

CAPVT III

TOPLJIVOST

Otapanje \neq Miješanje

ili

Otapanje \subset Miješanje

?

O vodi



WATER

from a Chemical Point of View

or

On Eccentricities and Peculiarities of
a Very Strange Liquid

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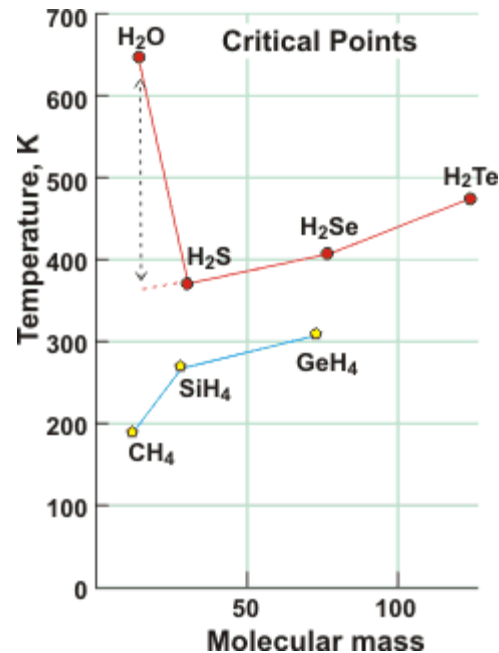
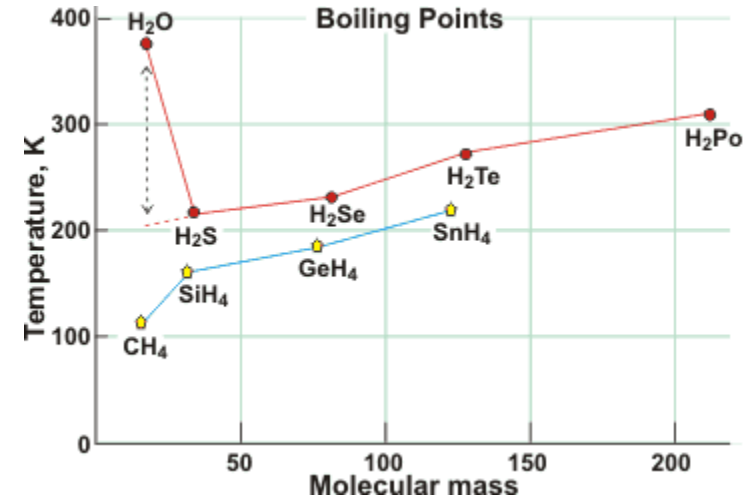
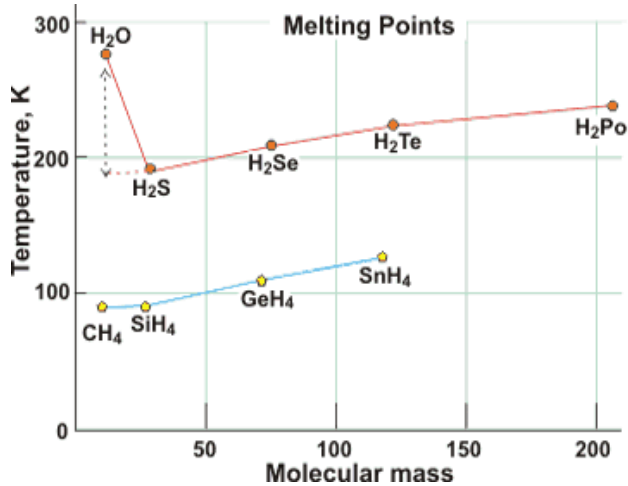


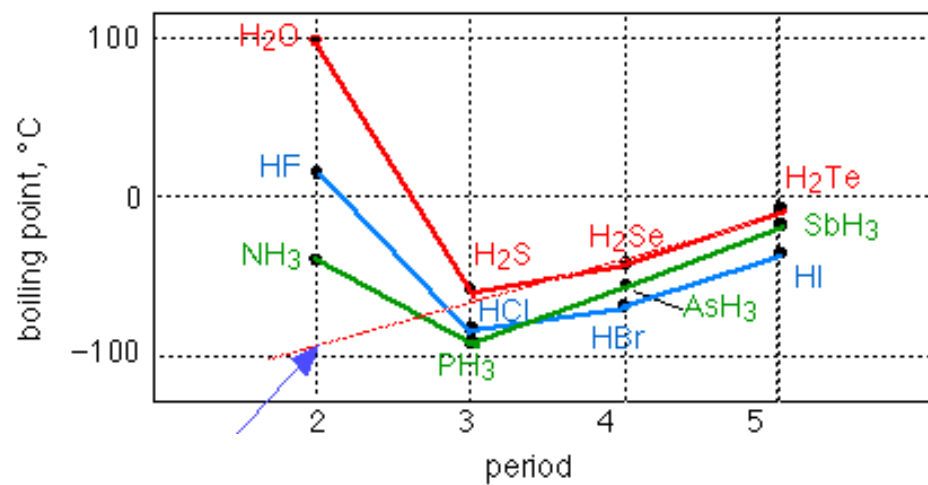
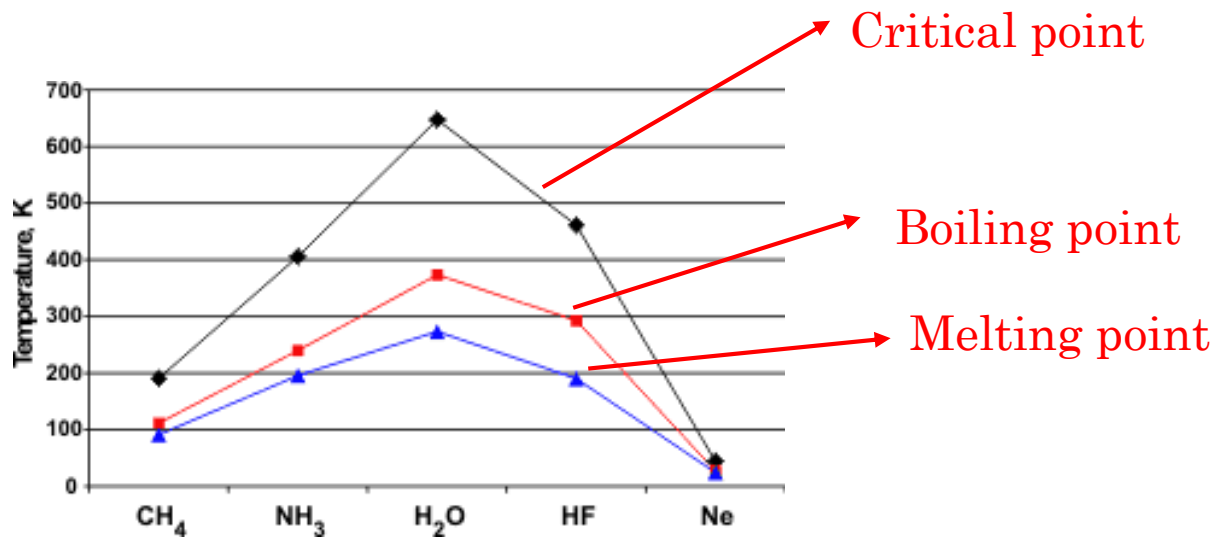
PART I:

What's so strange about it?

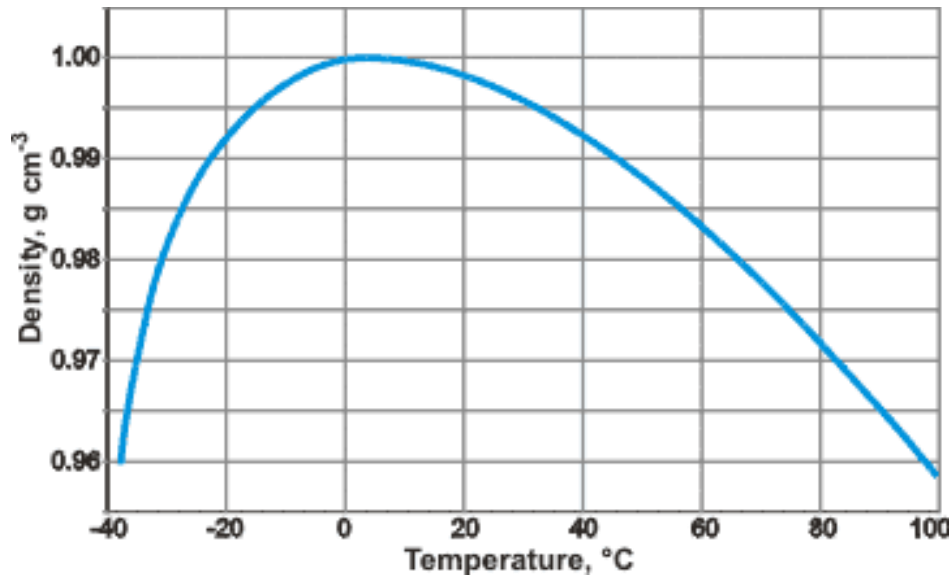


Unusually high melting point, boiling point and critical point.

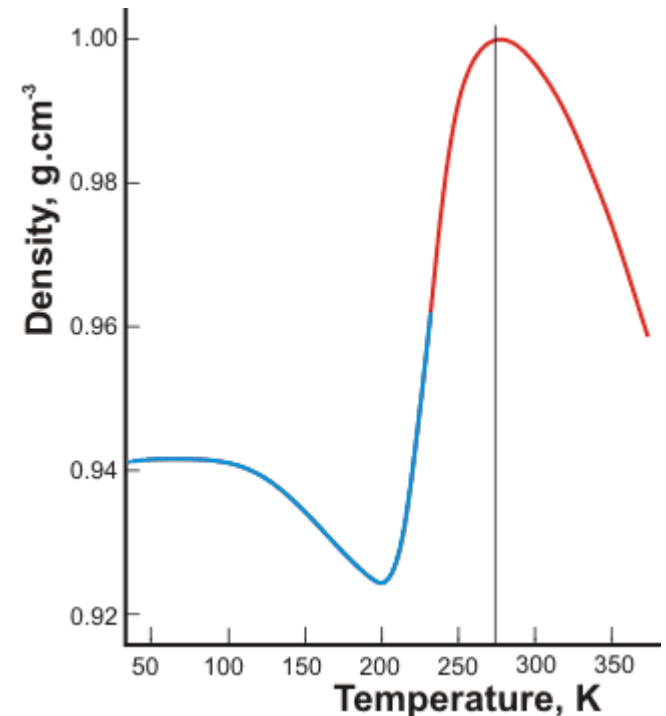




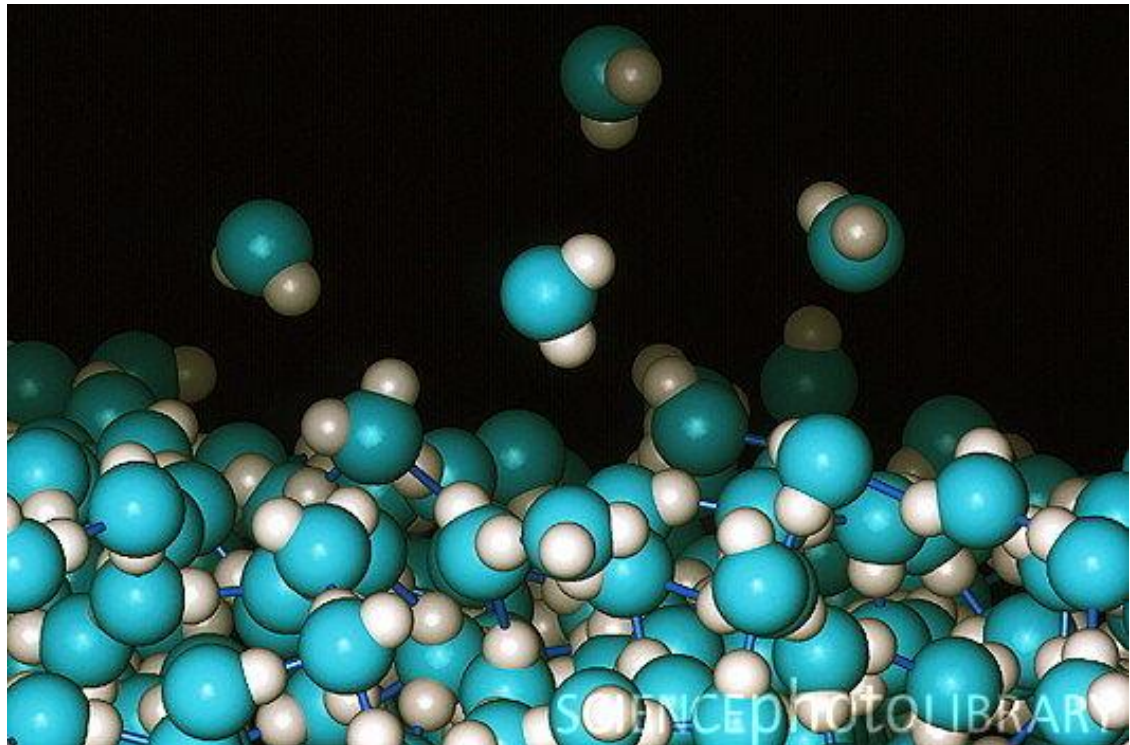
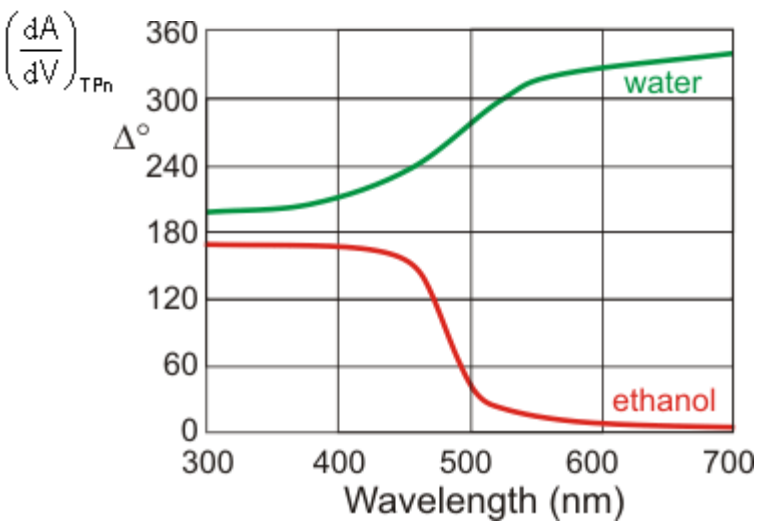
Liquid water has a high density that increases on heating (up to 3.984 °C).



