CAPVT IIII

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

Vladimir Stilinović
Department of Chemistry, Faculty of Science, University of Zagreb,
Horvatovac 102a, HR-10000 Zagreb, Croatia.
vstilinovic@chem.pmf.hr

PART I:

What’s so strange about it?

- 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?

Water is polar

What does that mean?

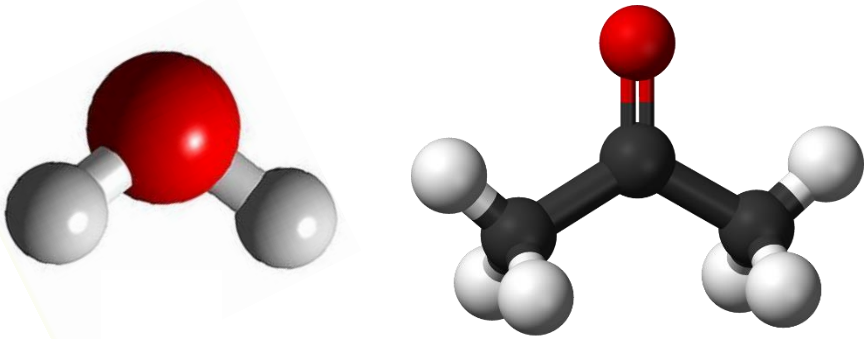
1. Water molecule has a polar geometry?

2. Water molecule das a large dipole moment?

3. Water has a large dielectric constant?

4. Something else?

What is more polar – water or acetone?

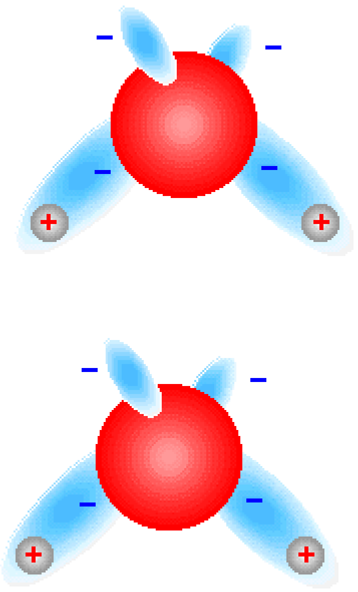


1. Molecular geometry	$C2_v$	$C2_v$	SAME
2. Dipole moment / D	1.85	2.88	acetone
3. Dielectric constant	80.4	20.7	water

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

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

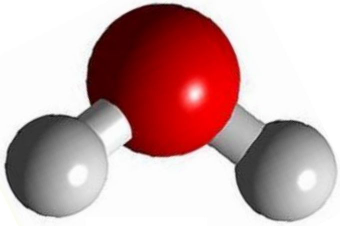
Dipole – dipole interaction

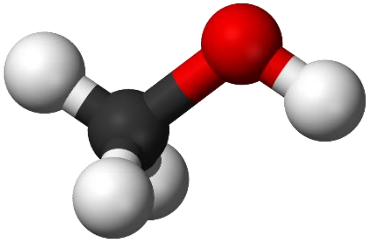


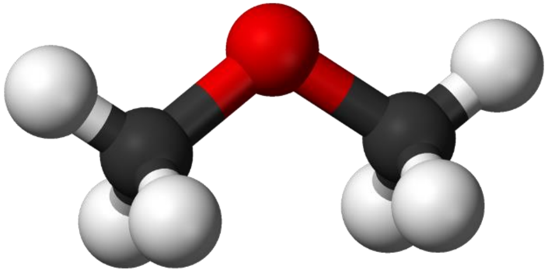
$$E = -\frac{\mu_1\mu_2}{4\pi\varepsilon_0 r_{12}^3}\left(\cos\varphi_{12} - 3\cos\varphi_1\cos\varphi_2\right)$$

For optimal dipole alignement – ca 0,5 kcal mol^{-1}

Dipole interactions?

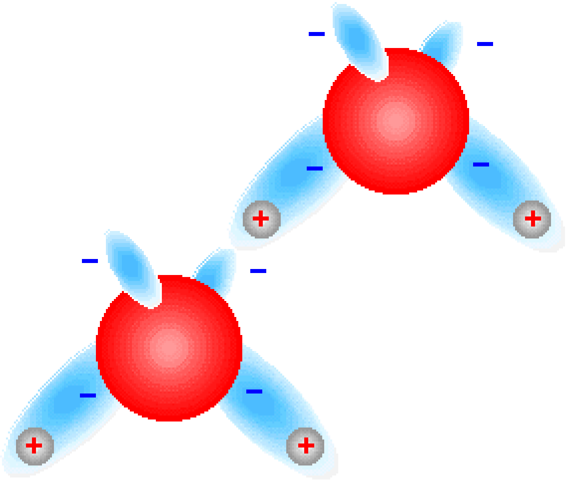






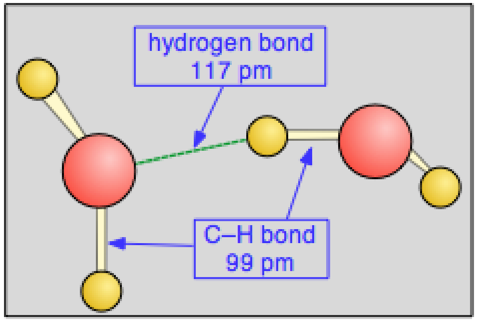
	Water	Methanol	Dimethyl ether
μ / D	1.85	1.62	1.43
Boiling point / °C	100	64.7	-23.6

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



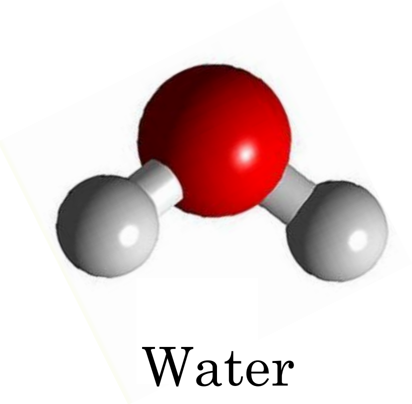
$$V(d) = 4\varepsilon\left(\left(\frac{\sigma}{d}\right)^{12} - \left(\frac{\sigma}{d}\right)^{6}\right)$$

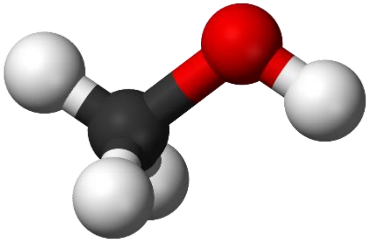
ca 5,0 kcal mol^{-1}

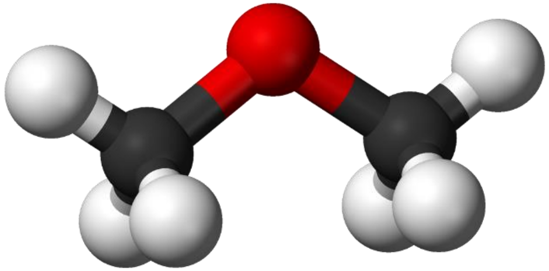


Hydrogen bonds include a minor electron exchange (partialy covalent) – **bond energies exceed dipole-dipole interactions by some 10x!**

Hydrogen bonds!

