \gamma_{-}^{m}\right)^{\frac{1}{n+m}}$ (52) mean activity coefficient of n:m electrolyte

$\mu_i = \mu_i^{ideal} + nRT \ln \gamma_{\pm}$ (53) chemical potential of an ion

Debye-Huckel theory

Provided theoretical means for the calculation of ionic activity coefficients

- *Debye-Huckel limiting law:*

$$\log \gamma_{\pm} = -|z_+ z_-| A \sqrt{I} \tag{54}$$

- *Ionic strength* of the solution:

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\varnothing}} \tag{55}$$

- *Ionic strength* of the solution (two types of ions):

$$I = \frac{1}{2} \sum_i \frac{\left(b_+ z_+^2 + b_- z_-^2\right)}{b^{\varnothing}} \tag{56}$$

- *Debye-Huckel constant:*

$$A = \frac{F^3}{4\pi N_A \ln 10} \left(\frac{\rho b^{\varnothing}}{2\varepsilon^3 R^3 T^3} \right)^{\frac{1}{2}} \tag{57}$$

F – Faraday constant ($F = eN_A = 96.485$ kC/mol)

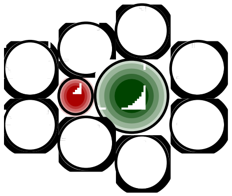
ρ - solvent mass density (in dilute solution [C] ≈ ρb)

ε - dielectric constant

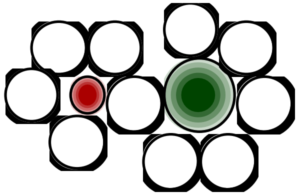
Applications of Debye-Huckel theory

	Water	***Supercritical water***
Temperature, T	298 K	750 K
Density, ρ	1.0 g/cm^3	0.3 g/cm^3
Dielectric constant, ε	78	~ 5
Debye-Huckel constant, A	0.509	~ 4.3

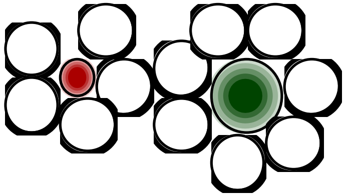
Electrolyte solution: molecular picture



Hydrated NaCl molecule

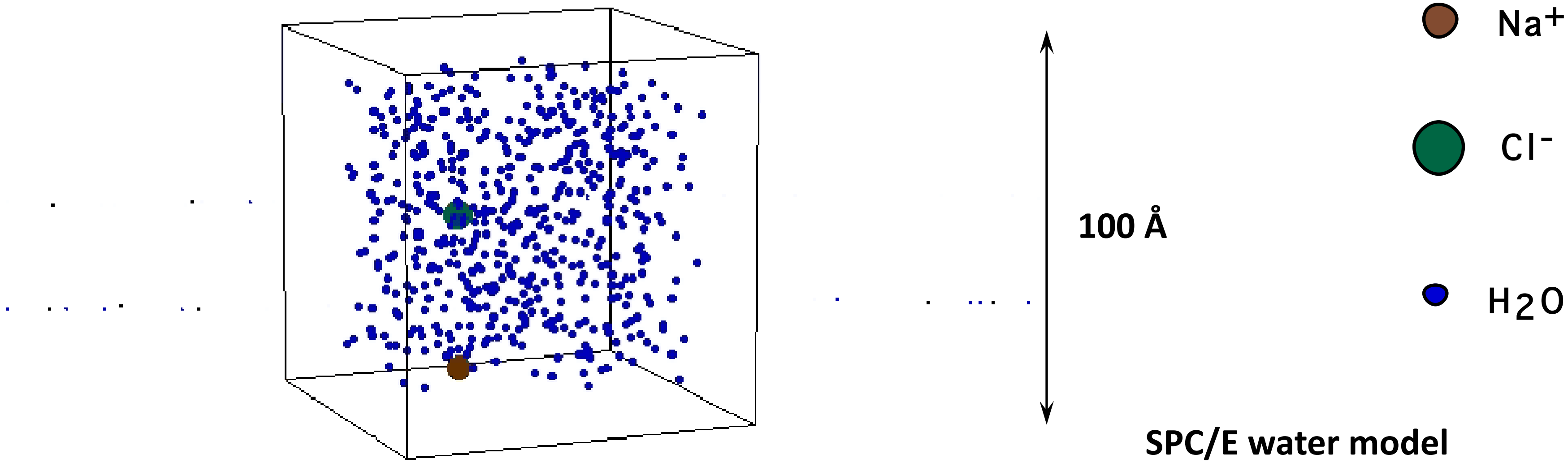


Solvent separated Na^+Cl^- ion pair



Fully dissociated Na^+Cl^- ion pair

Molecular dynamics simulation of ionic dissociation of NaCl in water



SPC/E water model
T=633 K and P=300 bar

Supercritical water (SCW)