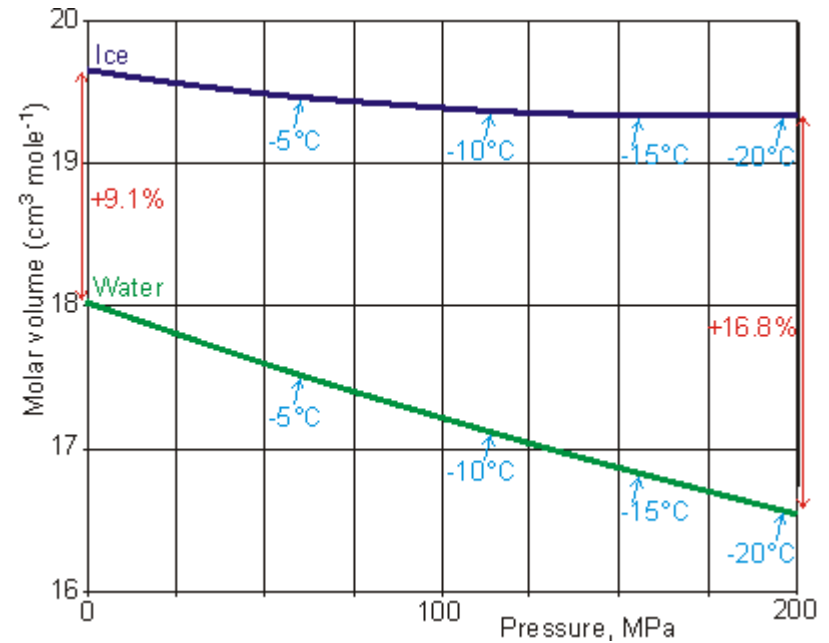
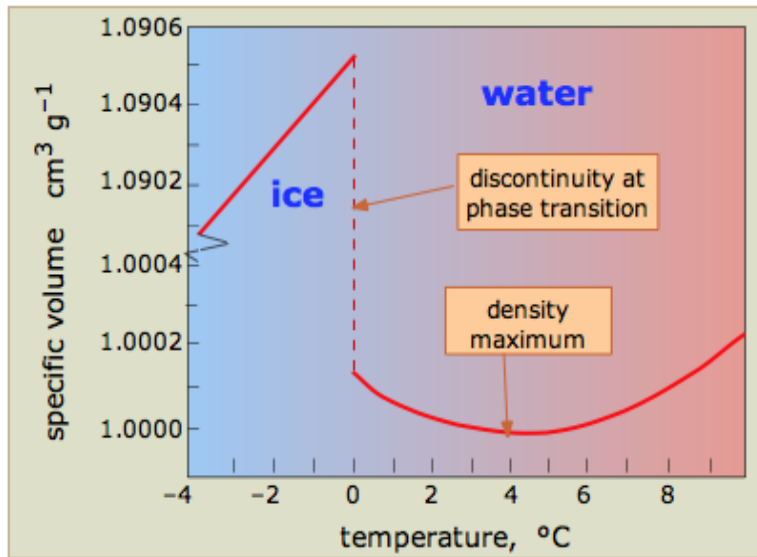
There is a minimum in the density of supercooled water



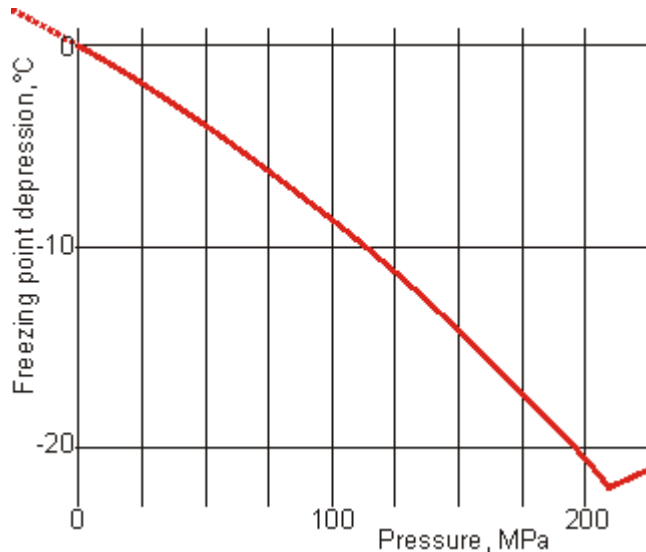
The surface of water is denser than the bulk



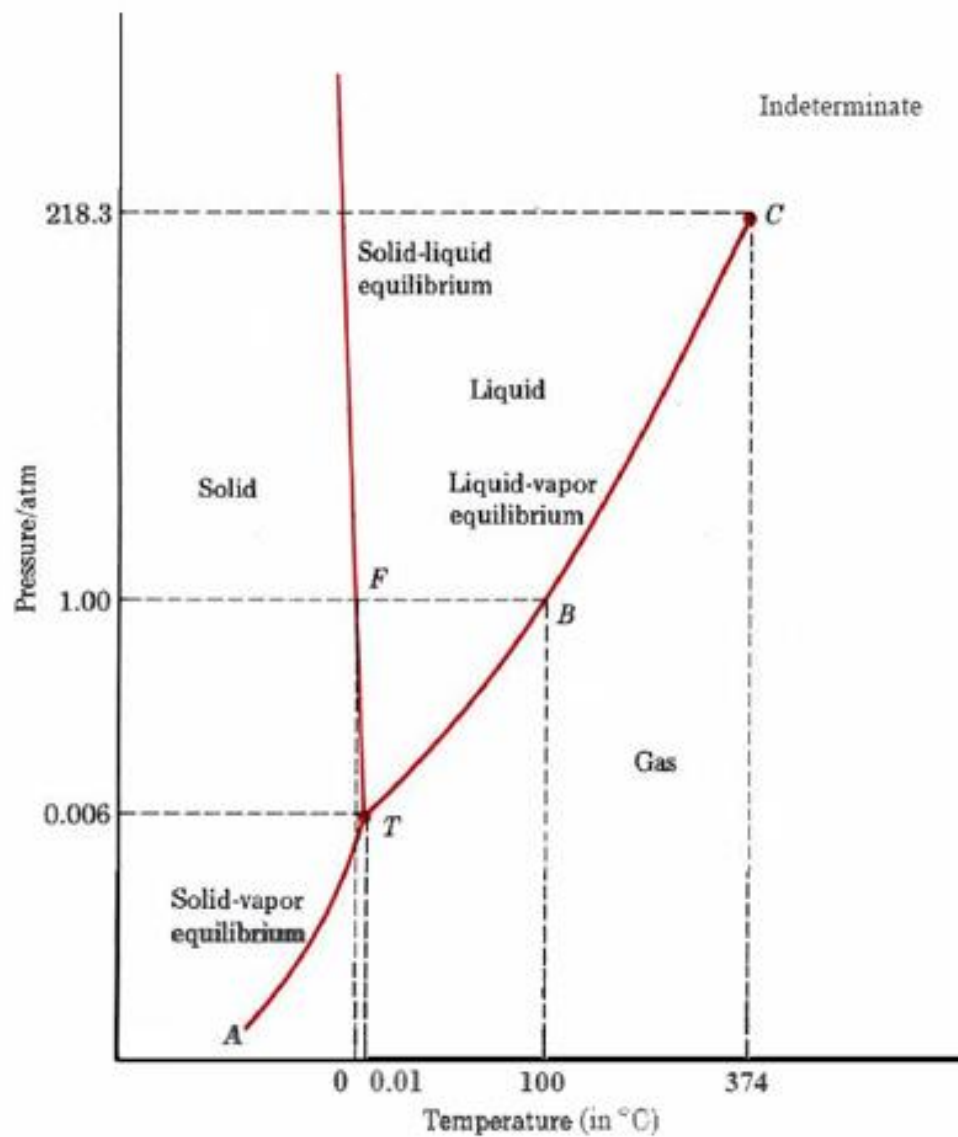
Water shrinks on melting.



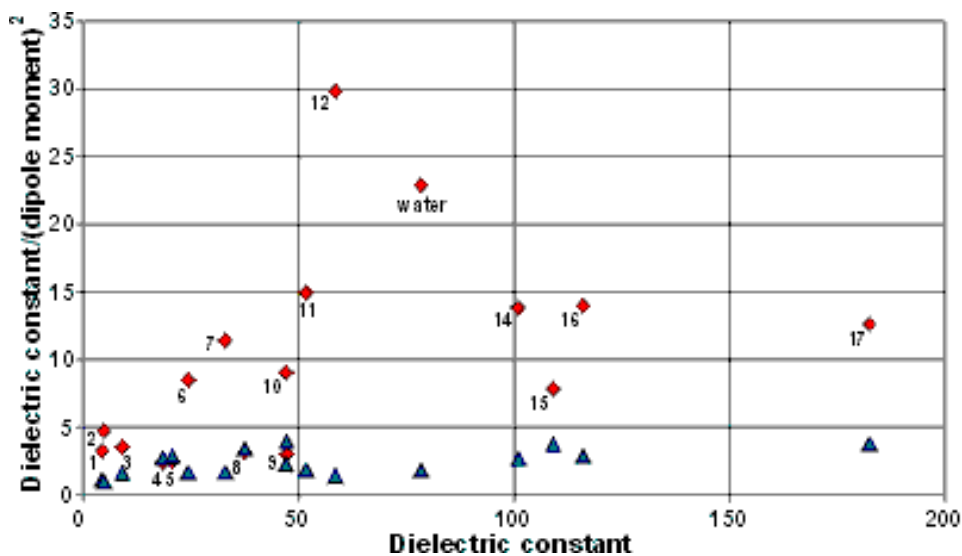
Pressure reduces ice's melting point.



$$\frac{dP}{dT} = \frac{Q}{T(V^I - V^{II})}$$



Unusually high dielectric constant

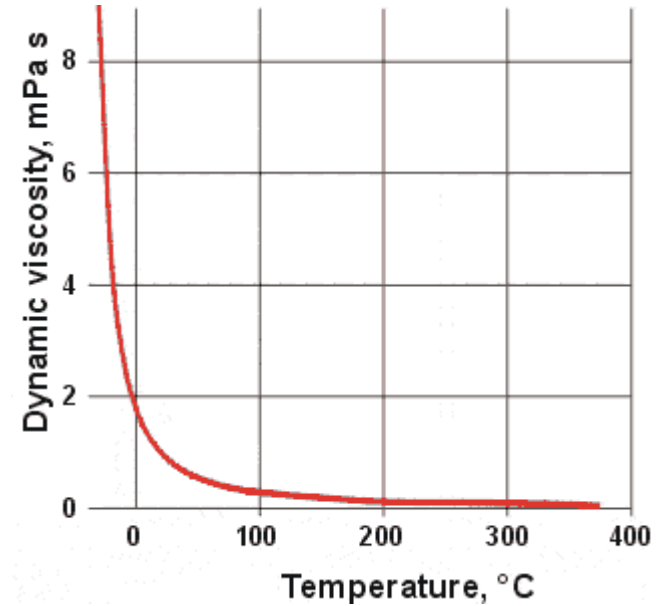
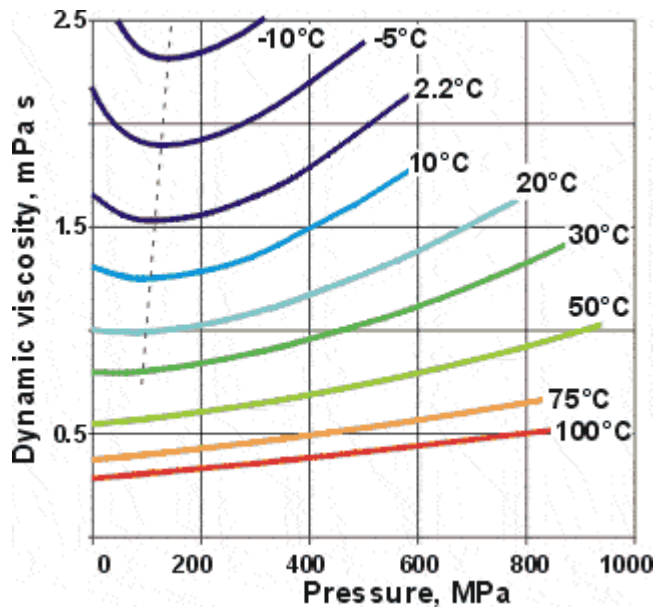


- 1, diethyl ether;
- 2, chloroform;
- 3, methylene dichloride;
- 4, methyl ethyl ketone;
- 5, acetone;
- 6, ethanol;
- 7, methanol;
- 8, acetonitrile;
- 9, ethylene glycol;
- 10, dimethyl sulfoxide;
- 11, hydrazine;
- 12, formic acid;
- 13, water;
- 14, sulfuric acid;
- 15, formamide;
- 16, hydrogen cyanide;
- 17, *N,N*-dimethylformamide

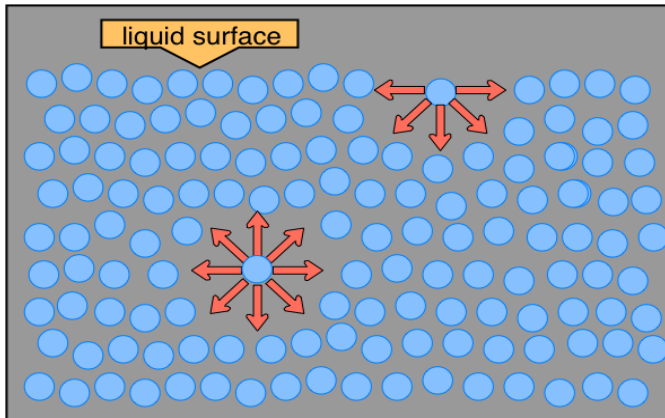
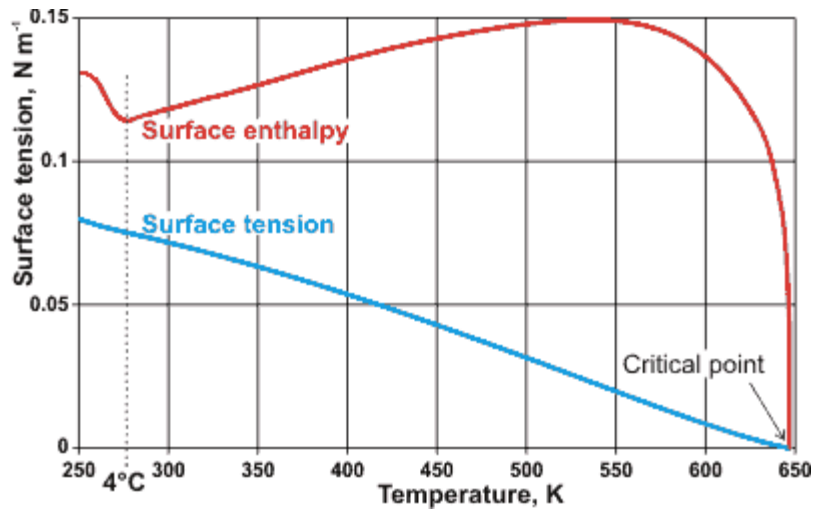
High viscosity

quickly increases with reduction of temperature

can decrease with pressure



Large surface tension

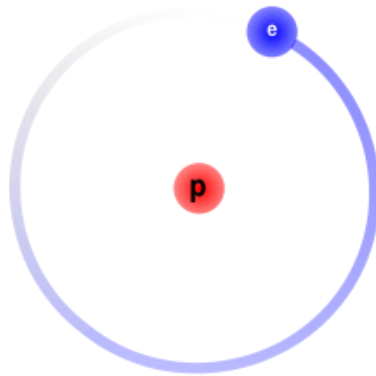


Unusually large isotopic effects.