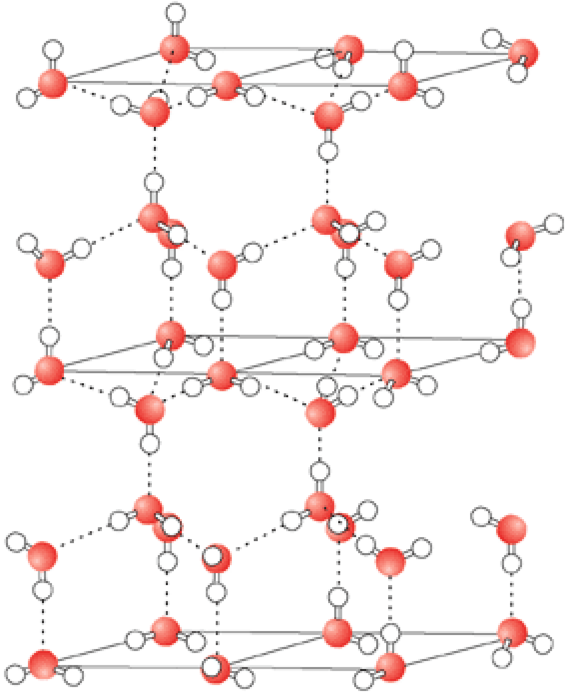






	Water	Methanol	Dimethyl ether
μ / D	1.85	1.62	1.43
N(possible hydrogen bonds per molecule)	4	2	0
Boiling point / °C	100	64.7	-23.6

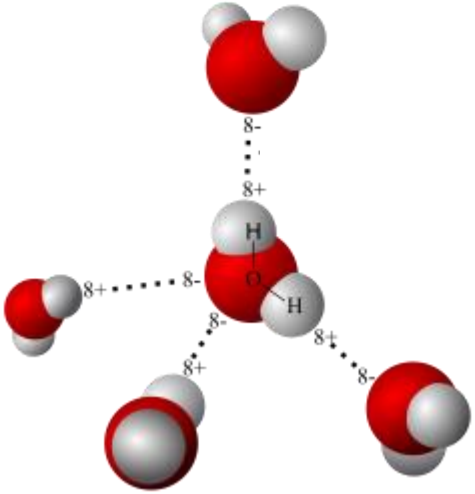
Hydrogen bonding in ice



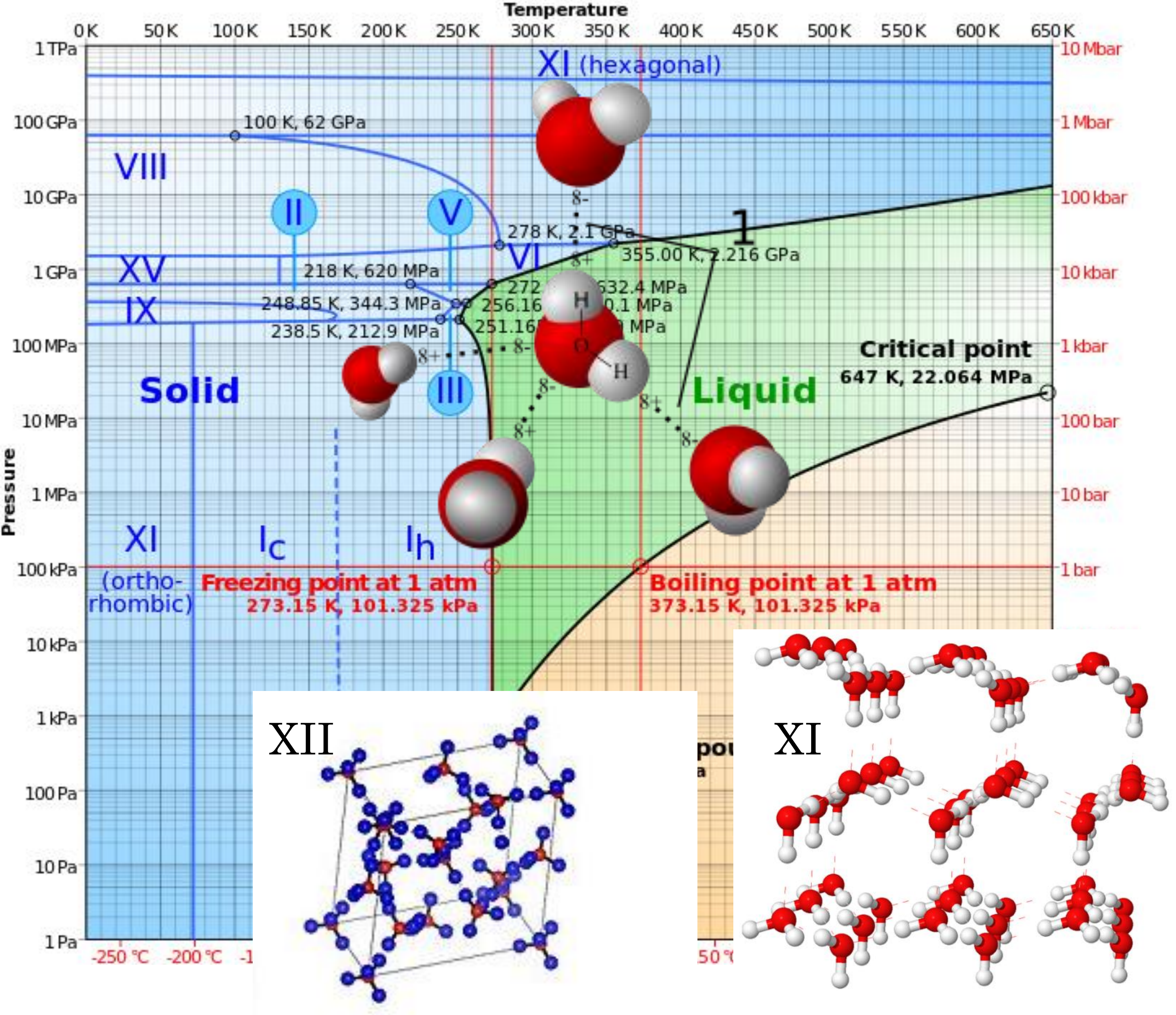
$d(\mathrm{O—O}) = 275\ \mathrm{pm}$

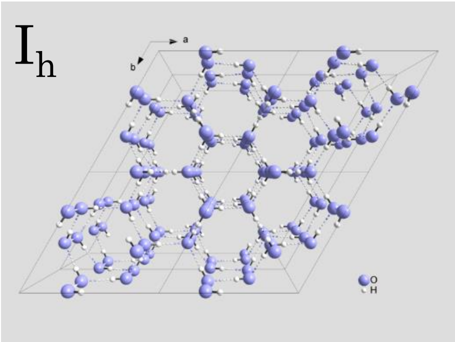
$\varphi(\mathrm{O—H} \cdots \mathrm{O}) = 180°$