SCW: water in a state above its critical pressure and temperature

Critical point: T_c = 374°C, P_c = 22.1 MPa, ρ_c = 0.32 g/cm^3

Unique physical-chemical properties

- Tunable reaction conditions: density, viscosity, dielectric constant

  Continuity of supercritical states

- Dissolves organic materials, normally insoluble: hydrocarbons

  Low dielectric constant, low density

- Complete miscibility of non-polar gases: O_2, N_2, H_2

  Low dielectric constant, low density

- Extraordinary fast kinetics

  No interphase boundaries, homogeneous medium

Supercritical water: solvent properties

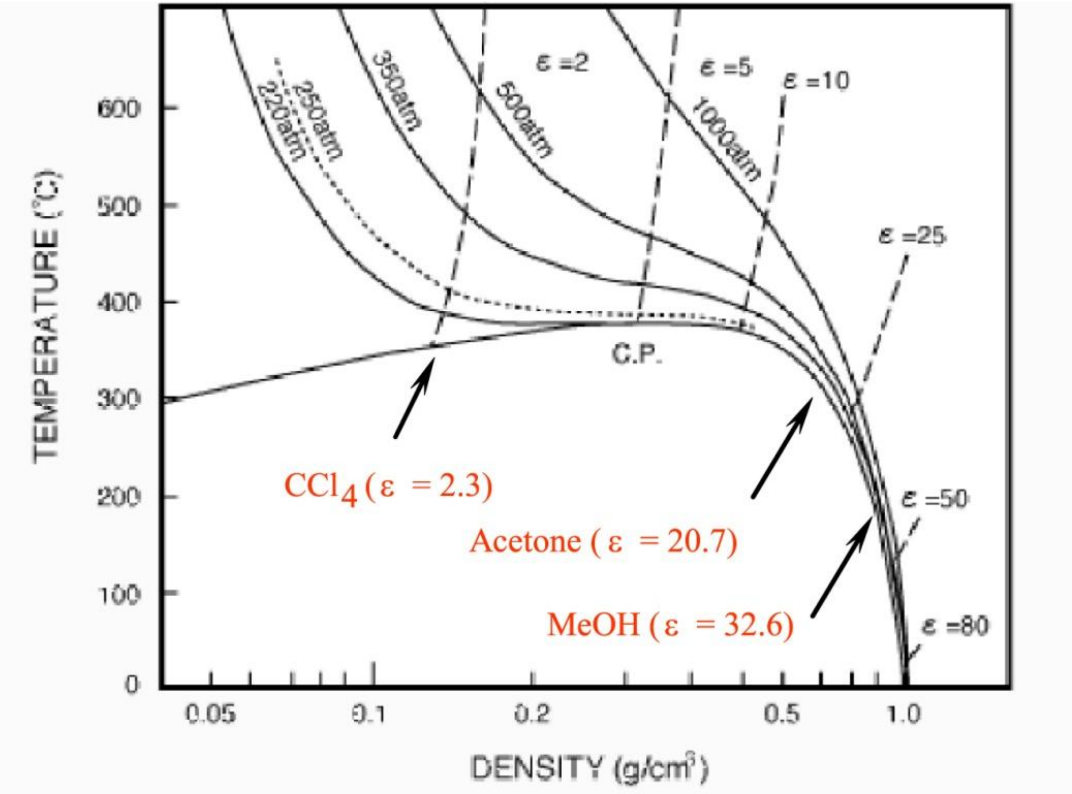
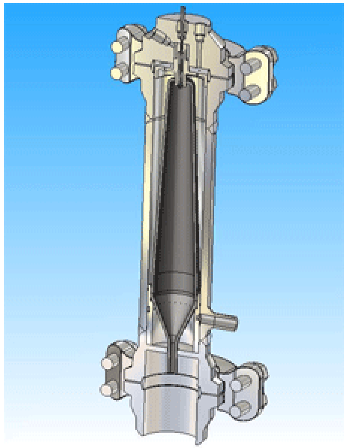


Figure 2: Phase diagram for water and dielectric constant

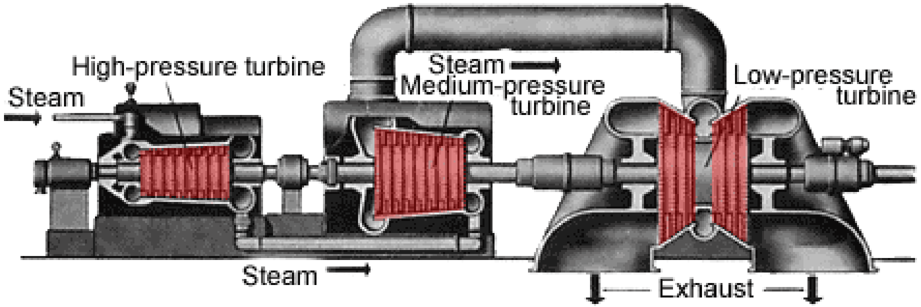
Hydrothermal technologies



Supercritical Water Oxidation
of hazardous organic waste (dioxins, PCBs, chemical warfare agents)

Recycling of plastics
Organic synthesis
Biomass conversion

Hydrothermal synthesis and processing of nanomaterials



Power generation (nuclear reactor coolant), steam turbines, water boilers

Supercritical water oxidation (SCWO)

Basic principle: *Total oxidation of organic waste compounds in supercritical water*

Oxidants: H_2O_2 or O_2

Target wastes: *PCBs, dioxins, chemical warfare agents, chemical sludge*

Process features:

- Rapid (Residence time < 60 s)
- Efficient (Degradation > 99.9 %)
- Environmentally Safe (no by-products)

Unique properties of supercritical water
(density, dielectric constant, viscosity)
+
No mass transfer limitations
=
Rapid and complete reactions !

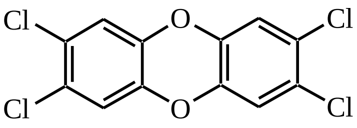
Key Advantage: ***Optimization of the reaction conditions can be achieved without changing solvent***

Supercritical water oxidation (SCWO)

Reaction conditions: T = 400 – 650 °C and P = 23 – 50 MPa

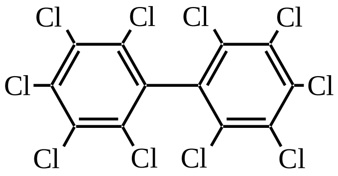
Completeness: up to 99.99%

Dioxin **(2,3,7,8-Tetrachloro-dibenzo[1,4]dioxine)**



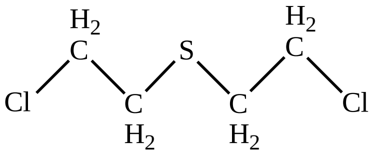
$+\ 22\ H_2O_2 \longrightarrow 12\ CO_2 + 22\ H_2O + 4\ HCl$

PCB (2,3,4,5,6,2',3',4',5',6'-Decachloro-biphenyl)