D₂O and T₂O differ significantly from H₂O in their physical properties.

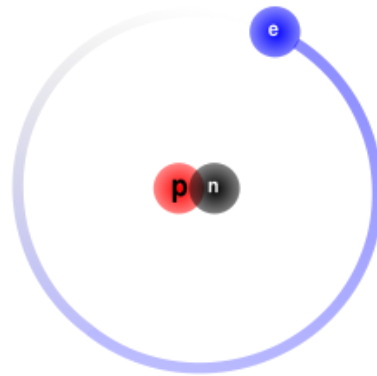
Liquid H₂O and D₂O differ significantly in their phase behavior.

H₂O and D₂O ices differ significantly in their quantum behavior.



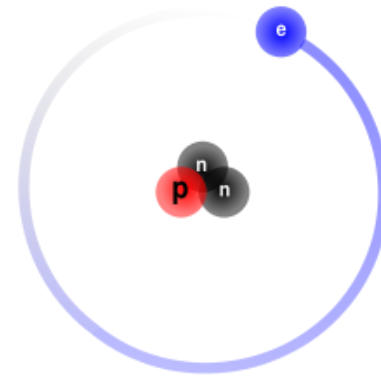
${}^1_1\text{H}$

(Normal) Hydrogen



${}^2_1\text{H} = \text{D}$

Deuterium



${}^3_1\text{H} = \text{T}$

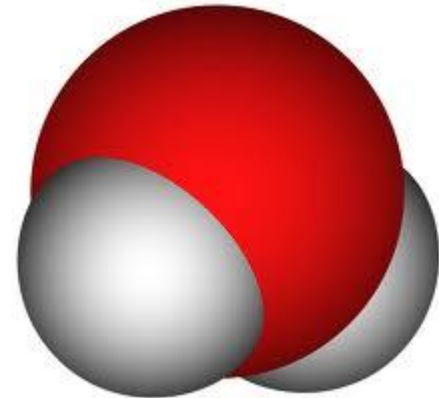
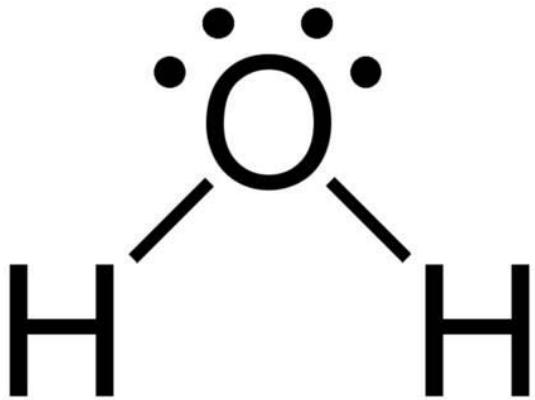
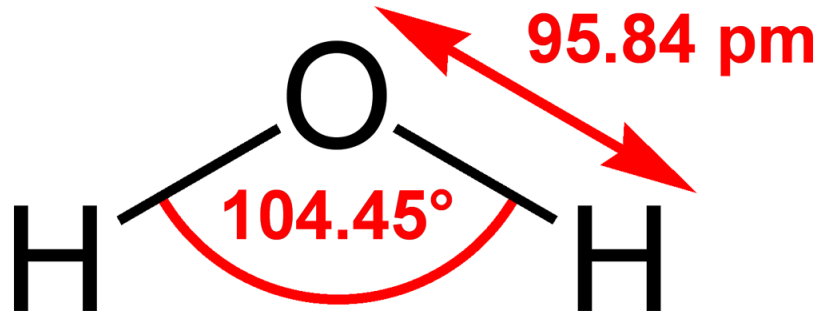
Tritium

And many other peculiarities...

- Water has unusually high melting point.
- Water has unusually high boiling point.
- Water has unusually high critical point.
- Solid water exists in a wider variety of stable (and metastable) crystal and amorphous structures than other materials.
- The thermal conductivity, shear modulus and transverse sound velocity of ice reduce with increasing pressure.
- The structure of liquid water changes at high pressure.
- Supercooled water has two phases and a second critical point at about -91 °C.
- Liquid water is easily supercooled but glassified with difficulty.
- Liquid water exists at very low temperatures and freezes on heating.
- Liquid water may be easily superheated.
- Hot water may freeze faster than cold water; the Mpemba effect.
- Warm water vibrates longer than cold water.
- The density of ice increases on heating (up to 70 K)
- Water shrinks on melting.
- Pressure reduces ice's melting point.
- Liquid water has a high density that increases on heating (up to 3.984 °C).
- The surface of water is denser than the bulk.
- Pressure reduces the temperature of maximum density.
- There is a minimum in the density of supercooled water.
- Water has a low coefficient of expansion (thermal expansivity).
- Water's thermal expansivity reduces increasingly (becoming negative) at low temperatures.
- Water's thermal expansivity increases with increased pressure.
- The number of nearest neighbors increases on melting.
- The number of nearest neighbors increases with temperature.
- Water has unusually low compressibility.
- The compressibility drops as temperature increases up to 46.5 °C.
- There is a maximum in the compressibility-temperature relationship.
- The speed of sound increases with temperature up to 74 °C.
- The speed of sound may show a minimum.
- 'Fast sound' is found at high frequencies and shows an discontinuity at higher pressure.
- NMR spin-lattice relaxation time is very small at low temperatures.
- The NMR shift increases to a maximum at low (supercool) temperatures
- The refractive index of water has a maximum value at just below 0 °C.
- The change in volume as liquid changes to gas is very large.
- No aqueous solution is ideal.
- D2O and T2O differ significantly from H2O in their physical properties.
- Liquid H2O and D2O differ significantly in their phase behavior.
- H2O and D 2O ices differ significantly in their quantum behavior.
- The mean kinetic energy of water's hydrogen atoms increases at low temperature.
- Solutes have varying effects on properties such as density and viscosity.
- The solubilities of non-polar gases in water decrease with temperature to a minimum and then rise.
- The dielectric constant of water is high.
- The relative permittivity shows a temperature maximum.
- Proton and hydroxide ion mobilities are anomalously fast in an electric field.
- The electrical conductivity of water rises to a maximum at about 230 °C.
- Acidity constants of weak acids show temperature minima.
- X-ray diffraction shows an unusually detailed structure.
- Under high pressure water molecules move further away from each other with increasing pressure.
- The heat of fusion of water with temperature exhibits a maximum at -17 °C [Water has over twice the specific heat capacity of ice or steam]
- The specific heat capacity (CP and CV) is unusually high]
- The specific heat capacity CP has a minimum at 36 °C]
- The specific heat capacity (CP) has a maximum at about -45 °C]
- The specific heat capacity (CP) has a minimum with respect to pressure]
- The heat capacity (CV) has a maximum.
- High heat of vaporization.
- High heat of sublimation.
- High entropy of vaporization.
- The thermal conductivity of water is high and rises to a maximum at about 130 °C.
- Water has unusually high viscosity.
- Large viscosity increase as the temperature is lowered.
- Water's viscosity decreases with pressure below 33 °C.
- Large diffusion decrease as the temperature is lowered.
- At low temperatures, the self-diffusion of water increases as the density and pressure increase.
- The thermal diffusivity rises to a maximum at about 0.8 GPa.
- Water has unusually high surface tension.
- Some salts give a surface tension-concentration minimum; the Jones-Ray effect.
- Some salts prevent the coalescence of small bubbles.
- The molar ionic volumes of salts show maxima with respect to temperature.

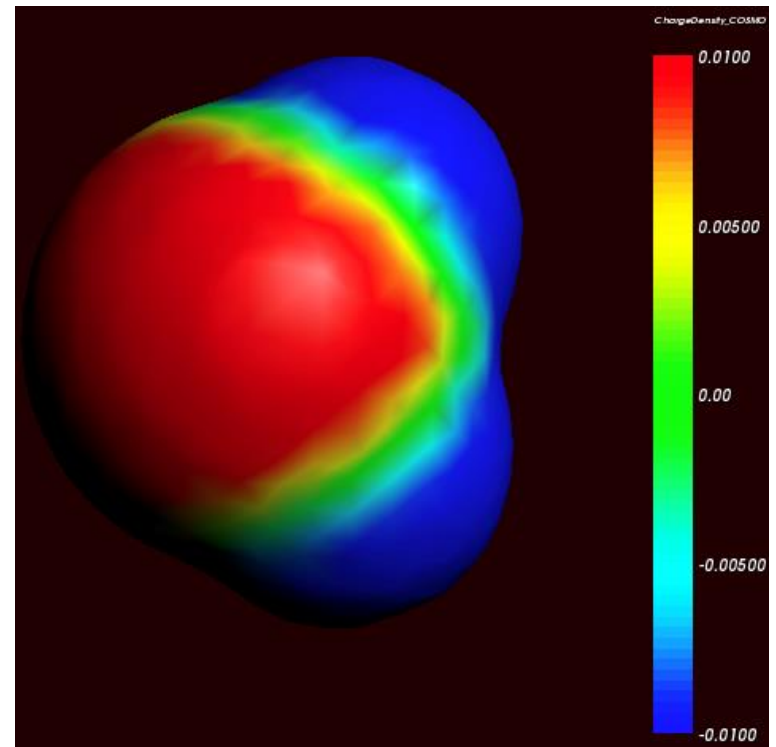
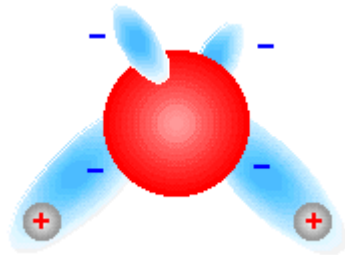
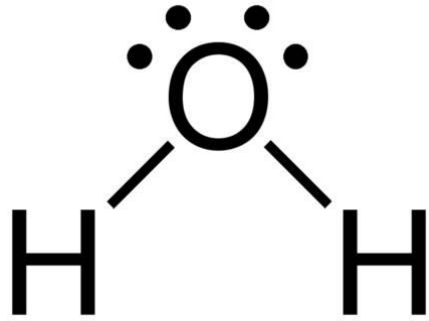
WHY?

The water molecule – H₂O



Piješ vodu kao vo'
Ne znaš što je ha-dva-o

Water is polar

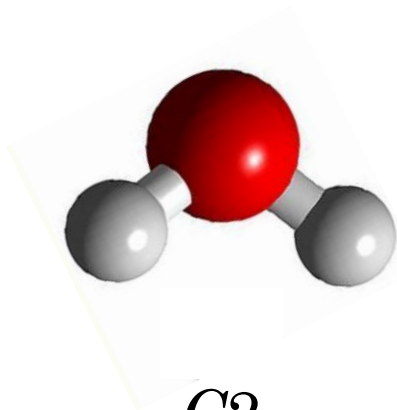


Water is polar

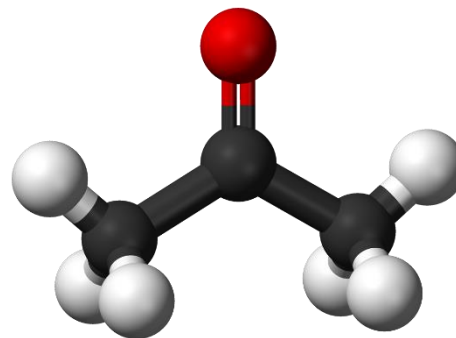
What does that mean?

1. Water molecule has a polar geometry?
2. Water molecule has a large dipole moment?
3. Water has a large dielectric constant?
4. Something else?

What is more polar – water or acetone?



C_{2v}



C_{2v}

1. Molecular geometry

2. Dipole moment / D

3. Dielectric constant

1.85

80.4

2.88

20.7

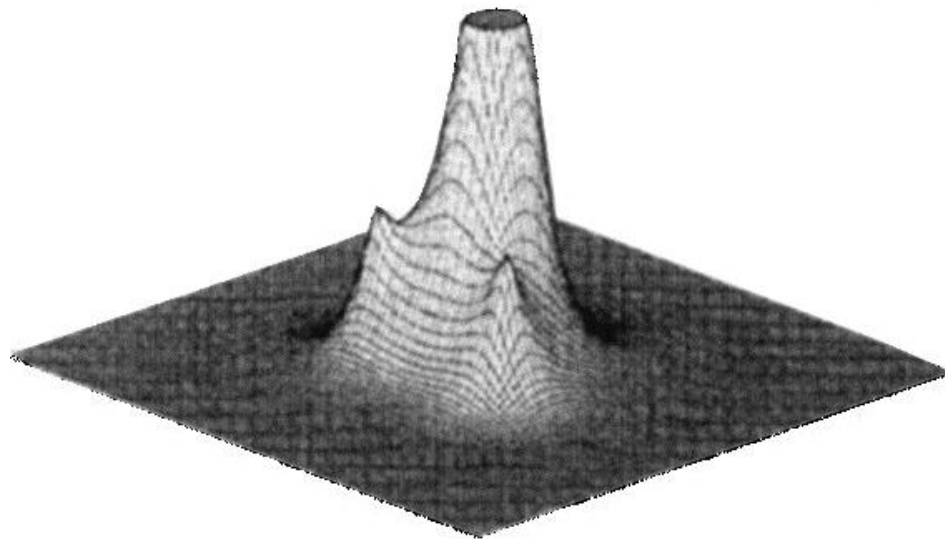
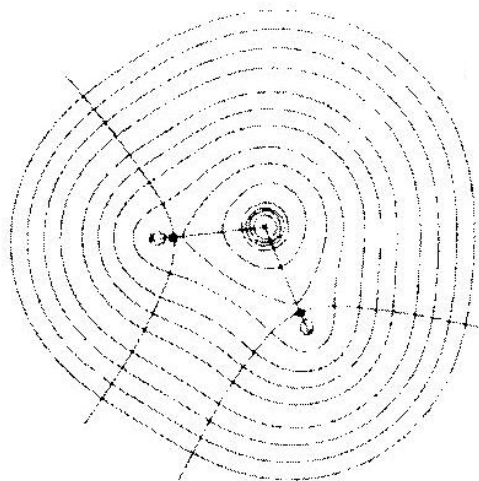
SAME