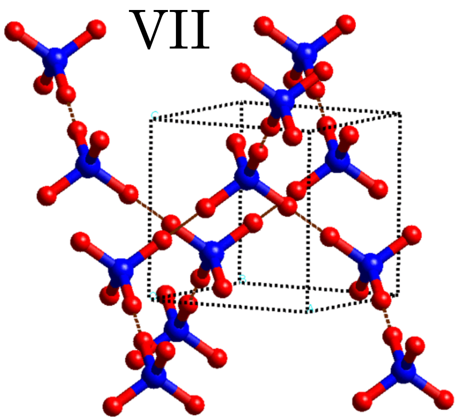
Hydrogen nuclei are disordered over two positions

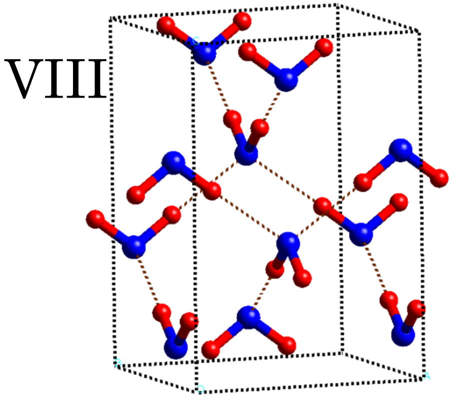


Which ice?

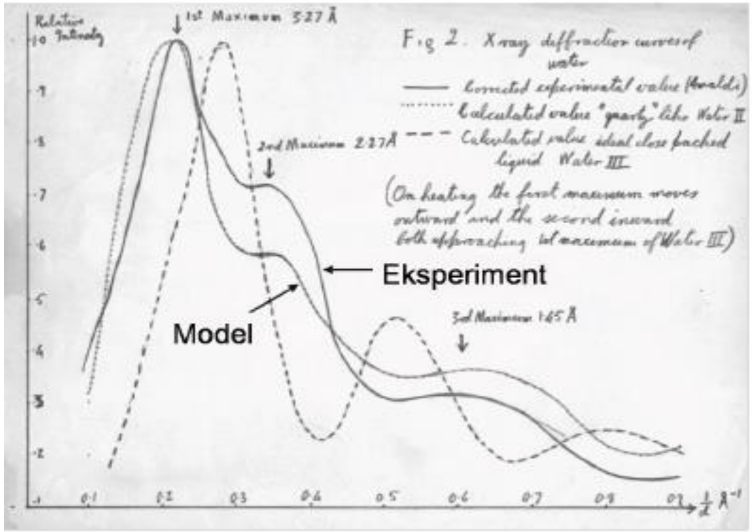

Temperature
0 K
50 K
100 K
150 K
200 K
250 K
300 K
350 K
400 K
450 K
500 K
550 K
600 K
650 K
Pressure
1 TPa
100 GPa
10 GPa
1 GPa
100 MPa
10 MPa
1 MPa
100 kPa
10 kPa
1 kPa
100 Pa
10 Pa
1 Pa
10 Mbar
1 Mbar
100 kbar
10 kbar
1 kbar
100 bar
10 bar
1 bar
XI (hexagonal)
100 K, 62 GPa
VIII
II
V
278 K, 2.1 GPa
1
355.00 K, 2.216 GPa
VI
XV
218 K, 620 MPa
272
632.4 MPa
248.85 K, 344.3 MPa
256.16
0.1 MPa
IX
251.16
MPa
238.5 K, 212.9 MPa
δ-
δ+
H
O
H
Critical point
647 K, 22.064 MPa
Solid
III
Liquid
XI
(ortho-
rhombic)
Ic
Ih
Freezing point at 1 atm
273.15 K, 101.325 kPa
Boiling point at 1 atm
373.15 K, 101.325 kPa
-250 °C
-200 °C
XII
XI


Ih
a
b
O
H

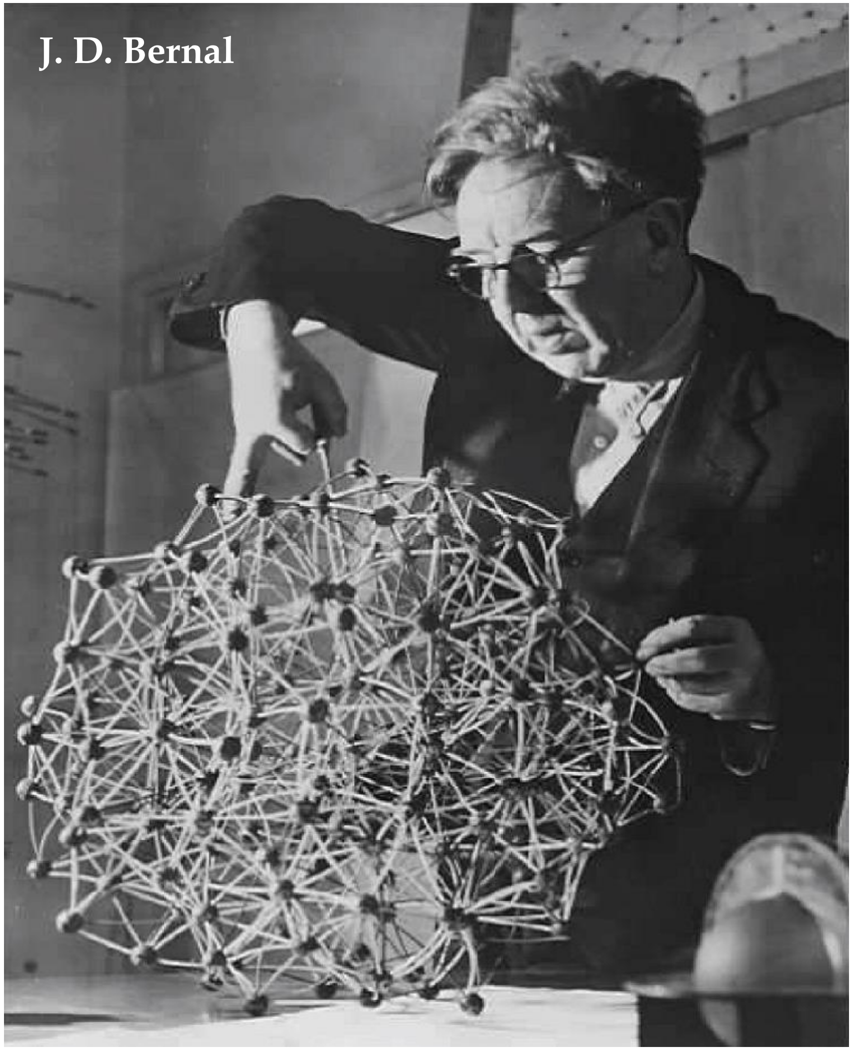

VII


VIII

The structure of liquid water – something ice-like?