$+\ 22\ H_2O_2 \longrightarrow 12\ CO_2 + 14\ H_2O + 10\ HCl$

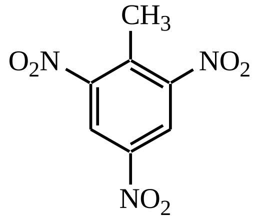
Nerve Agent HD



$+\ 14\ H_2O_2 \longrightarrow 4\ CO_2 + 16\ H_2O + 2\ HCl + H_2SO_4$

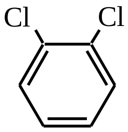
TNT

2



$+\ 21\ H_2O_2 \longrightarrow 14\ CO_2 + 26\ H_2O + 3\ N_2$

o-Dichlorobenzene



$+\ 13\ H_2O_2 \longrightarrow 6\ CO_2 + 14\ H_2O + 2\ HCl$

Organic chemical reactions in SCW

- Dehydration of alcohols to olefins

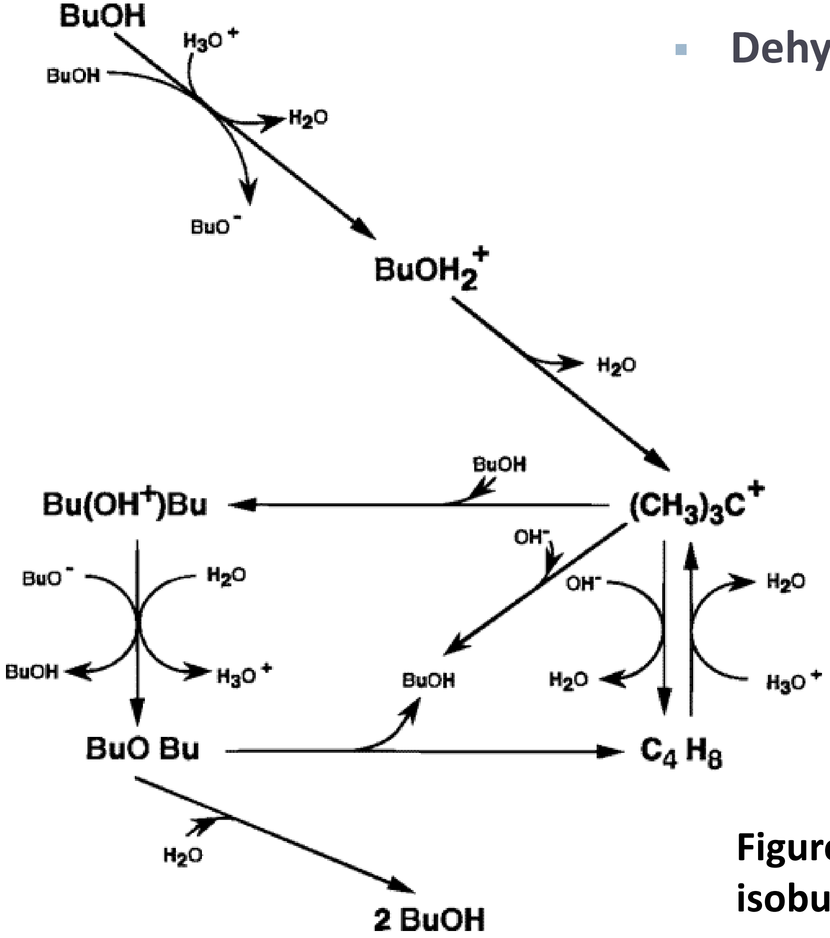
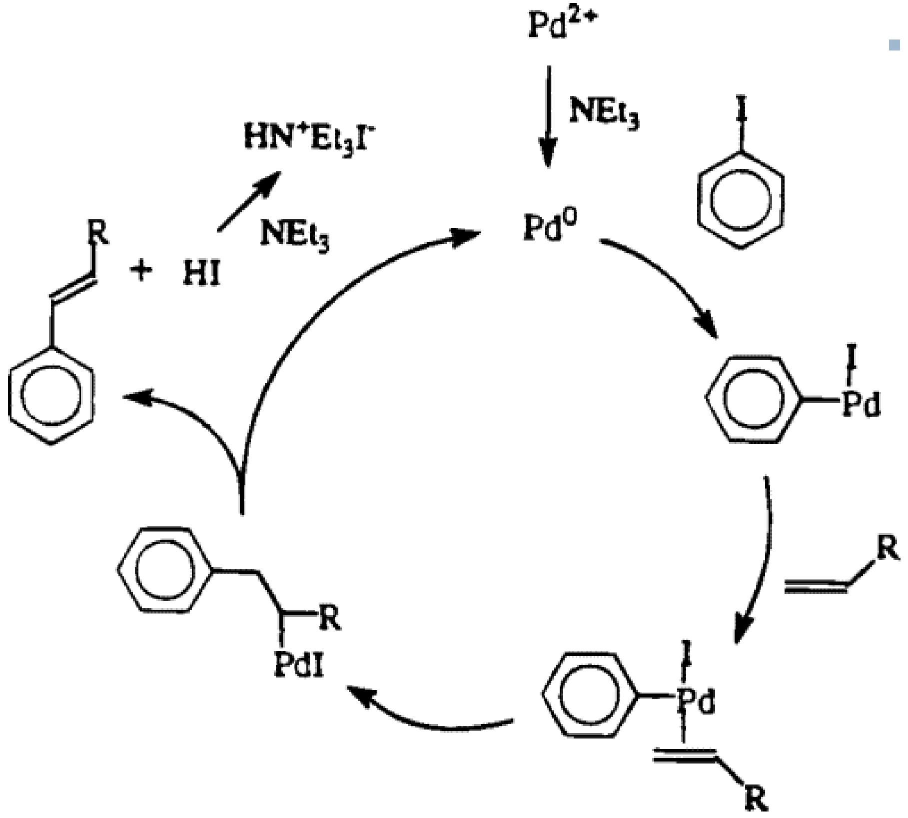