acetone

water

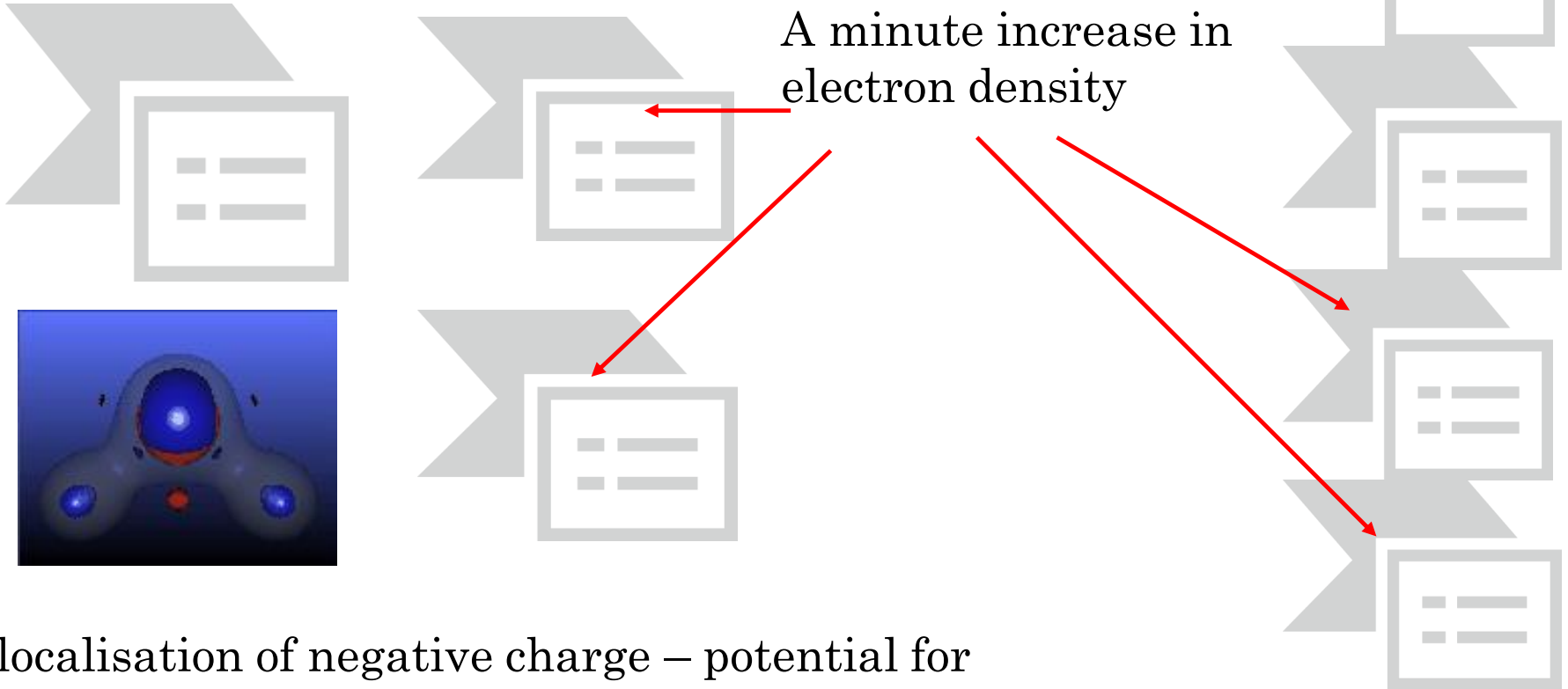
Dipole moment is a property of a molecule,
dielectric constant of a substance!

A closer look at a water molecule – electron density distribution



An even closer look at a water molecule – Laplacian of electron density

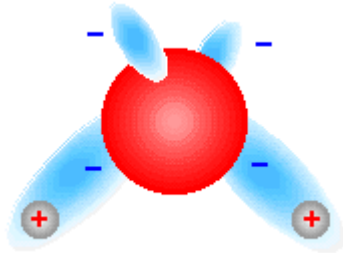
$$\text{Laplacian} - \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$



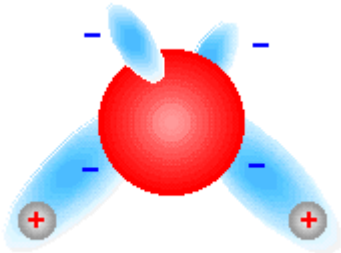
localisation of negative charge – potential for
hydrogen bonding

The structure of liquid water – what holds the molecules together – Dipole interactions?

Dipole – dipole interaction

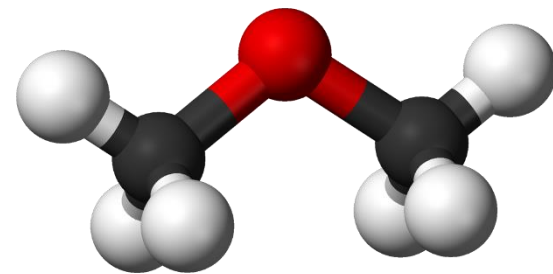
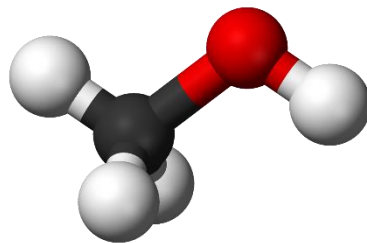
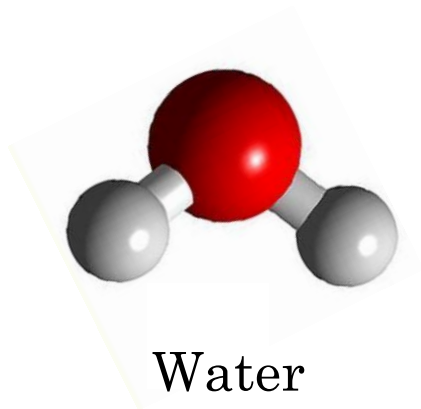


$$E = -\frac{\mu_1\mu_2}{4\pi\epsilon_0 r_{12}^3} (\cos \varphi_{12} - 3 \cos \varphi_1 \cos \varphi_2)$$



For optimal dipole alignment –
ca 0,5 kcal mol⁻¹

Dipole interactions?



μ / D

1.85

1.62

1.43

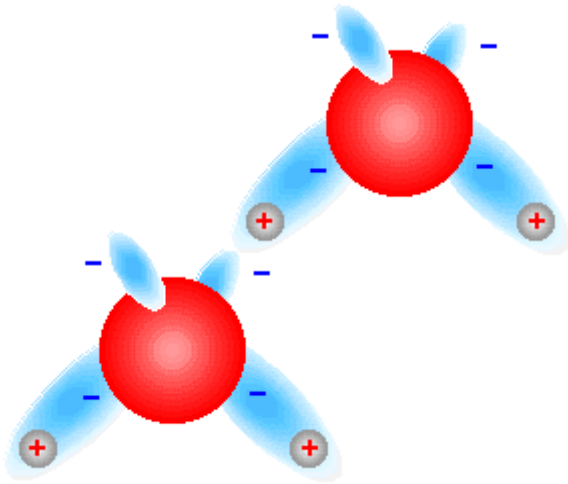
Boiling point / °C

100

64.7

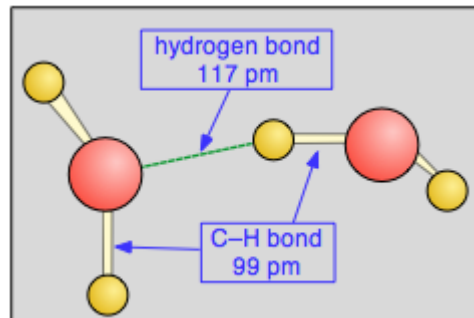
-23.6

The structure of liquid water – what holds the molecules together – Hydrogen bonds?



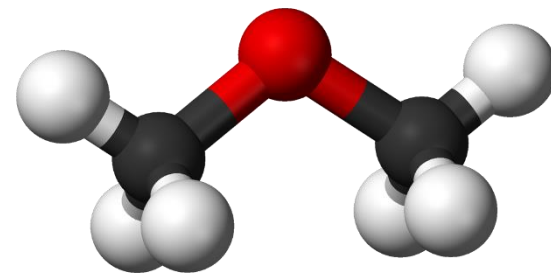
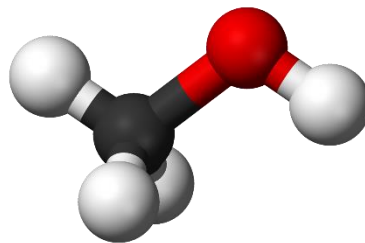
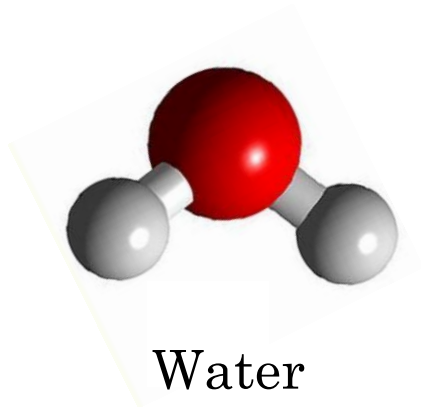
$$V(d) = 4\epsilon \left(\left(\frac{\sigma}{d} \right)^{12} - \left(\frac{\sigma}{d} \right)^6 \right)$$

ca 5,0 kcal mol⁻¹



Hydrogen bonds include a minor electron exchange (partially covalent) – **bond energies exceed dipole-dipole interactions by some 10x!**

Hydrogen bonds!



μ / D

1.85

1.62

1.43

N (possible hydrogen bonds per molecule)

4

2

0

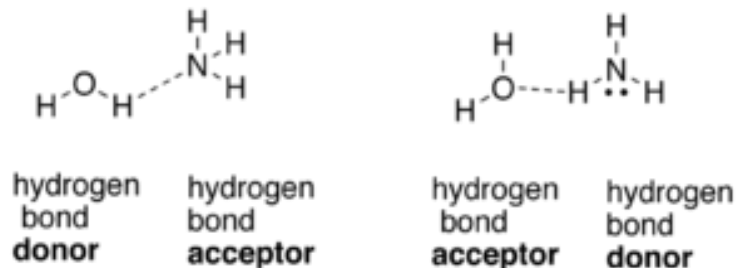
Boiling point / °C

100

64.7

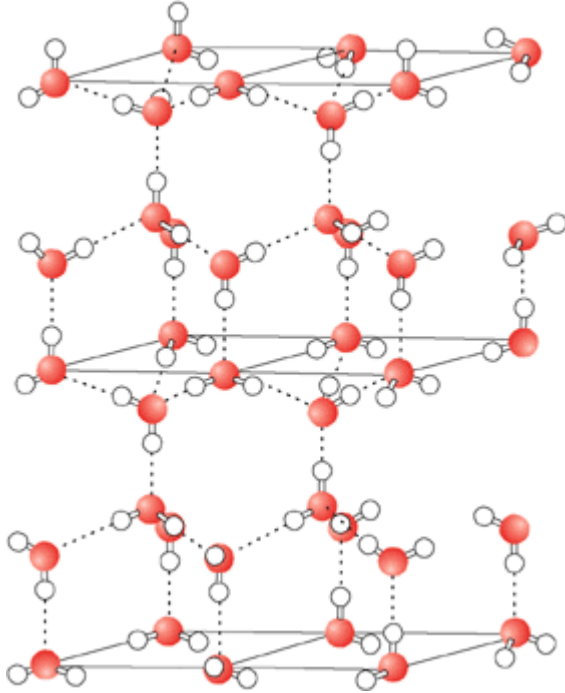
-23.6

The nature of hydrogen bond



1. A hydrogen atom acts as a bridge between two (electronegative) atoms (*hydrogen donor*, D and *hydrogen acceptor*, A)
2. Can be as strong as covalent bonds ($\approx 40 \text{ kcal mol}^{-1}$)
3. Highly directional (D—H \cdots A angles as close to 180° as possible)
4. Reliable – if in a system hydrogen donors and acceptors exist, they will form hydrogen bonds
5. Responsible for many inorganic, organic and biological structures.