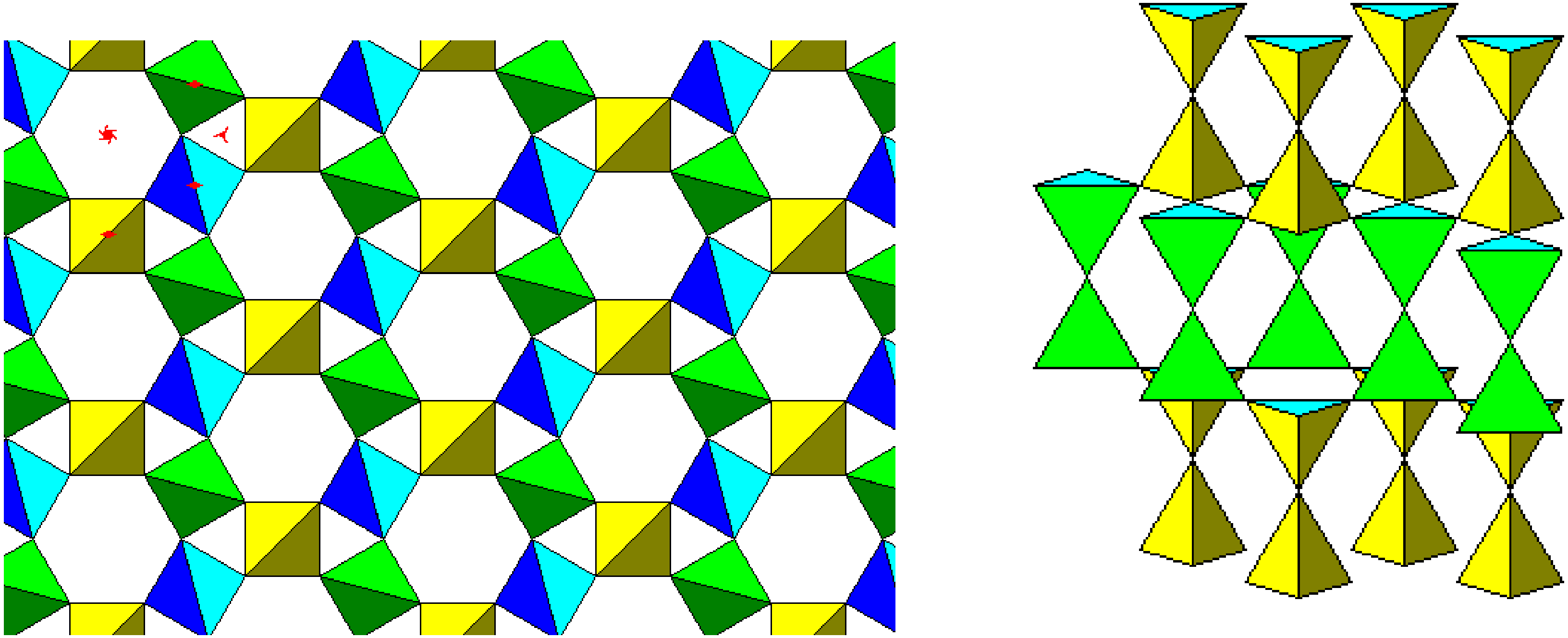


1933. Bernal – the first model of water structure, based on X-ray diffraction on liquid water and spactroscopic measurements



The Bernal model:

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



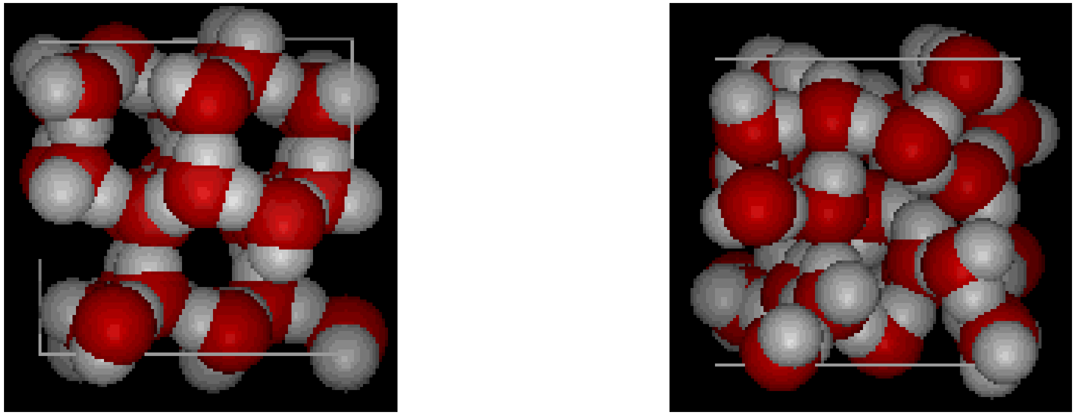
From X-ray diffraction data:

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 acctually present

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

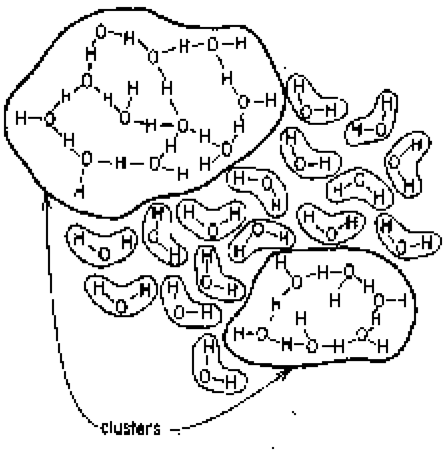


More modern models

Clusters (1950):

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

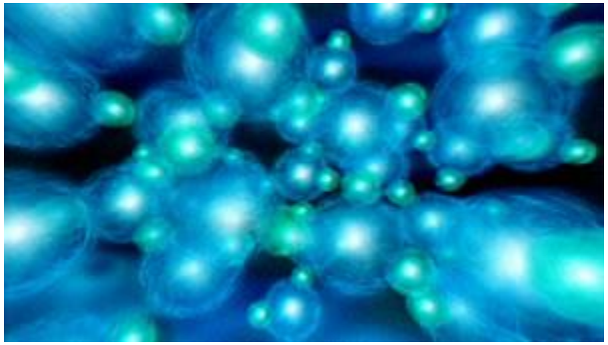
Clusters are not permanent – the exchange of molecules bteween clusters and interlayers is extremely fast