Figure: Conversion of *tert*-butyl alcohol to isobutylene

P. Savage, *Chem. Rev.,* 1999, 2, 603-622

Organic chemical reactions in SCW

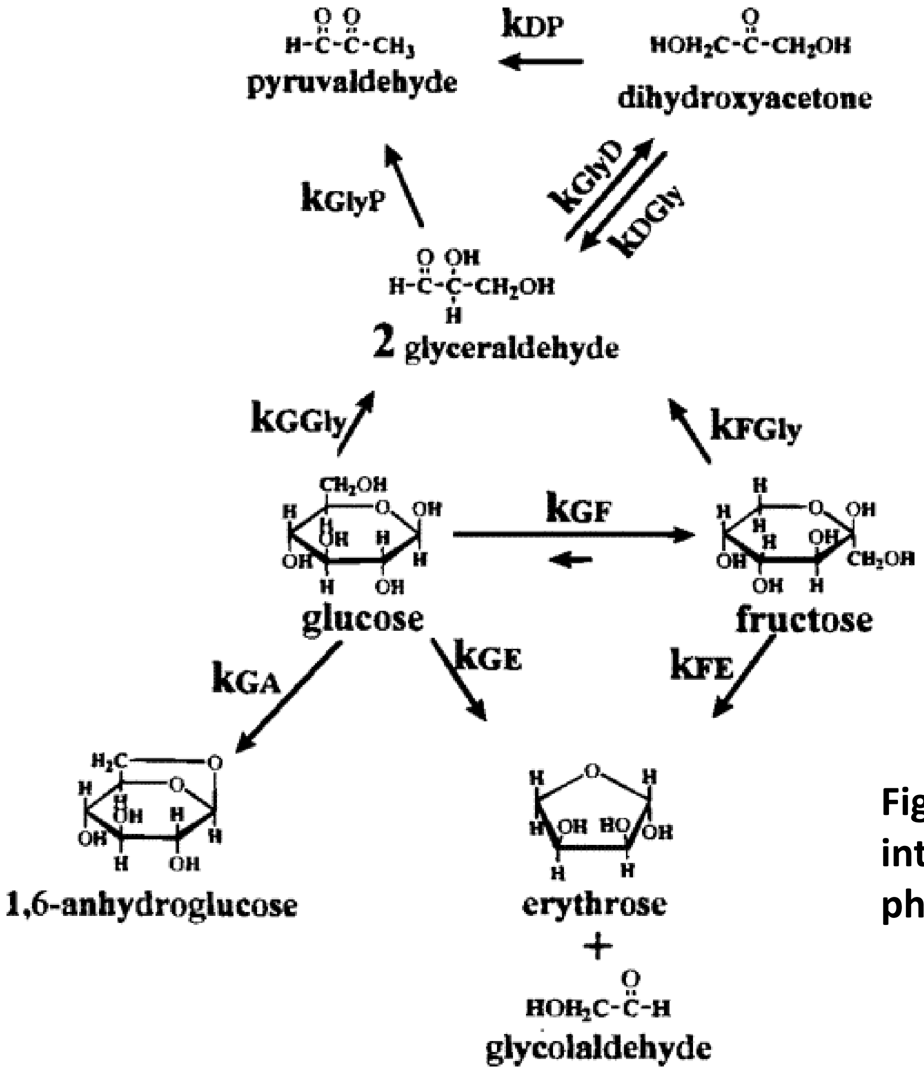


- C-C bond formation

Figure: Heck coupling reaction for iodobenzene with an alkene

P. Savage, *Chem. Rev.,* 1999, 2, 603-622

Organic chemical reactions in SCW

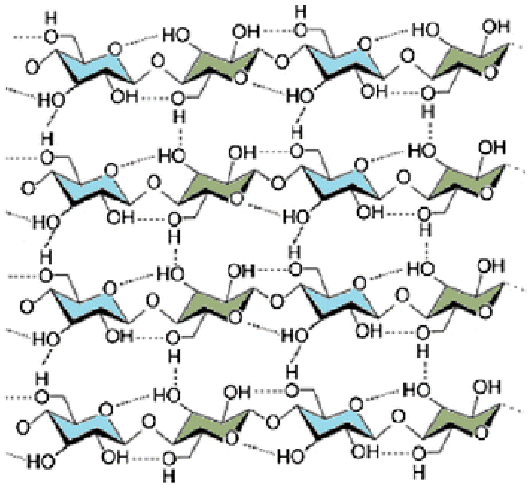


- Glucose conversion

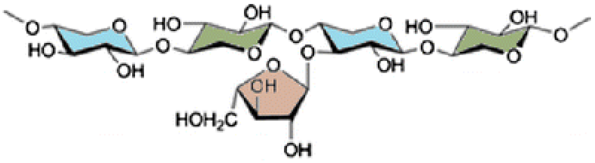
Figure: Glucose (sugar water) decomposition into erythrose (used in fine chemicals, pharmaceuticals)

P. Savage, *Chem. Rev.,* 1999, 2, 603-622

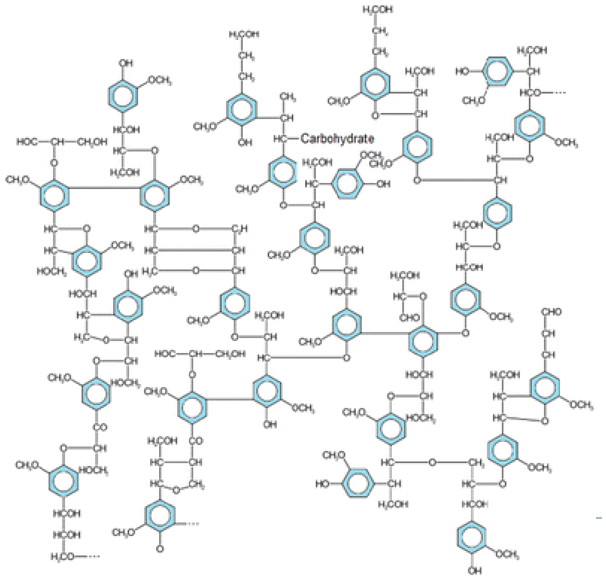
Biomass conversion in SCW



a



b



c

a) cellulose

b) hemicellulose

c) lignin

S. Nanda, *Biomass Conversion and Biorefinery*, 2017, 2, 157-191

Biomass conversion in SCW

- Non catalytic gasification pathways

Cellulose → Sugars (mainly glucose) → Syngas (Reactions 1-2)