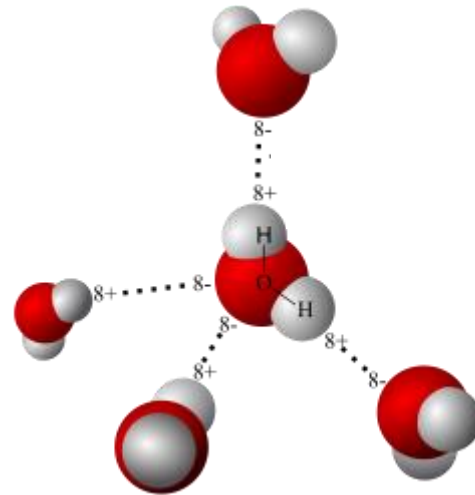
Hydrogen bonding in ice



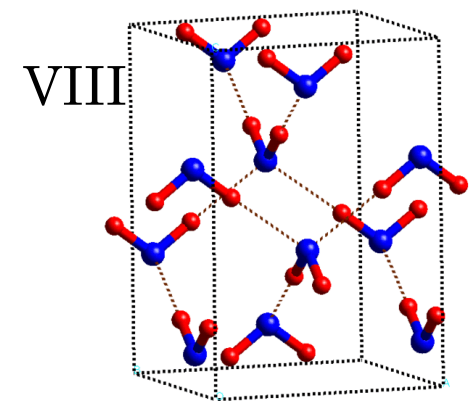
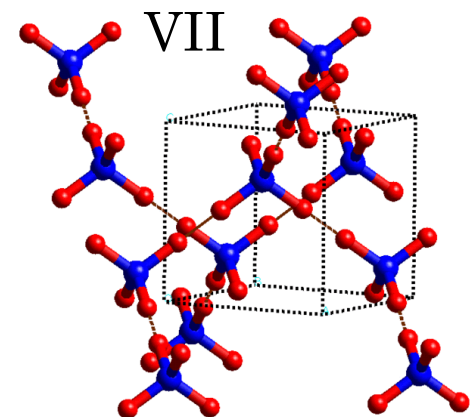
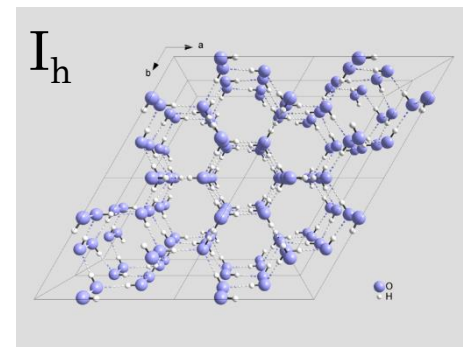
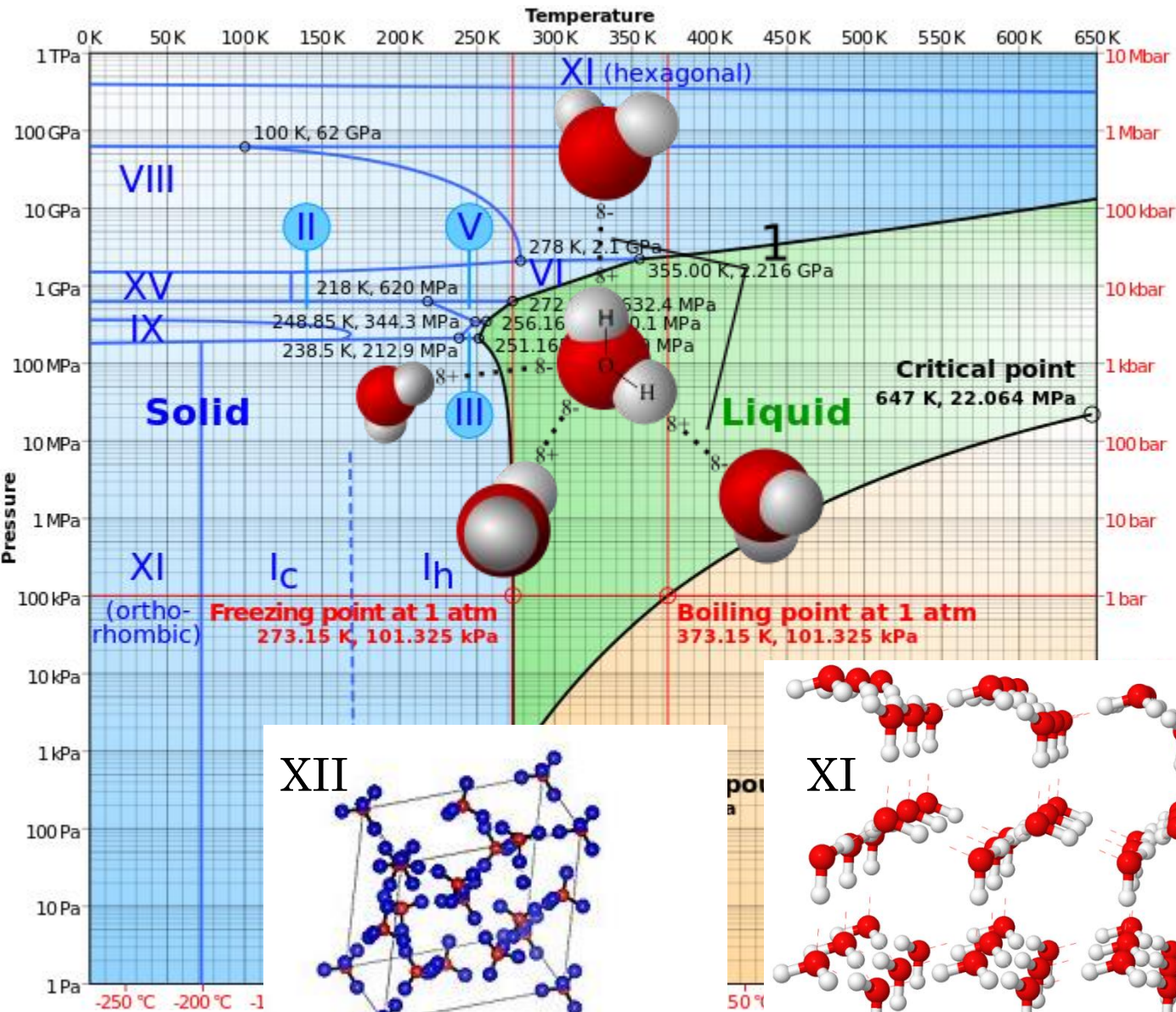
$$d(\text{O—O}) = 275 \text{ pm}$$

$$\varphi(\text{O—H} \cdots \text{O}) = 180^\circ$$

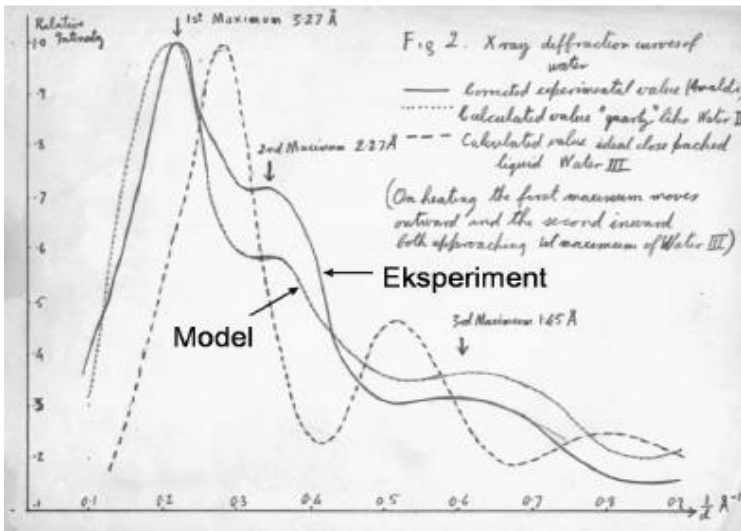
Hydrogen nuclei are disordered over two positions



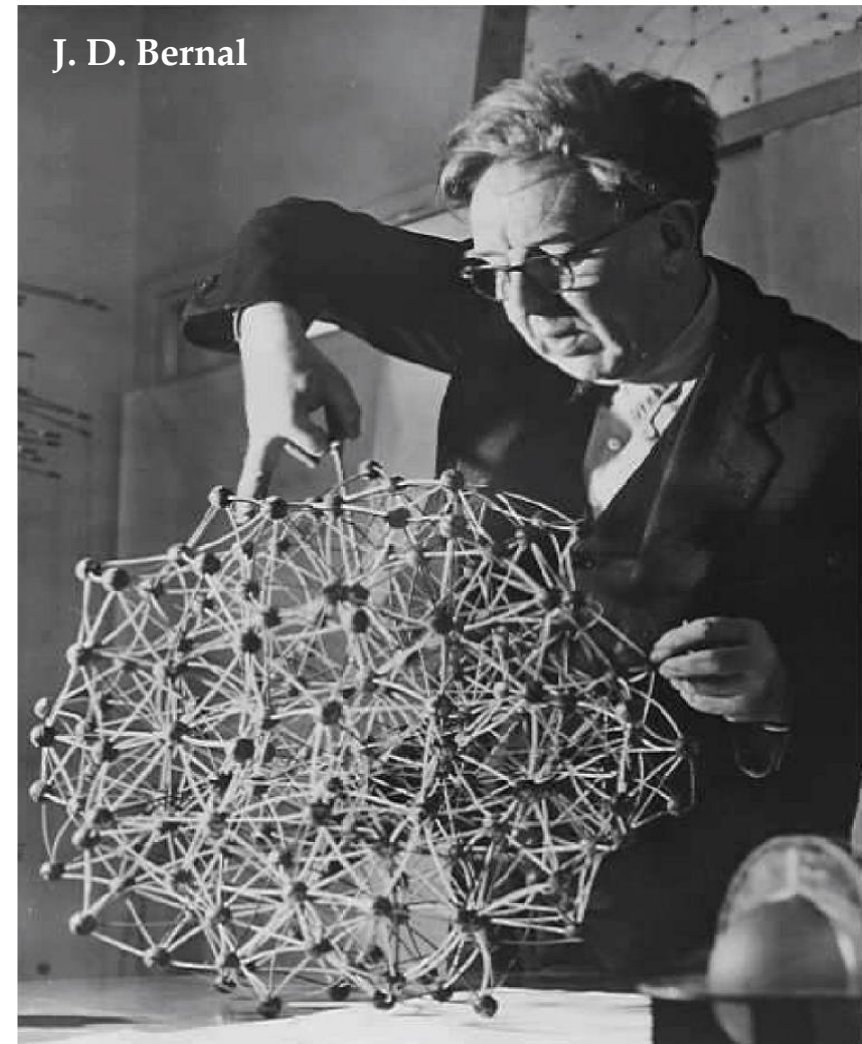
Which ice?



The structure of liquid water – something ice-like?

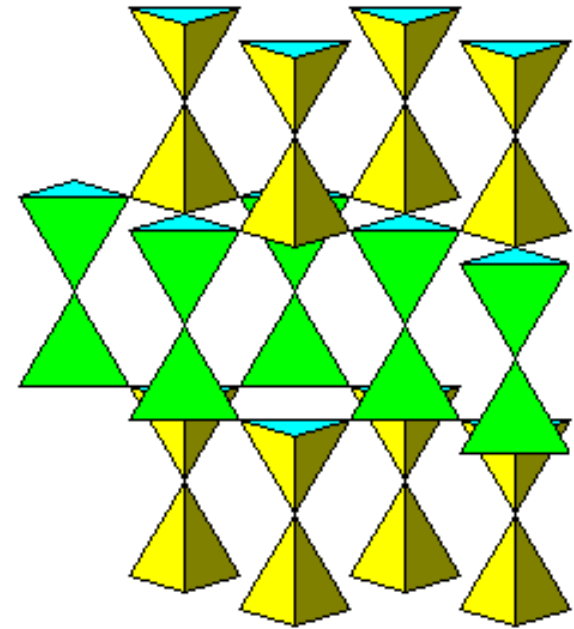
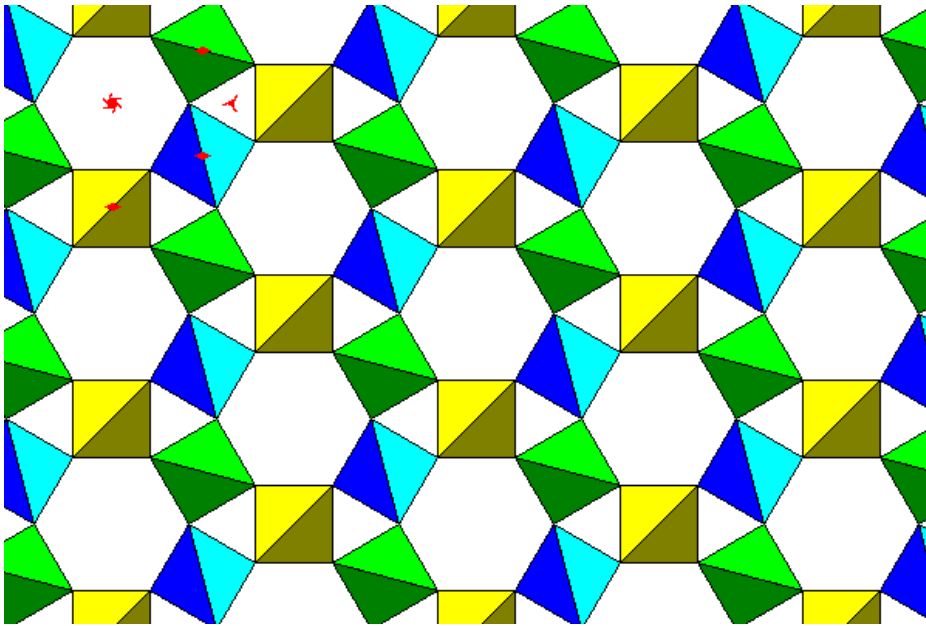


1933. Bernal – the first model of water structure, based on X-ray diffraction on liquid water and spectroscopic measurements



The Bernal model:

Water molecules tend to be surrounded by 4 other molecules forming tetrahedra (similar to silicates) – the structure can be modelled as a disordered intermediary between quartz and trypdimite structures



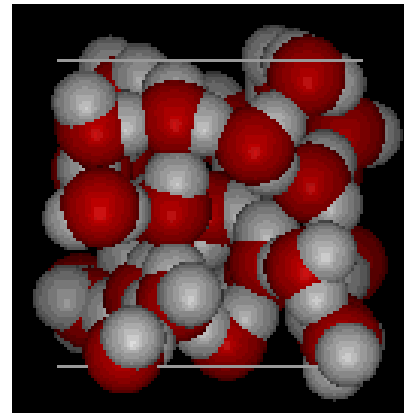
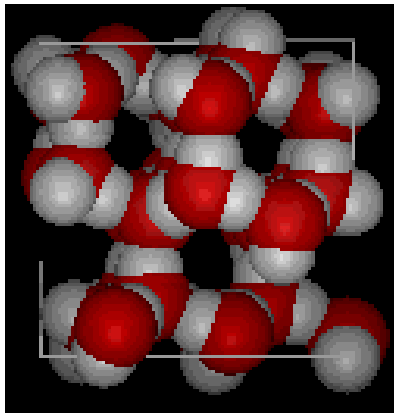
From X-ray diffraction data:

The closest neighbors to a molecule are ca 290 pm apart, with an average of 3,2 molecules

The second neighbors are at 466 pm, (average 13,4 molecules), with 4,6 molecules in distances below 400 pm.

Between 77 % i 100 % of the possible hydrogen bonds are actually present

The structure of liquid water is similar to a distorted structure of ice, with additional molecules occupying the voids in the structure

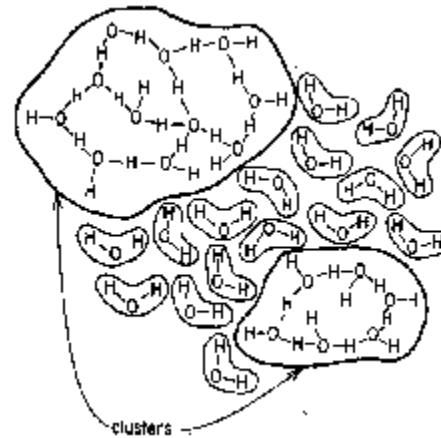


More modern models

Clusters (1950):

Water comprises clusters of “bernaloid” structure with areas with no ordering between them.

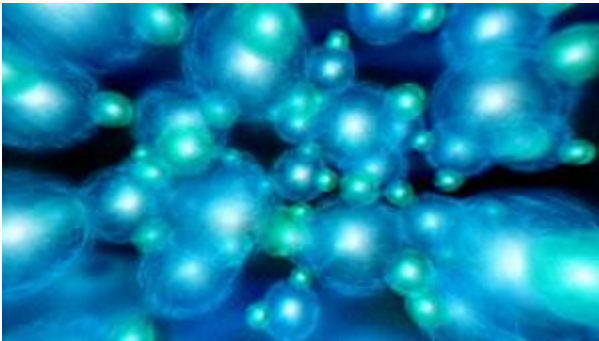
Clusters are not permanent – the exchange of molecules between clusters and interlayers is extremely fast



More modern models

Irregular network (1980):

On a very short time scale (less than a ps), water is more like a "gel" consisting of a single, huge hydrogen-bonded cluster. On a 10^{-12} - 10^{-9} s time scale, rotations and other thermal motions cause individual hydrogen bonds to break and re-form in new configurations, inducing ever-changing local discontinuities whose extent and influence depends on the temperature and pressure.