More modern models

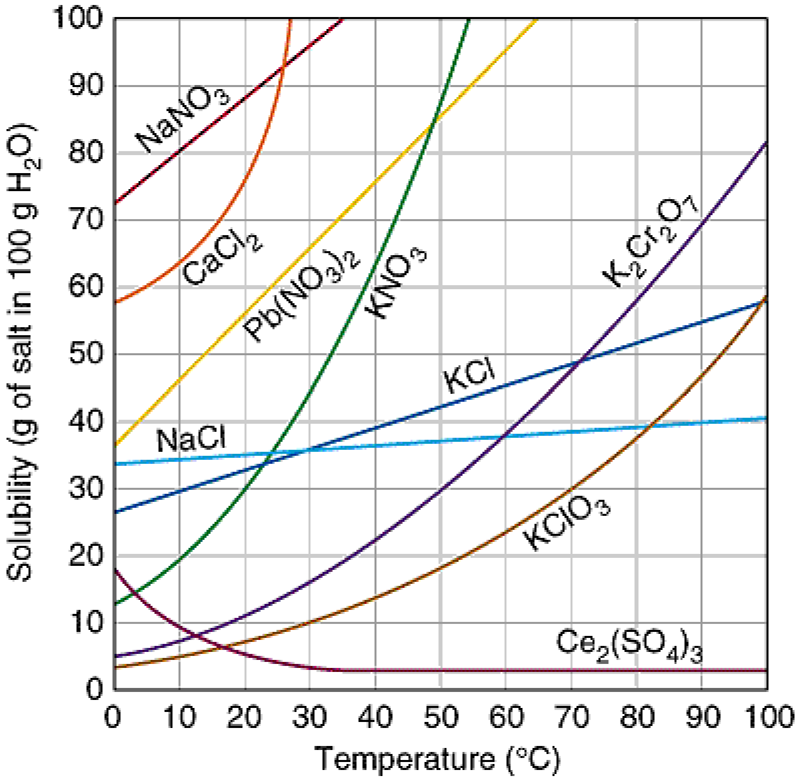
Irregular network (1980):

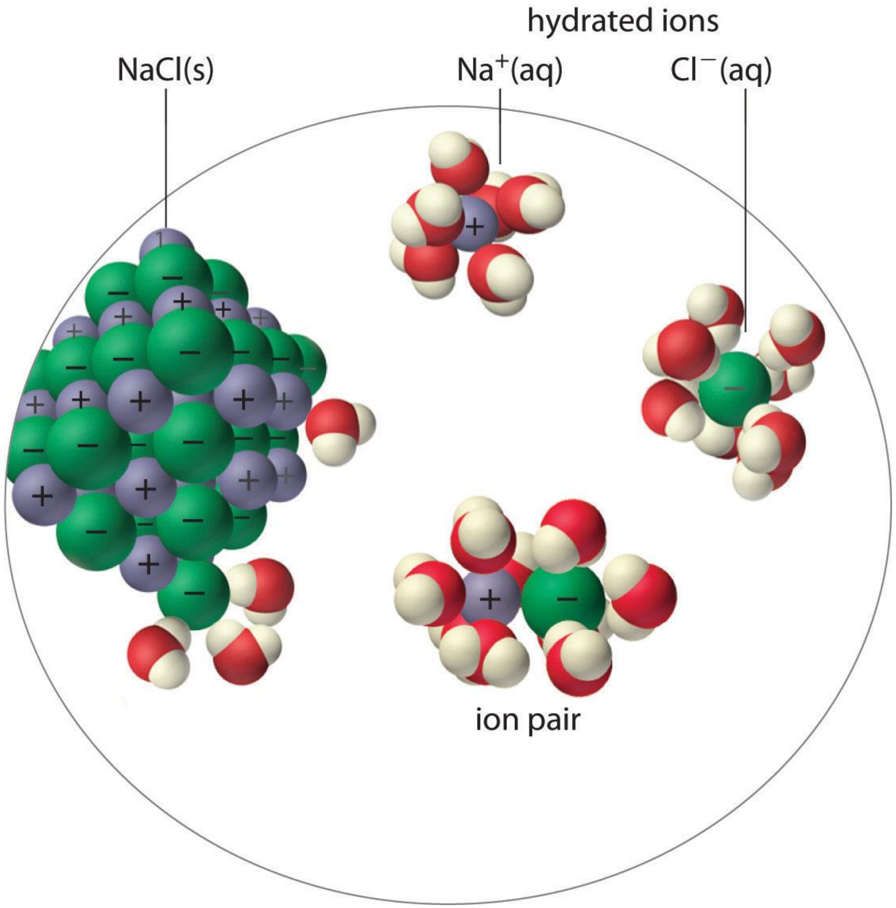
On a very short time scale (less than a ps), water is more like a "gel" consisting of a single, huge hydrogen-bonded cluster. On a 10^{-12}-10^{-9} s time scale, rotations and other thermal motions cause individual hydrogen bonds to break and re-form in new configurations, inducing ever-changing local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



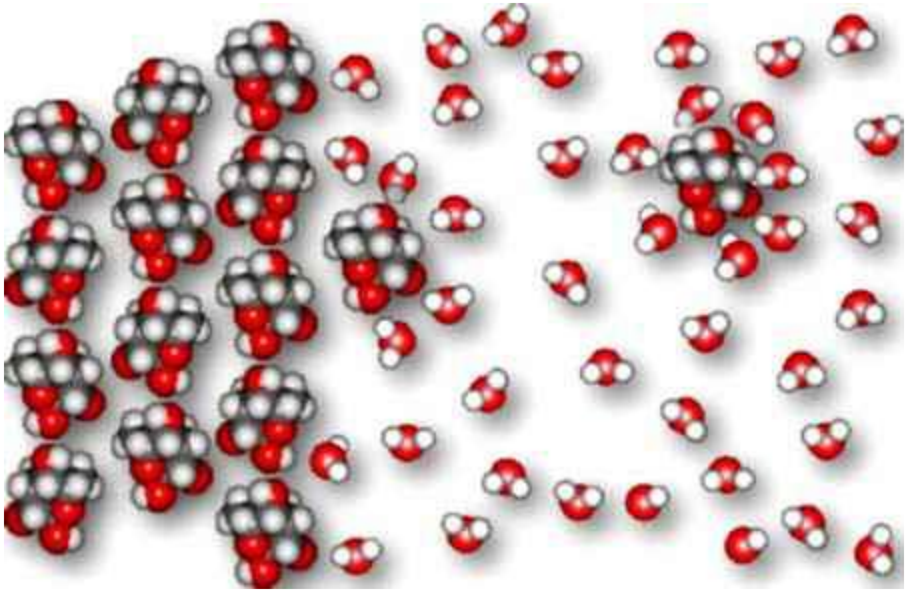
Hydrogen bonds in liquid water break and re-form so rapidly (often in distorted configurations) that the liquid can be regarded as a continuous network of hydrogen-bonded molecules.