Lignin → Phenolic compounds → Gaseous products (Reactions 3-8)

$(C_6H_{10}O_5)_n + n\ H_2O \rightarrow n\ C_6H_{12}O_6$ (1)

$C_6H_{12}O_6 \rightarrow 6\ CO + 6\ H_2$ (2)

$(C_{10}H_{10}O_3)_n + n\ H_2O \rightarrow n\ C_{10}H_{12}O_4$ (3)

$C_{10}H_{12}O_4 \rightarrow$ Phenolics (4)

Phenolics + $H_2O \rightarrow CO + CO_2 + H_2$ (5)

$CO + H_2O \rightarrow CO_2 + H_2$ (6)

$CO + 3\ H_2 \rightarrow CH_4 + H_2O$ (7)

$CO + 2\ H_2 \rightarrow CH_4 + 0.5\ O_2$ (8)

Biomass conversion in SCW

- **Catalytic liquefaction of syngas into a fuel (Fischer-Tropsch reaction)**

Noble metal catalysts (Rh, Ru and Re) show higher activity

Non-noble metal catalysts (Zn, Mo, Fe, Mn, Co and Cr) produce a mixture of alcohols

$2CO + 4H2 \rightarrow C_2H_5OH + H_2O$ (13)

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (14)

$CO + 2H_2 \rightarrow CH_3OH$ (15)

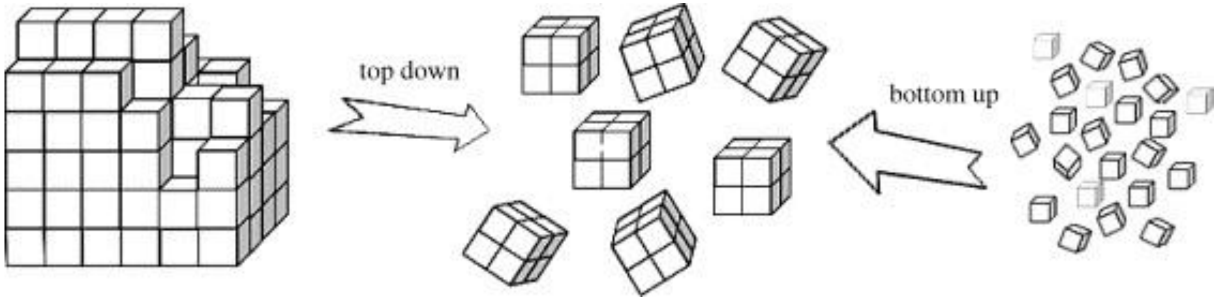
$CH_3OH + CO + H_2 \rightarrow C_2H_5OH$ (16)

$nCO + (2n+1)H_2 \rightarrow C_nH_{2(n+1)} + nH_2O$ (17)

$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$ (18)

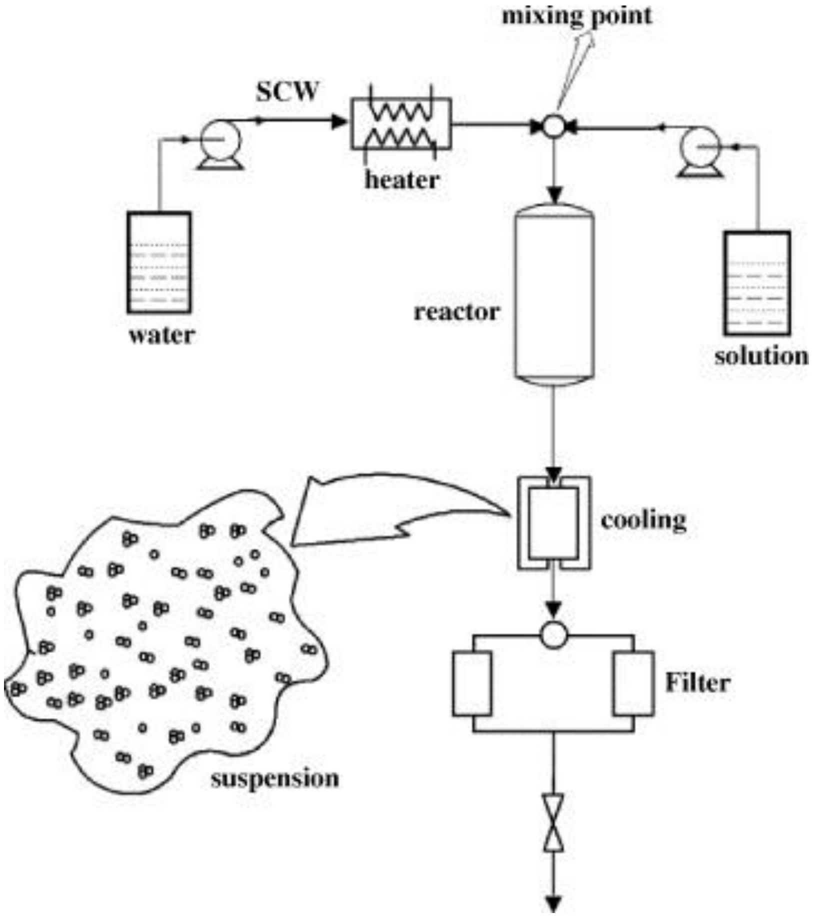
$C_2H_{2n-1}OH + CO + 2H_2 \rightarrow CH_3(CH_2)_nOH + H_2O$ (19)

Supercritical water: synthesis of nanomaterials



- Bottom-up approach (synthesis)
- Nanoproducts should have at least one dimension smaller than 100 nm

HTS-SCW process



Lay-out of the HTS-SCW process

Hydrothermal synthesis in supercritical water (HTS-SCW)