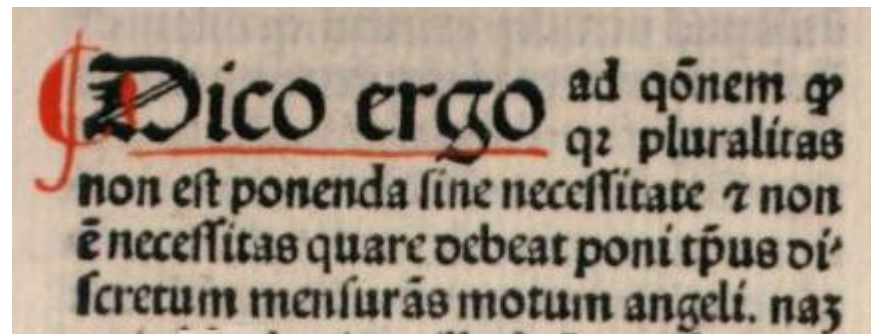
Hydrogen bonds in liquid water break and re-form so rapidly (often in distorted configurations) that the liquid can be regarded as a continuous network of hydrogen-bonded molecules.

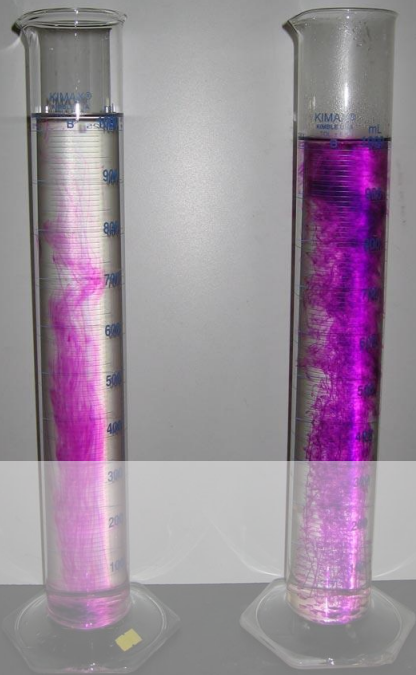
HOWEVER

Although the 1933 Bernal model fails to explain some experimental observations made on a short time-scale, all the “normal” water properties can be equally well accounted by it, as by the more recent models.

Unlike later models, Bernal’s is almost entirely based on experimental data, rather than on theoretical computation.

It is by far the simplest and easiest model to handle.





PART II:

Water in company



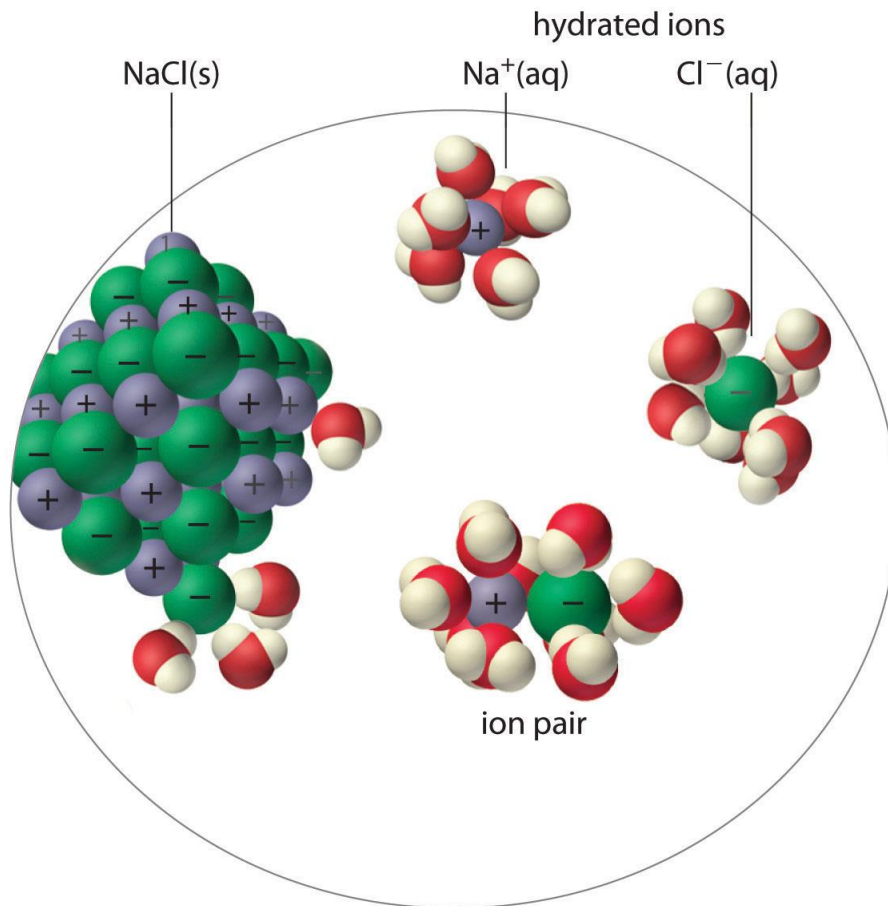
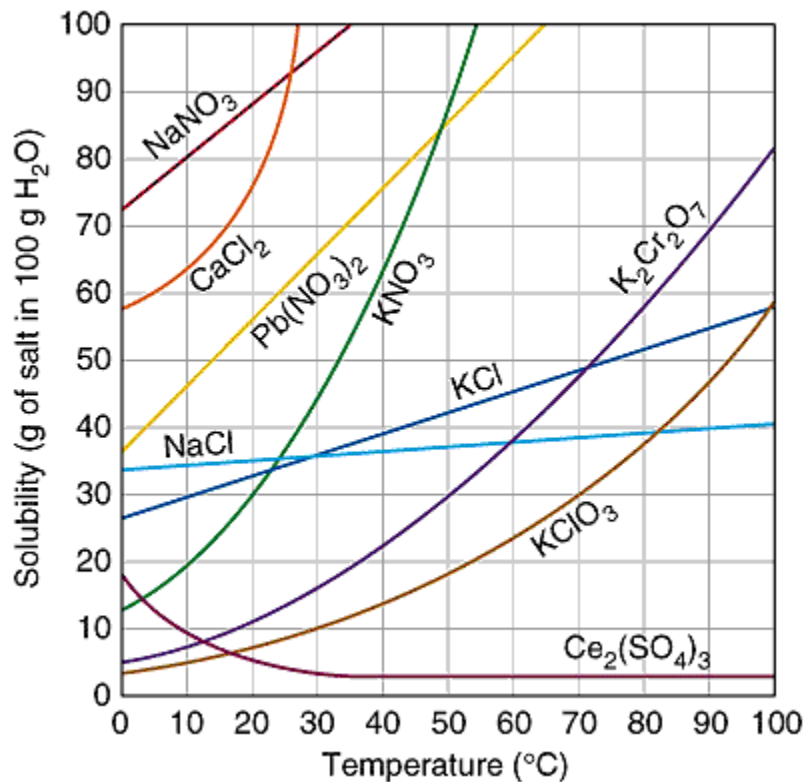
Water is THE solvent

Water is an excellent solvent for numerous inorganic and organic compounds

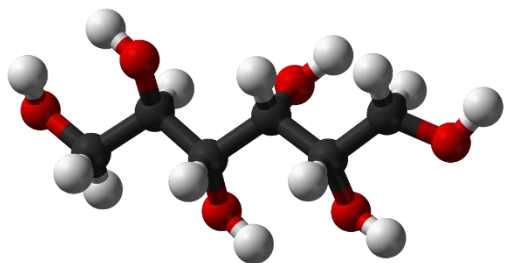
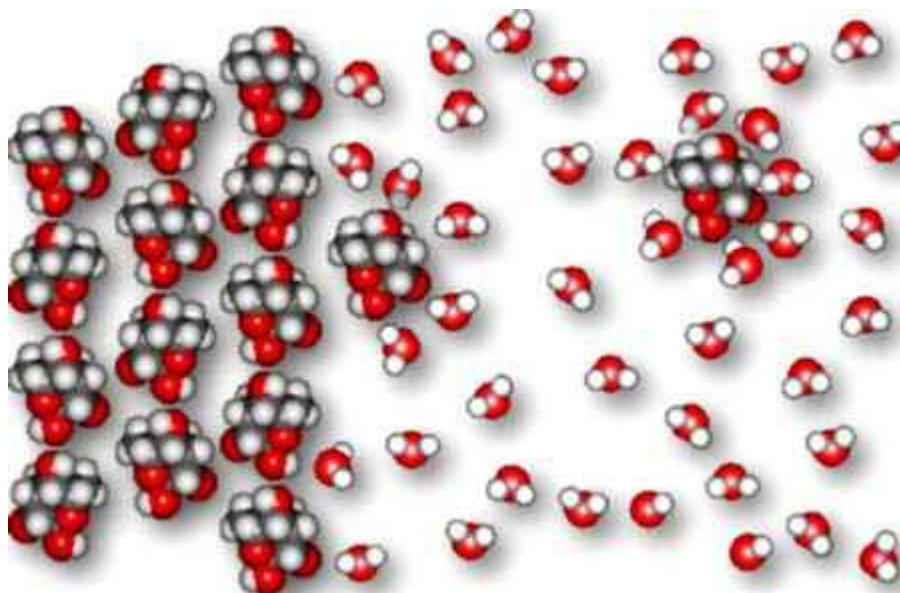
Water is the most important reaction medium in chemistry, industry and nature

Water is an omnipresent catalyst

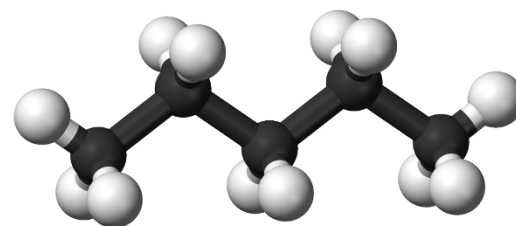
Solubility in water – salts



Solubility in water – molecular compounds



soluble



insoluble

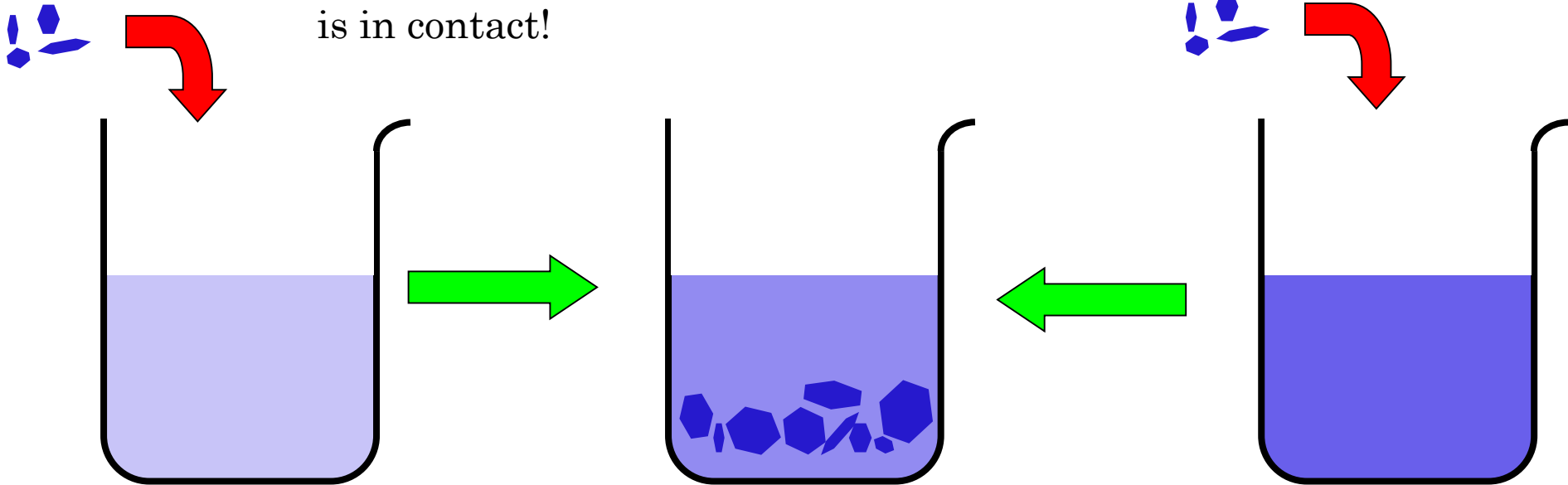
Quantification of solubility

1. Add in excess the substance whose solubility is to be studied
2. Adjust temperature and wait for dissolution to stop
3. Take a sample of the solution of an exact mass or volume
4. Evaporate the solvent (water) and weigh the residue.

$$c_x = \frac{m_x}{M_x V}$$

How much does it dissolve – saturation & equilibrium

dissolution continues until equilibrium
between solution and the solid with which it
is in contact!