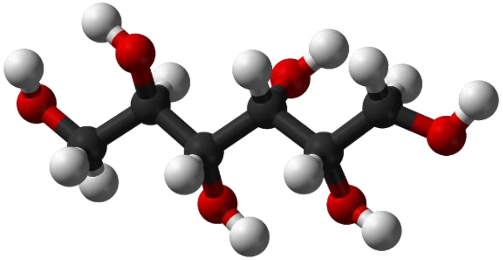
Solubility in water – salts



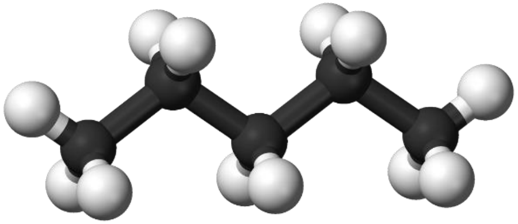


Solubility in water – molecular compounds



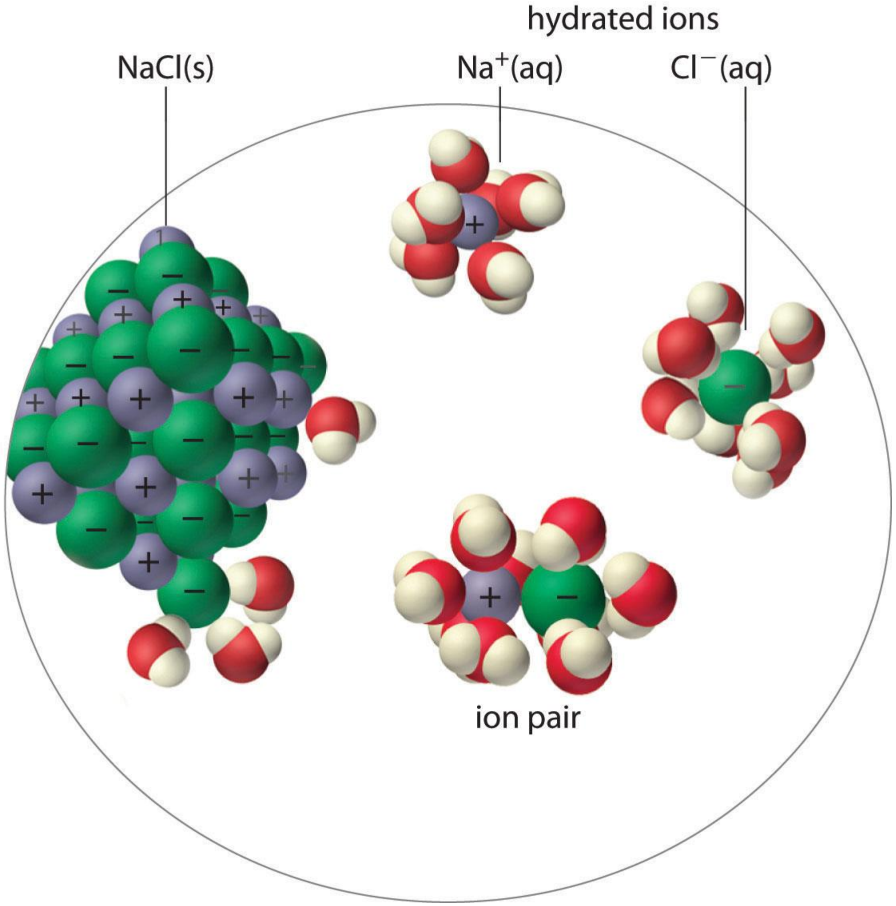


soluble



insoluble

A short analisys – what is in dissolution?



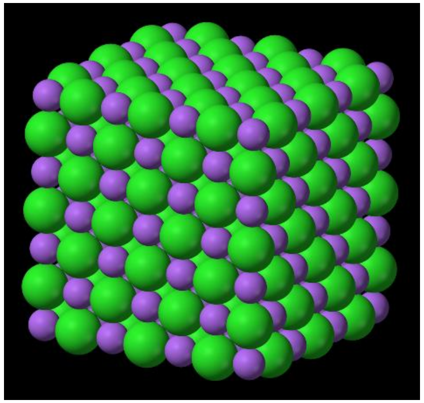
1. Distruction of a crystal

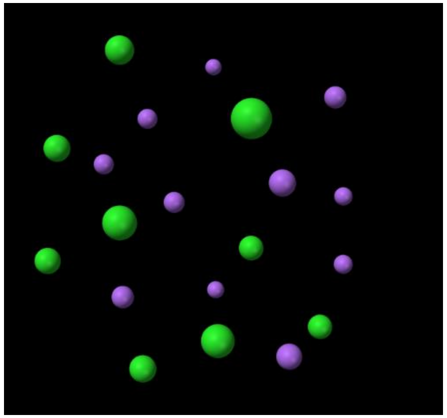
(2. Dissotiation of ion pairs)

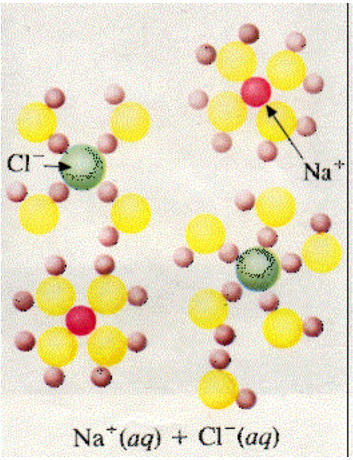
3. Solvation of the molecules (formation of bonds between atoms/ions/molecules os the solute and water molecules

The effects on heat of dissolution

1. Distruction of a crystal → Energy required
2. Dissotiation of ion pairs → Energy required
3. Solvation of the molecules (formation of bonds between atoms/ions/molecules os the solute and water molecules → Energy released