- HTS is used to produce synthetic materials imitating natural geothermal processes
- Pressurized metal salt solution and a SCW stream are combined in a mixing point, which leads to rapid heating and subsequent reaction
- The reaction equilibrium changes with temperature and results in the formation (precipitation) of fine particles of metal hydroxides or oxides

HTS-SCW process

Material	Particle dimensions (nm)	
	Range	Mean size
Co_3O_4		100
TiO_2	10–1000	20
CeO_2	20–300	180
$Al_5(Y + Tb)_3O_{12}$	20–600	
$LiCoO_2$	40–400	
Fe_3O_4 + Fe		40–92
$CoFe_2O_4$		39–72
$NiFe_2O_4$		28–43
α-Fe_2O_3	30–60	
Co_3O_4	30–60	
ZnO	120–320	
ZrO_2	3–5	

Table: Compounds produced in nanoparticles by HTS-SCW

Water treatment

- Water treatment method depends on intended use and source of water

- Drinking water
- Industrial use
- Sewage wastewater

Water quality

Major drinking water quality (WQ) parameters and source of water

WQ Parameter	Groundwater	Surface water
DO	low	high
BOD	lower	higher
particulates	low	high
H_2S, CH_4	possible	low
alkalinity	lower	higher
hardness	possible	possible
Fe^{2+}	high	low
bacteria count	lower	higher

Water quality

Special concerns for drinking water quality - hazardous chemicals

Small organics - chlorinated solvents, BTX (benzene, toluene, xylenes)

Large organics - pesticides, pharmaceuticals

Nitrate

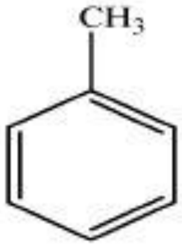
Phosphate, NTA and EDTA (detergent builders)

Heavy metals (organometallic forms)

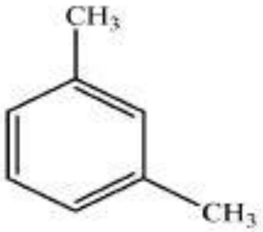
Hazardous chemicals

Benzene and its derivatives (BTX), PCP

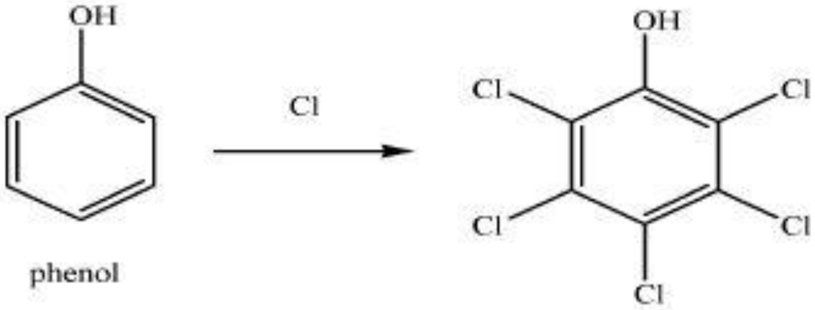
more soluble in water, 1.78 g/L



toluene



xylene **(toxic)**



PCP: pentachlorophenol

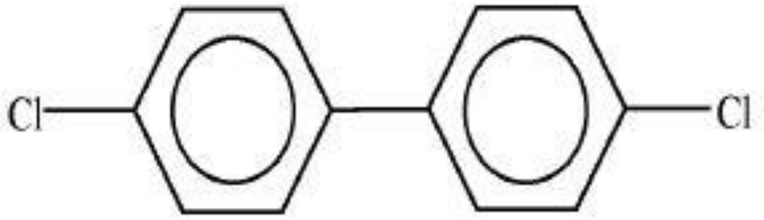
wood preservative, very toxic

Hazardous chemicals

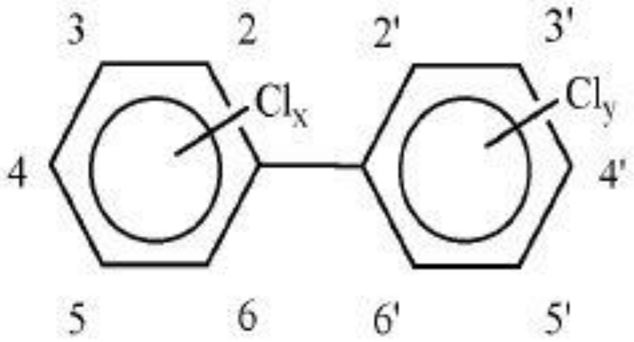
Chlorinated hydrocarbons

Saturated:
Trihalomethanes (THM), $CHCl_3$

Aromatic:
polychlorinated biphenyls (PCBs) - transformer fluids, flame retardants