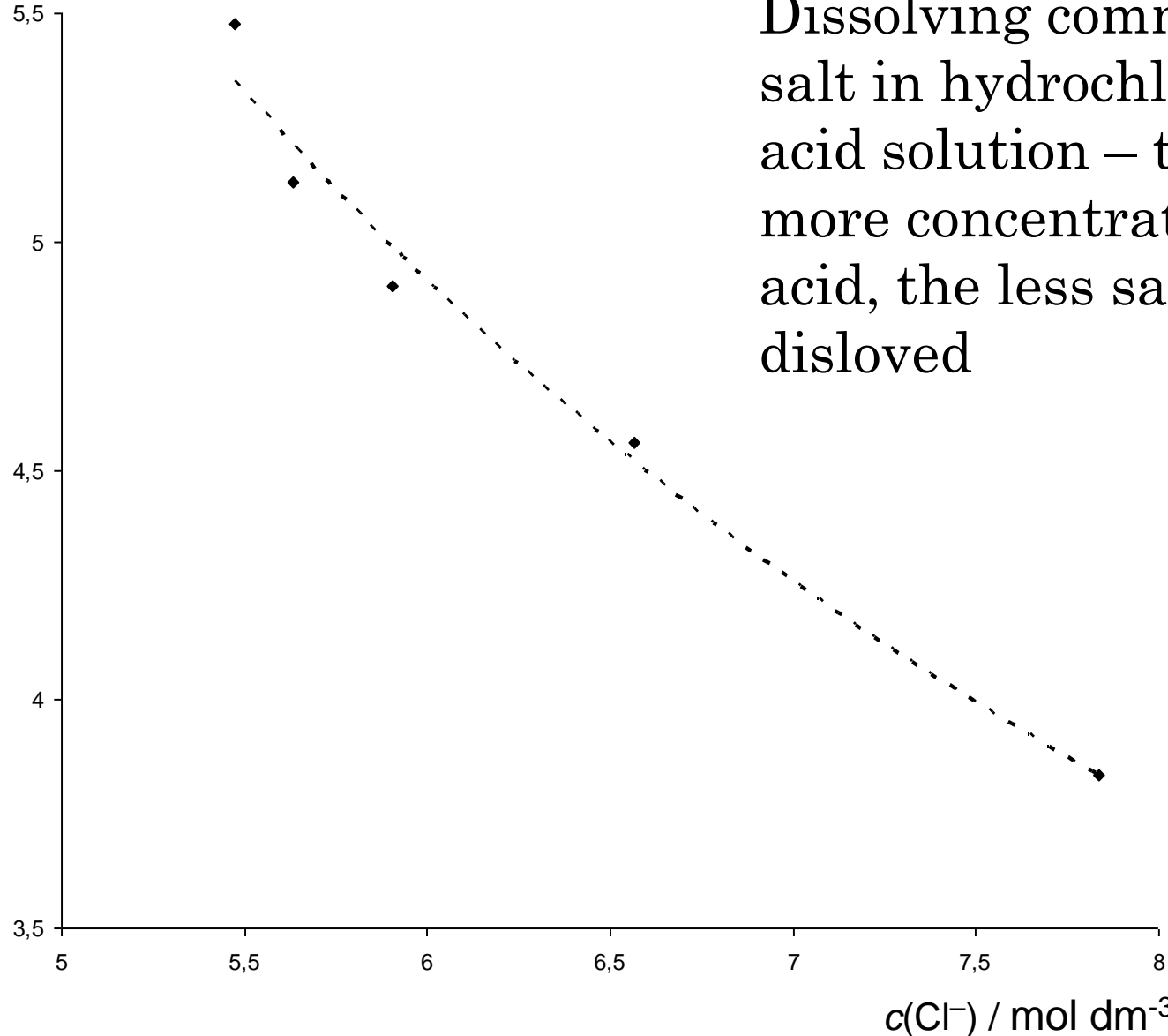
Undersaturated solution – less dissolved than in saturated.
Added solid dissolves → solution and solid are not in equilibrium.

Saturated solution – solution in contact with the solid – the amount of solid neither increases nor decreases → solution and solid are in equilibrium.

Supersaturated solution – more dissolved than in saturated.
Added solid grows → solution and solid are not in equilibrium.

Common-ion effect

$c(\text{NaCl}) / \text{mol dm}^{-3}$



And now...

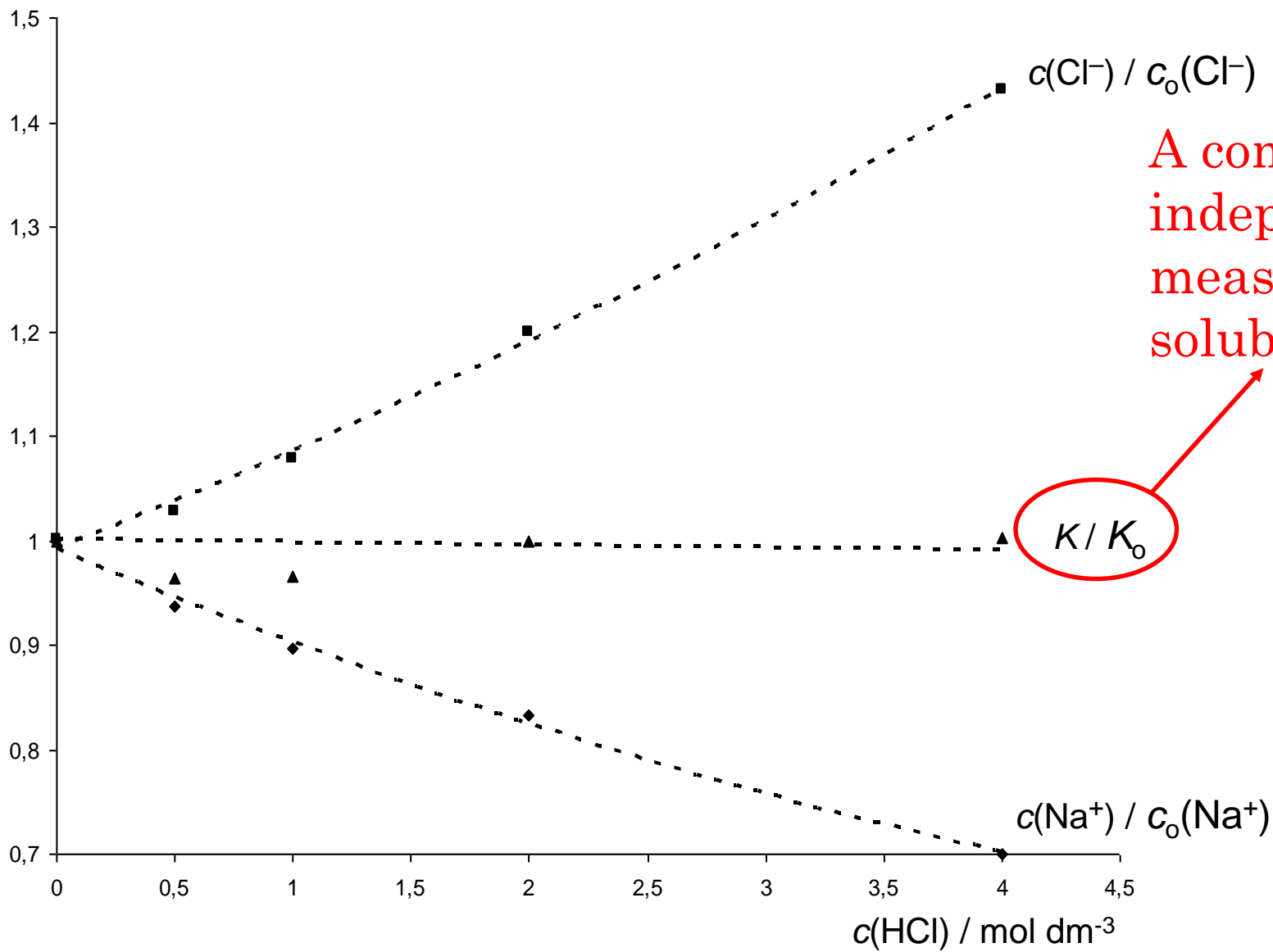
Calculate the concentrations of ions

$$c_{\text{Na}^+} = c_{\text{NaCl}}$$

$$c_{\text{Cl}^-} = c_{\text{NaCl}} + c_{\text{HCl}}$$

And multiply them

$$K = c_{\text{Cl}^-} c_{\text{Na}^+}$$



A composition independent measure of solubility

K / K_0

Additional benefit of K

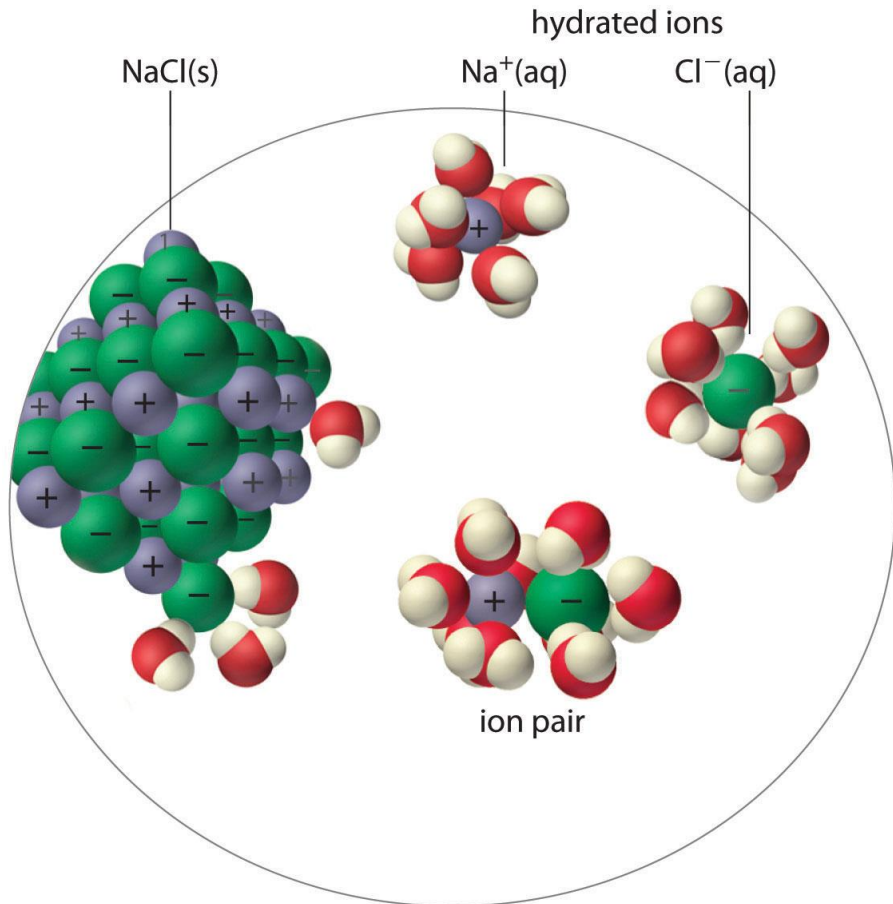
K is directly connected to the free energy of a process

$$\ln K = \frac{-\Delta_r G^\ominus}{RT}$$

and therefrom the heat and entropy of dissolution

$$\Delta G = \Delta H - T\Delta S$$

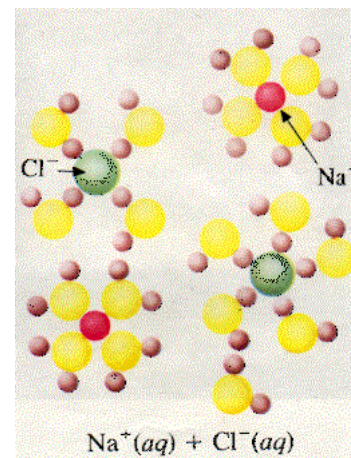
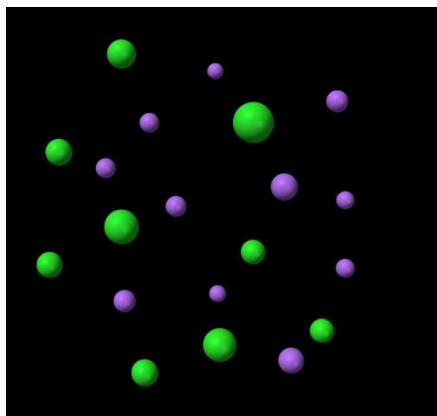
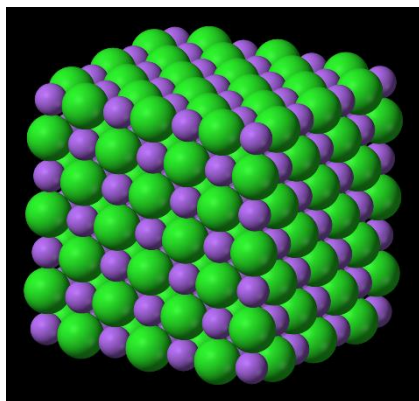
A short analysis – what is in dissolution?



1. Destruction of a crystal
- (2. Dissociation of ion pairs)
3. Solvation of the molecules (formation of bonds between atoms/ions/molecules of the solute and water molecules)

The effects on heat of dissolution

1. Destruction of a crystal \longrightarrow Energy required
2. Dissociation of ion pairs \longrightarrow Energy required
3. Solvation of the molecules (formation of bonds between atoms/ions/molecules and the solute and water molecules) \longrightarrow Energy released



Entalpija rešetke

- Teško mjerljiva i donekle izračunljiva

$$E = N_A \left[M \frac{1}{4\pi\epsilon_0} \frac{Z_+ Z_-}{r} + \frac{B}{r^n} \right]$$

$$E = N_A M \frac{1}{4\pi\epsilon_0} \frac{Z_+ Z_-}{r} \left(1 - \frac{1}{n} \right)$$



Ionski radijusi i Madelungova konstanta

Radius Ratio (Cation/Anion)	Lattice Type	Coordination Number of		Madelung Constant	Reduced ^a Madelung Constant
		Cation	Anion		
A. 1:1 Stoichiometry of Salt (MX)					
0.225–0.414	Wurtzite (ZnS)	4	4	1.63805	1.63805
	Zinc blende (ZnS)	4	4	1.64132	1.64132
0.414–0.732	Rock salt (NaCl)	6	6	1.74756	1.74756
0.732–1.000	CsCl	8	8	1.76267	1.76267
B. 1:2 Stoichiometry of Salt (MX ₂)					
0.225–0.414	Beta-quartz (SiO ₂)	4	2	2.201	1.467
0.414–0.732	Rutile (TiO ₂)	6	3	2.408 ^a	1.605
0.732–1.000	Fluorite (CaF ₂)	8	4	2.51939	1.6796
C. 2:3 Stoichiometry of Salt (M ₂ X ₃)					
0.414–0.732	Corundum (Al ₂ O ₃)	6	4	4.1719 ^b	1.6688
D. Other Stoichiometries and Lattice Types					
Never favored	Ion pair	1	1	1.00000	1.0000
0.000–0.155		2			
0.155–0.225		3			
0.225–0.414		4			
0.414–0.732		6			
0.732–1.000		8			
1.000		12			

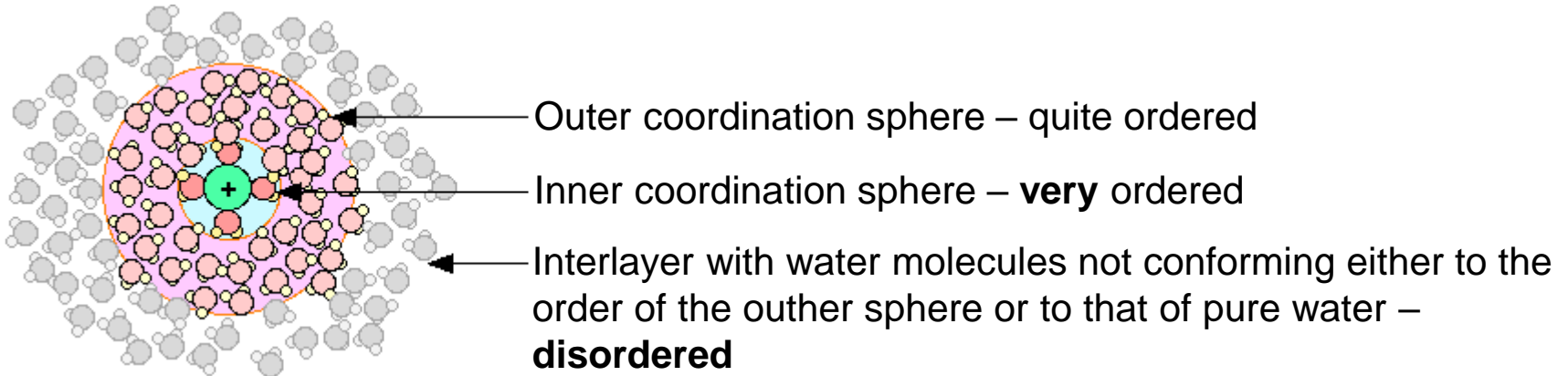
^aReduced Madelung constant = Madelung constant $\times 2/p$, where p = number of ions in the simplest formula of the salt.