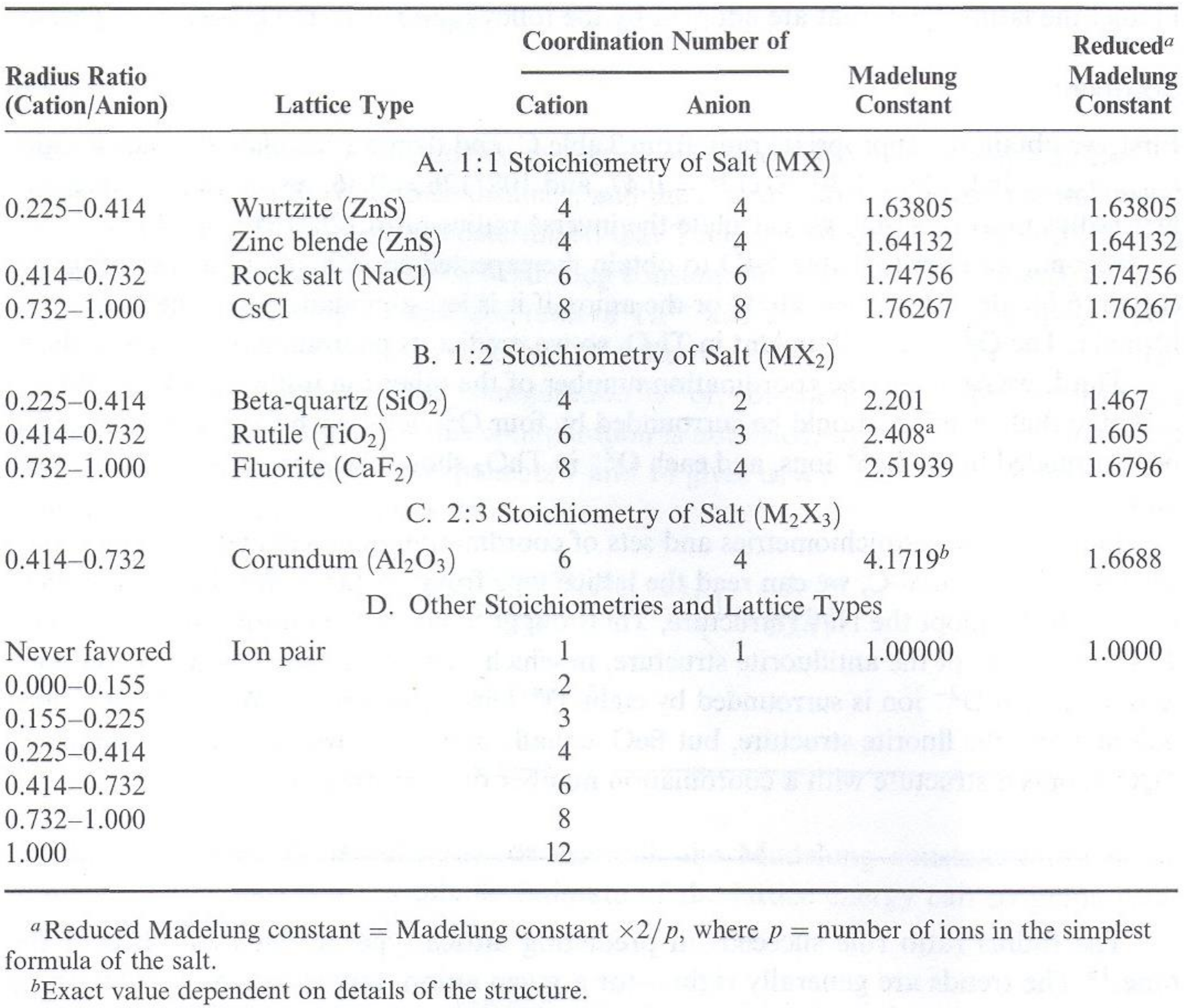
Entalpija rešetke

- Teško mjerljiva i donekle izračunljiva

$$E = N_{\mathrm{A}}\left[M\frac{1}{4\pi\varepsilon_0}\frac{Z_+Z_-}{r}+\frac{B}{r^n}\right]$$

$$E = N_{\mathrm{A}}M\frac{1}{4\pi\varepsilon_0}\frac{Z_+Z_-}{r}\left(1-\frac{1}{n}\right)$$

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_2X_3)				
0.414–0.732	Corundum (Al_2O_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			

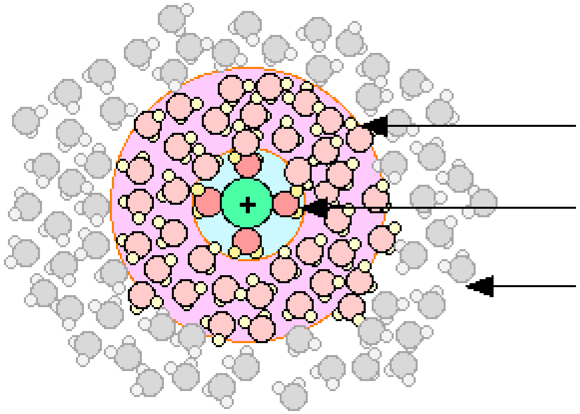
[a] Reduced Madelung constant = Madelung constant $\times 2/p$, where p = number of ions in the simplest formula of the salt.

[b] Exact 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 os the solute and water molecules → entropy somewhat decreases

Water has its structure!



Outer coordination sphere – quite ordered

Inner coordination sphere – **very** ordered

Interlayer with water molecules not conforming either to the order of the outher sphere or to that of pure water – **disordered**

Bulk water – structured as pure water

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

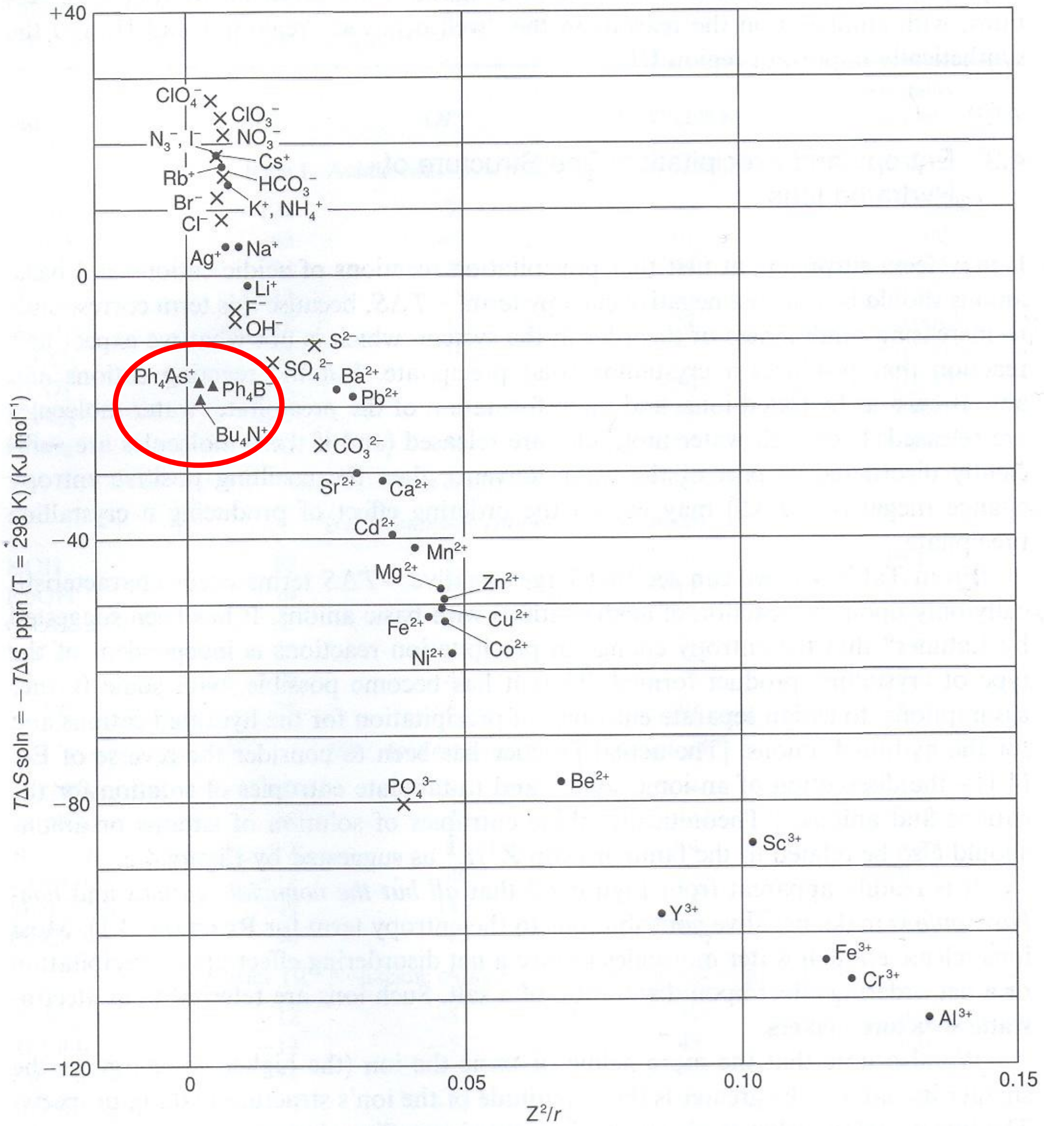


Figure 4.2
The 298 K entropy terms ($T\Delta S_{soln} = -T\Delta S_{pptn}$) for cations and anions as a function of Z^2/r. Crosses equal anions; dots equal metal cations; triangles equal organic ions. Thermodynamic data from Cox and Parker[7]; thermochemical radii of oxo anions from E. A. Keiter, R. L. Keiter, and J. E. Huheey, *Inorganic Chemistry*, Harper-Collins, New York, 1993; p. 118.