4,4'-dichlorobiphenyl

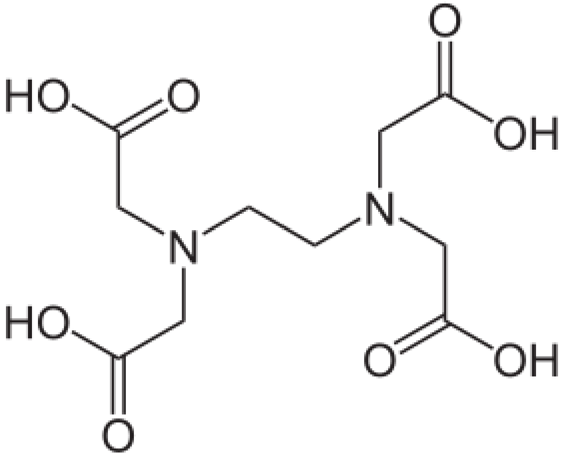


PCB congeners - family of PCBs

- **Halogenated hydrocarbons are toxic, persistent and tend to bioaccumulate**

Hazardous chemicals

Detergent builders - NTA and EDTA



EDTA

- **Strong chelating agents, solubilise and bind heavy metals**

Hazardous chemicals

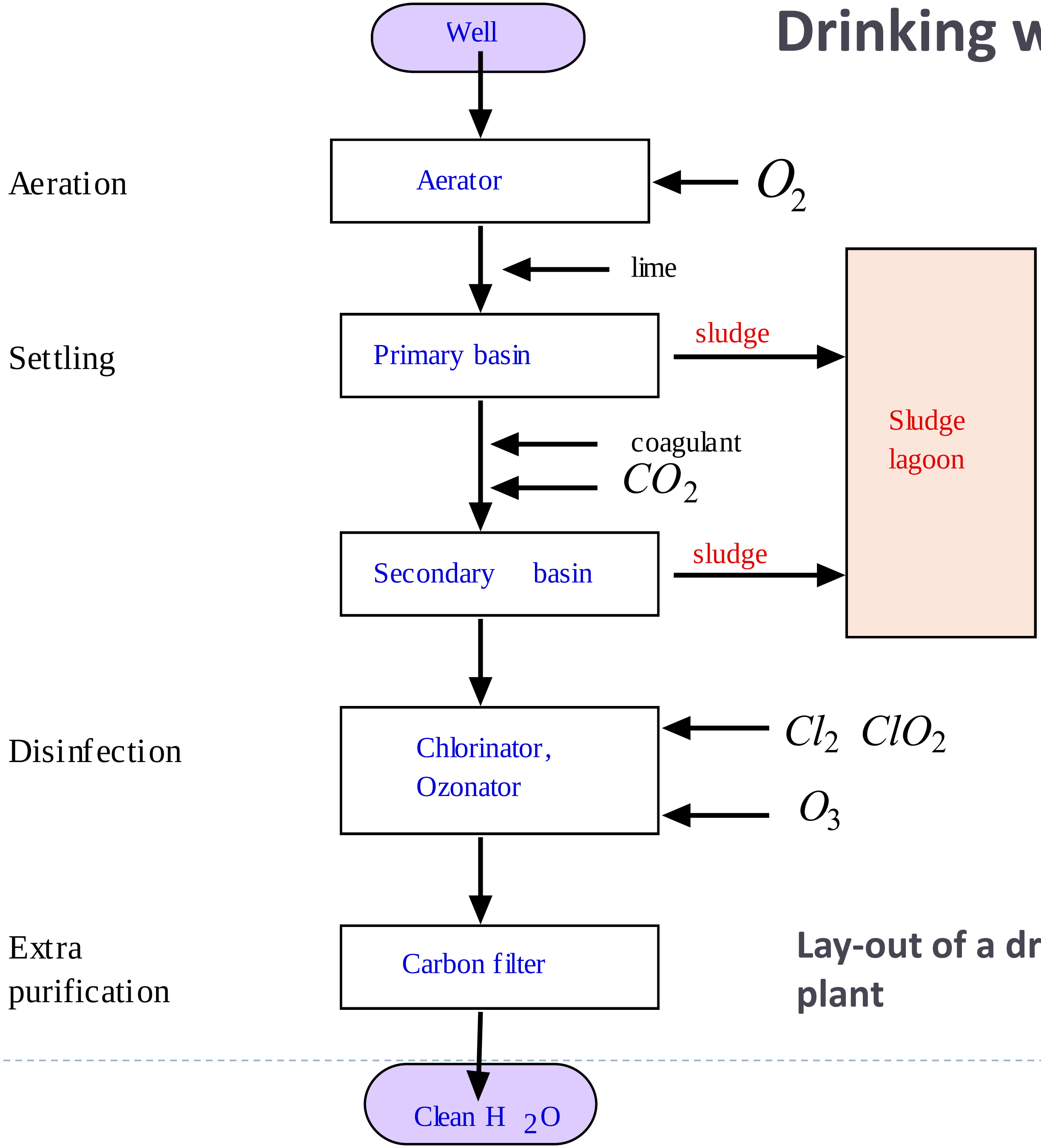
Organometallic derivatives of heavy metal compounds are particularly hazardous

tetraethyllead, TEL, $Pb(C_2H_5)_4$ - gasoline additive, toxic, affects central nervous system

tributyltin chloride, TBT, $Sn(C_4H_9)_3Cl$ - insecticide, very toxic

methylmercury chloride, $Hg(CH_3)Cl$ - product of bacterial activity, extremely toxic