^bExact value dependent on details of the structure.

What of entropy?

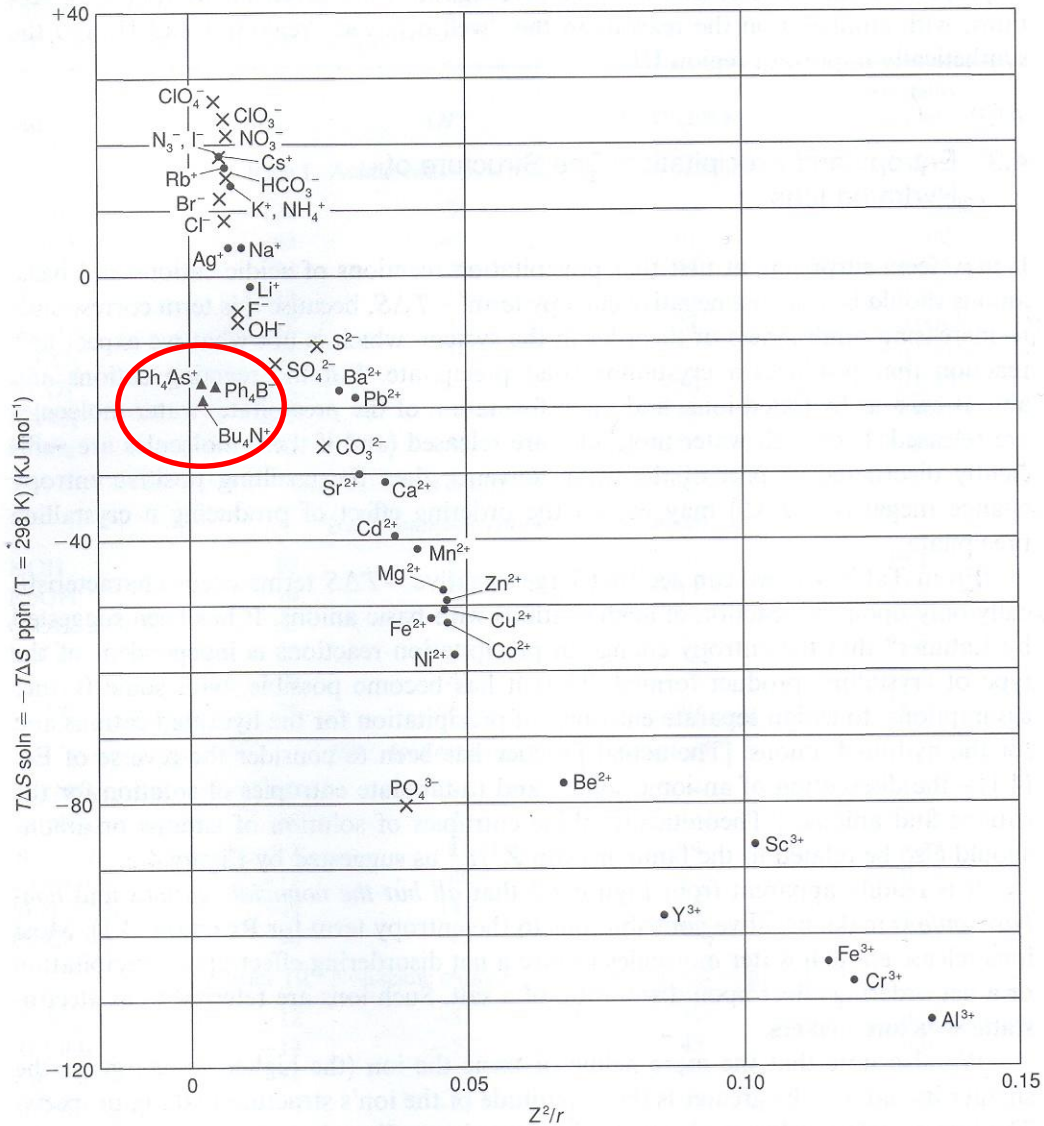
1. Destruction of a crystal  entropy increases
2. Solvation of the molecules
(formation of bonds between
atoms/ions/molecules of the
solute and water molecules  entropy somewhat
decreases

Water has its structure!



Bulk water – structured as pure water

Entropy of hydration will depend on the relative sizes of the 3 layers



The smaller the size of an ion and the larger its charge the entropy of hydration becomes more negative

Figure 4.2
 The 298 K entropy terms ($T\Delta S_{\text{soln}} = -T\Delta S_{\text{pptn}}$) for cations and anions as a function of Z^2/r . Crosses equal anions; dots equal metal cations; triangles equal organic ions. Thermodynamic data from Cox and Parker⁷; thermochemical radii of oxo anions from E. A. Keiter, R. L. Keiter, and J. E. Huheey, *Inorganic Chemistry*, Harper-Collins, New York, 1993; p. 118.

What will not dissolve well in water

Substances with large crystal lattice energies (salts of small and highly charged ions, oxides, covalent solids...)

Substances which increase the ordering (decrease entropy) of water – ions with large charges (large ordered hydration spheres) and organic molecules incapable of hydrogen bonding (remove disordered water from the voids of the hydrogen bonded array of water molecules)

Pravila topljivosti

ANIONS: CATIONS:	Nonbasic	Feebly basic	Moderately basic	Very strongly basic	
Nonacidic	III	II A			
Feebly acidic		IV C	IV A		
Weakly acidic		I			
Moderately acidic	II B				IV B
Strongly acidic					
Very strongly acidic					

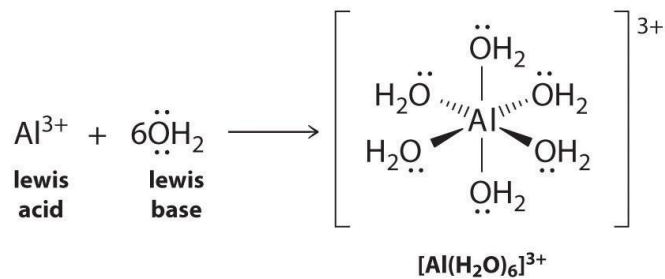
I – S jako raste pri otapanju (ponekad i u **IV**)

II – ΔS je zanemariva; male entalpije rešetke (različite dimenzije kationa i aniona) – topljivost je uvjetovana negativnom entalpijom otapanja, kristaliziraju kao hidrati (ponekad i u **IV**)

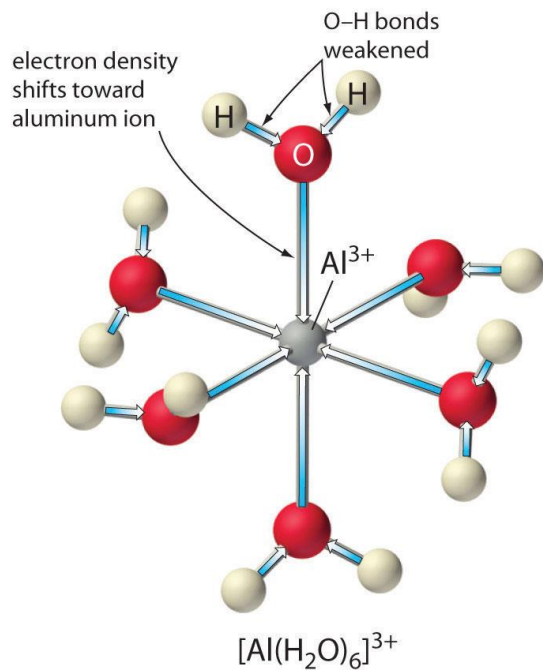
III – ΔS je zanemariva; velike entalpije rešetke (slični radijusi kationa i aniona) – netopljivost uvjetovana pozitivnom promjena entalpije pri otapanju

III i **IV** – soli su često slabo topljive / djelomično netopljive (ΔH i $T\Delta S$ bliskog iznosa i suprotnih predznaka)

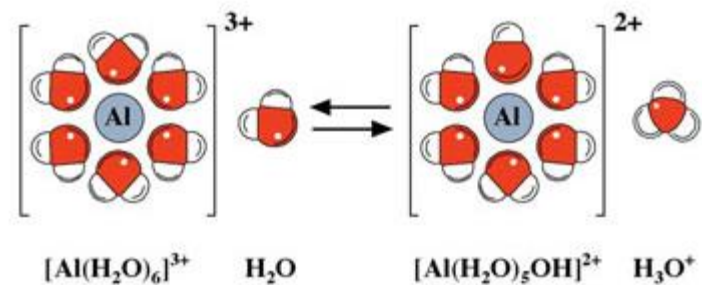
Acidity of cations



(a)

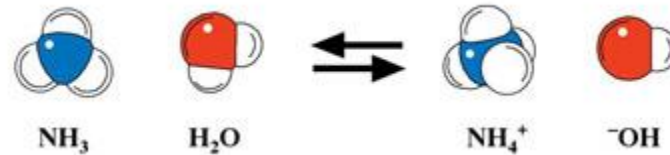
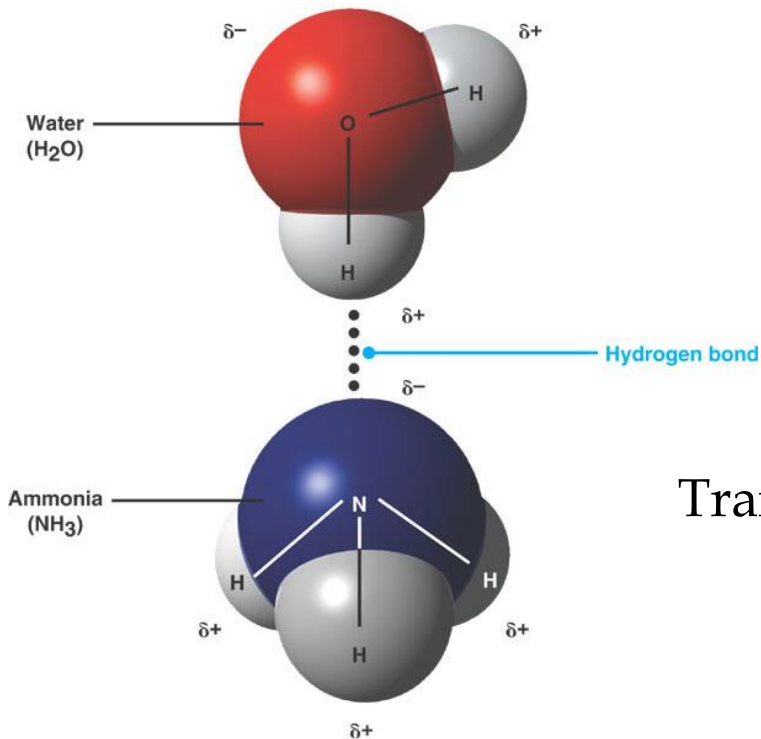
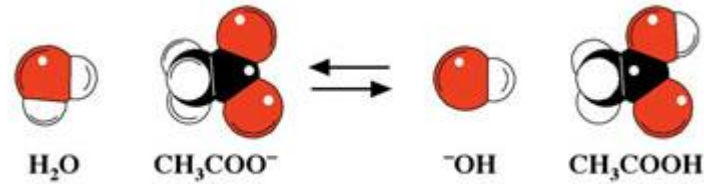


(b)



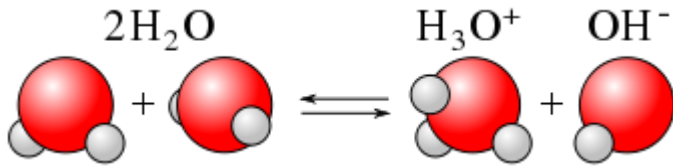
$$K_a = 1,1 \cdot 10^{-5}$$

Basicity of anions



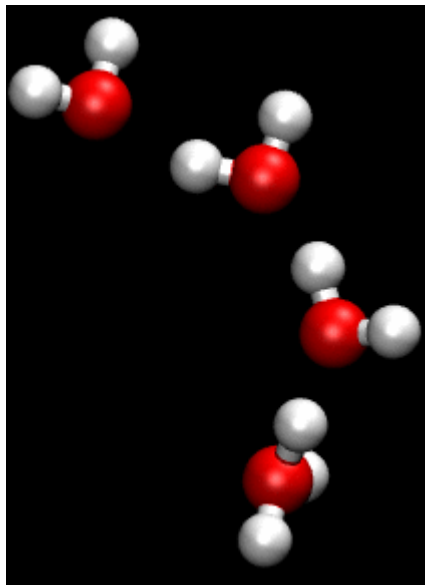
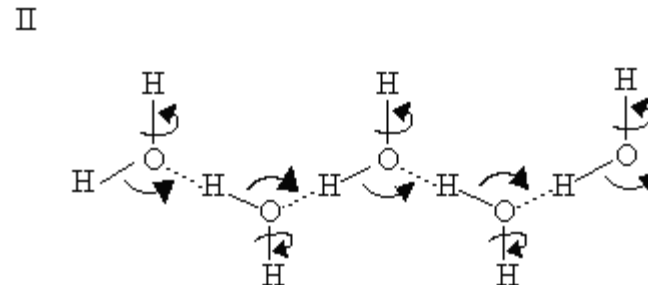
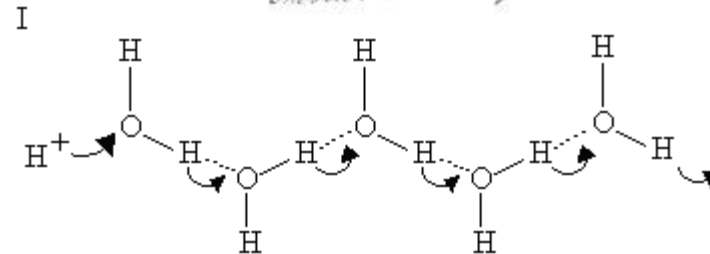
Transfer of a H⁺ along the hydrogen bond

H⁺ transfer in water itself?



Barun Christian Johann
Dietrich Theodor von
Grotthuss (1785.–1822.)

Theodor v. Grotthuss



High electric conductivity of acidic and
basic solutions

Nevodena otapala

- Protična, aprotična
- Polarna i nepolarna
- Strukturirana i bezstrukturna