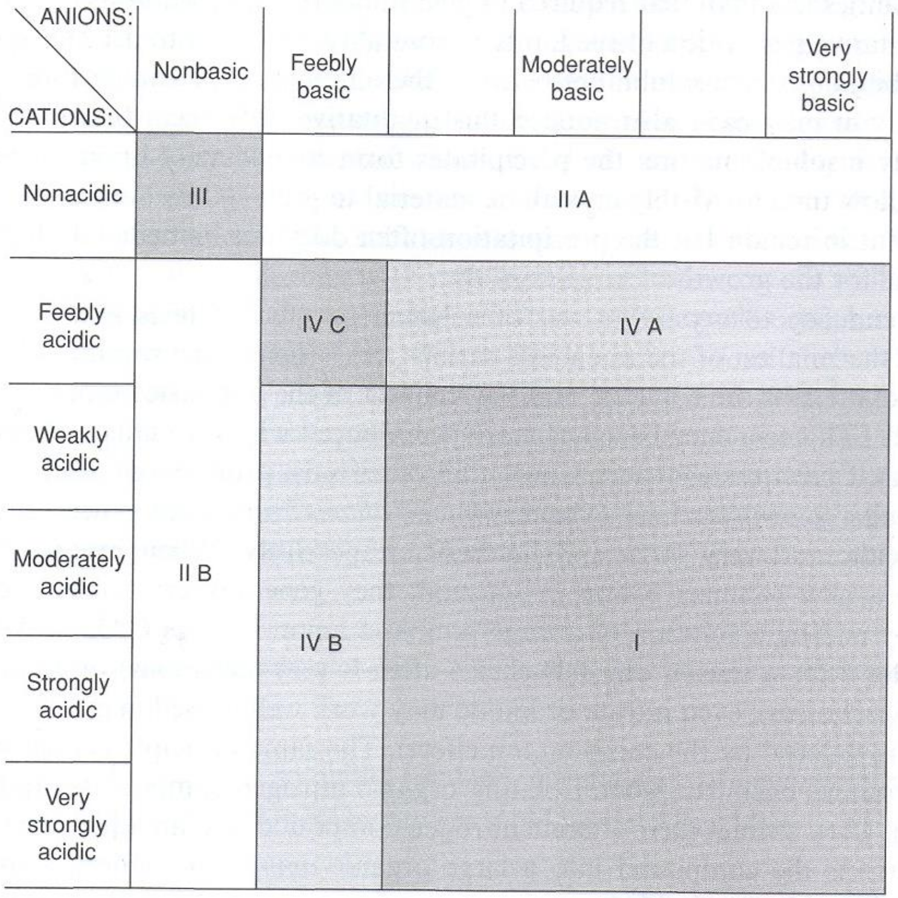
The smaller the size of an ion and the larger its charge the entropy of hydratation becomes more negative

What will not disolve well in water

Substances with large crystal lattice enegries (salts of small and highly charged ions, oxydes, covalent solids…)

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

Pravila topljivosti



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

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

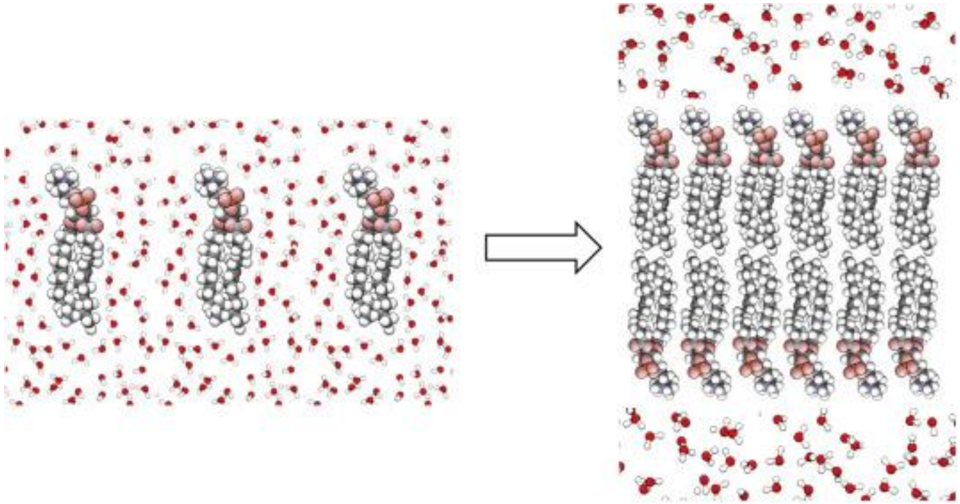
III – Δ*S* je zanemariva; velike entalpije rešetke (slični radijusi kationa i aniona) – netopljivost uvjetovana pozitivnom promjena entalpije pri otapanju

III i **IV** – soli su često slabo topljive / djelomično netopljive (Δ*H* i *T*Δ*S* bliskog iznosa i suprotnih predznaka)

Hidrofobnost

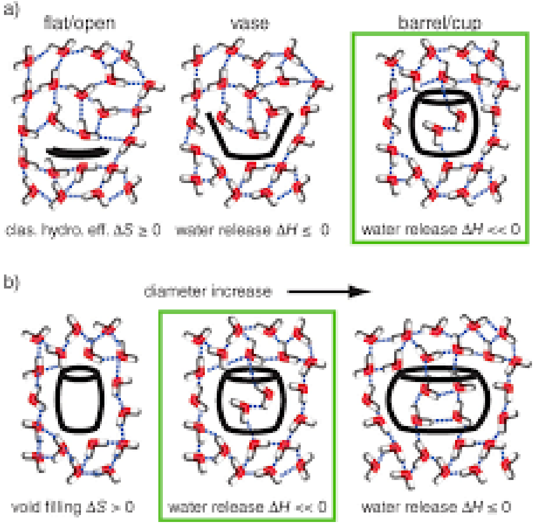
Klasična

- entropijski efekt – slabo sovatirani solut uređuje strukturu vode



Neklasična

- entalpijski efekt – molekule vode u unutrašnjosti kavezastih molekula tvore manje vodikovih veza od onih izvan



Nevodena otapala

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