Drinking water treatment



Well

Aeration

Aerator ← O_2

← lime

Settling

Primary basin → sludge

← coagulant

← CO_2

Secondary basin → sludge

Sludge lagoon

Disinfection

Chlorinator, Ozonator ← Cl_2 ClO_2

← O_3

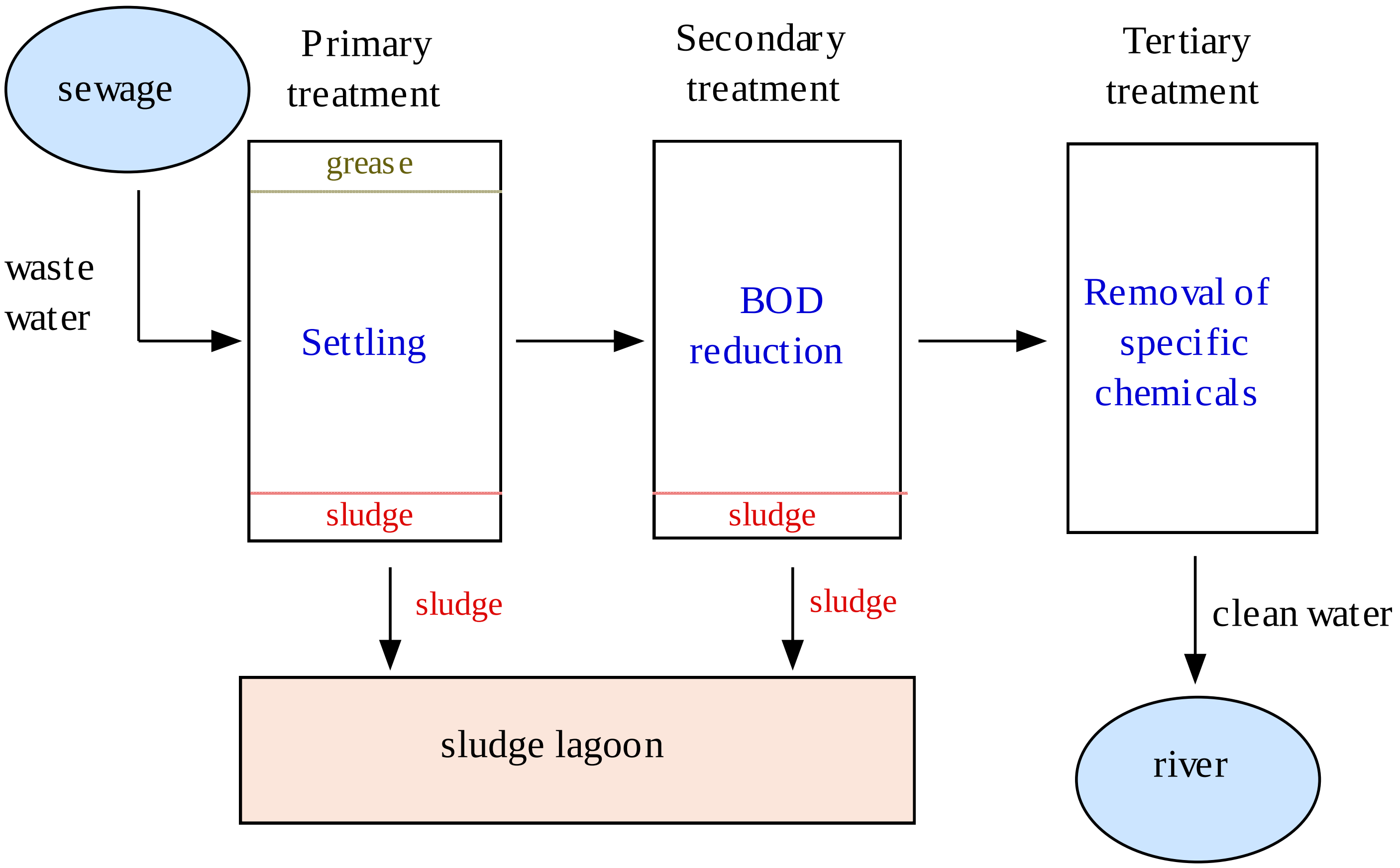
Extra purification

Carbon filter

Clean H_2O

Lay-out of a drinking water treatment plant

Wastewater treatment



Lay-out of a wastewater treatment plant

Advanced Oxidation Methods

Advanced Oxidation Methods (Processes) (abbreviation: AOM, AOP) refer to a set of chemical treatment procedures designed to remove waste materials by oxidation.

Contaminants are oxidized by three different reagents: ozone, hydrogen peroxide and oxygen, in precise, pre-programmed dosages, sequences, and combinations. These procedures may also be combined with UV irradiation and specific catalysts.

AOM examples

- **Fenton reagent** – solution of hydrogen peroxide and an iron catalyst
- **Photocatalysis** – acceleration of a photoreaction in the presence of a catalyst
- **Wet Air Oxidation** (WAO) - oxidation of dissolved or suspended organic compounds in water vapor using oxygen (air) as the oxidizer at T= 400-600 K and P = 10-150 bar
  - Catalytic Wet Air Oxidation (CWAO)
- **Supercritical Water Oxidation** (SCWO) – oxidation of organic compounds in supercritical water using oxygen or hydrogen peroxide as the oxidizer

Chemical methods of ·OH(aq) generation

- **By mixing H_2O_2 solution with waste water and UV irradiation**

$$H_2O_2 \xrightarrow{UV} 2 \cdot OH \qquad (1)$$

Fe^{2+} can be used as a catalyst for H_2O_2 decomposition (Fenton reagent)

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot OH + OH^- \qquad (2)$$

- **Alternatively, by adding O_3 together with H_2O_2**

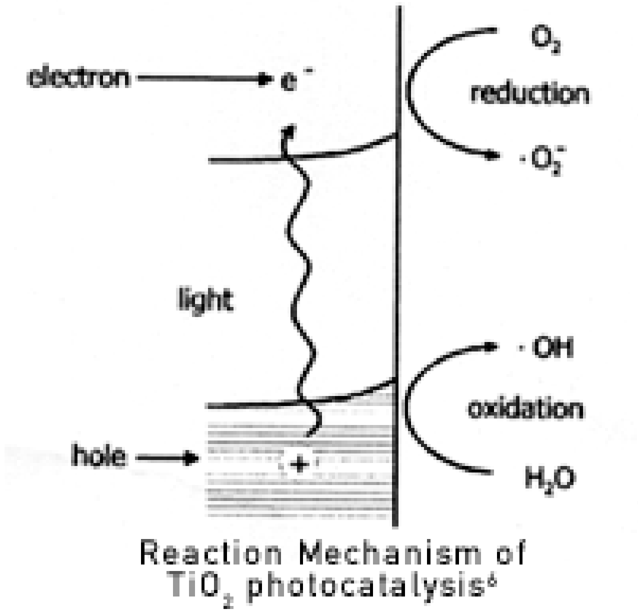
$$2O_3 + H_2O_2 \longrightarrow 2 \cdot OH + 3O_2 \qquad (3)$$

- **Or, simply, by thermal decomposition of H_2O_2**

$$H_2O_2 \xrightarrow{high\ T} 2 \cdot OH \qquad (4)$$

Physical methods of ·OH(aq) generation

- **By using suspensions of photocatalytic substances (titanium dioxide, TiO_2)**



Light absorption in TiO_2 at $\lambda < 385$ nm effects the promotion of an electron from the valence band to the conduction band of the semiconductor. This excitation process creates an electronic charge carrier in the conduction band and an electron vacancy (a hole) in the valence band. The hole is a very powerful oxidizing agent, capable of oxidizing a variety of organic molecules as well as generating hydroxyl radicals in water.

Reaction mechanism of TiO_2 photocatalysis