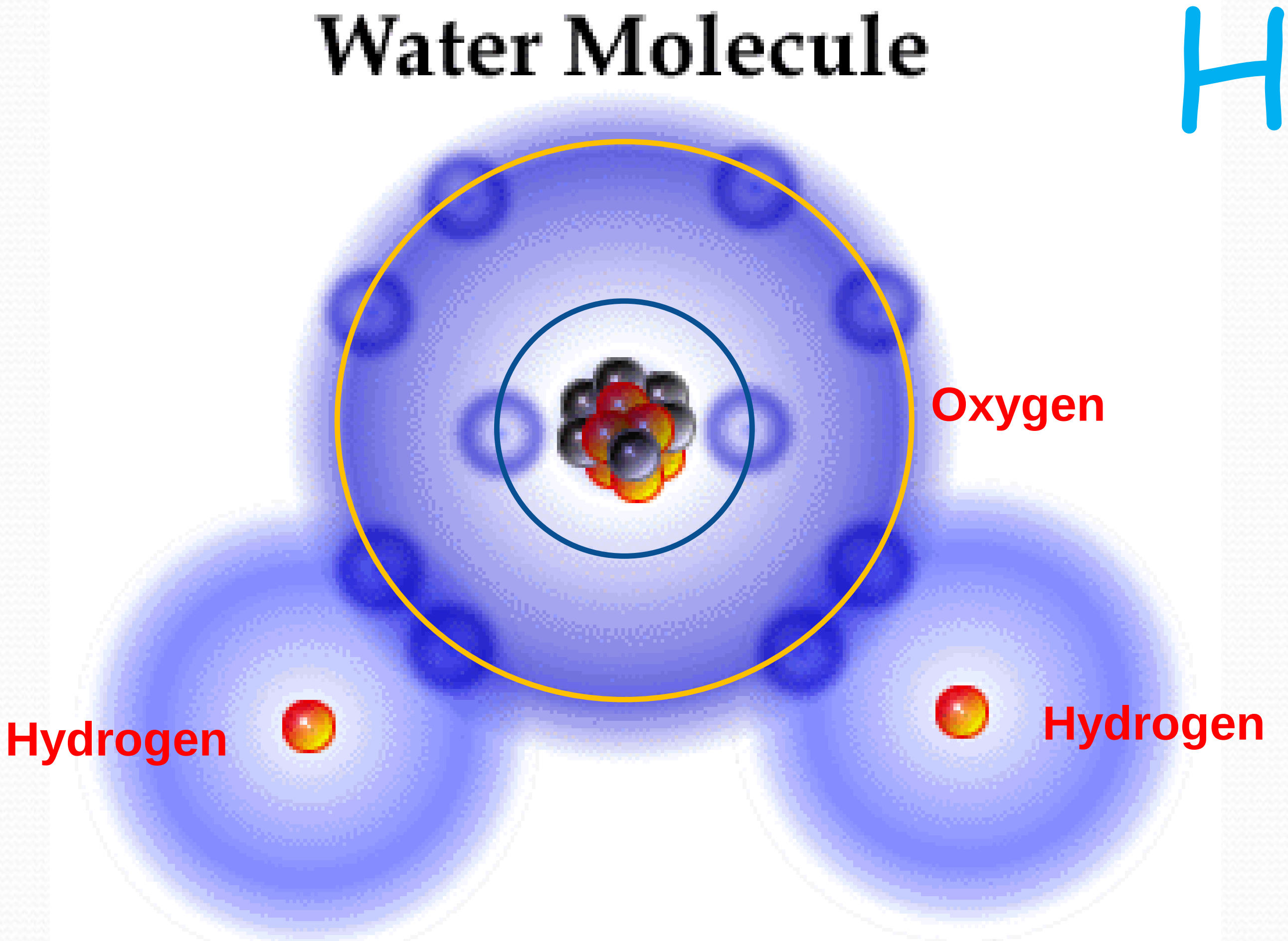
WATER:

One of the most extraordinary substances known to man

H_2O



http://eps.mcgill.ca/~courses/c220/

Isotopic composition of water

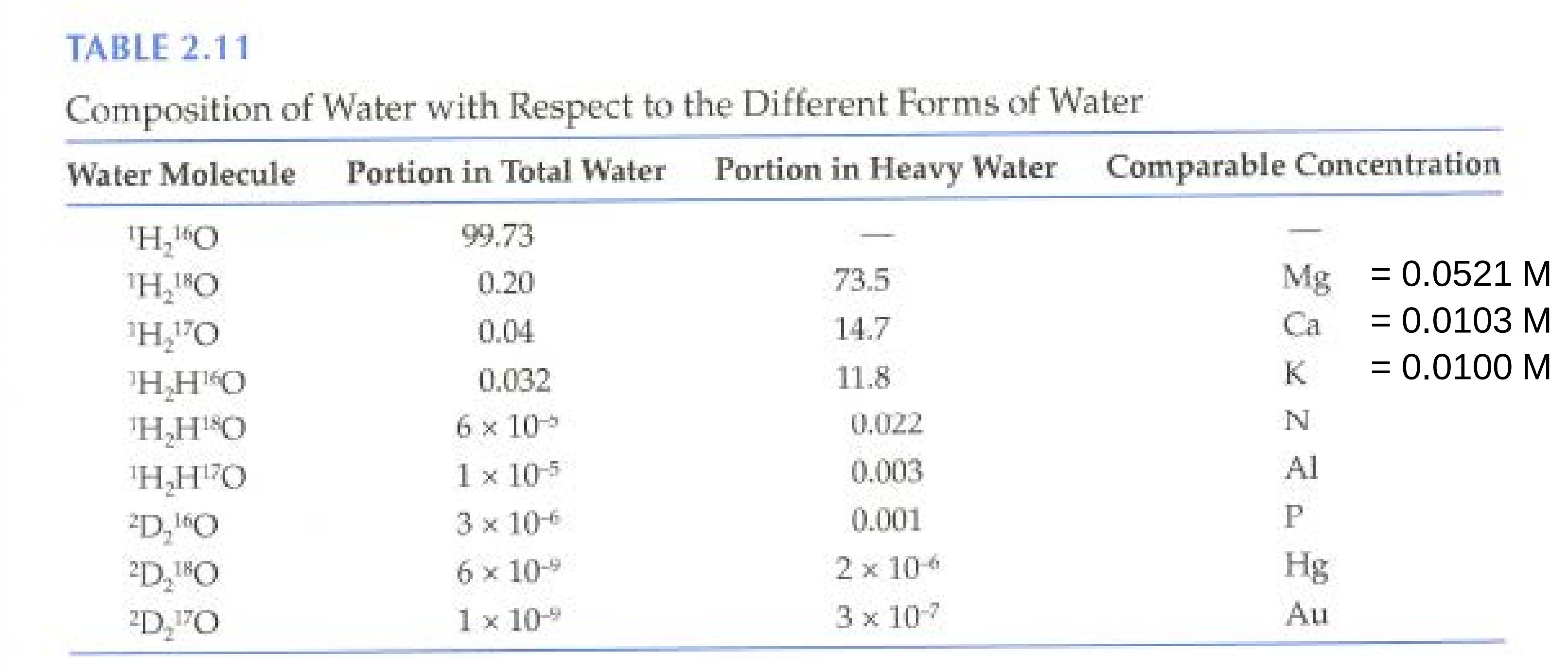
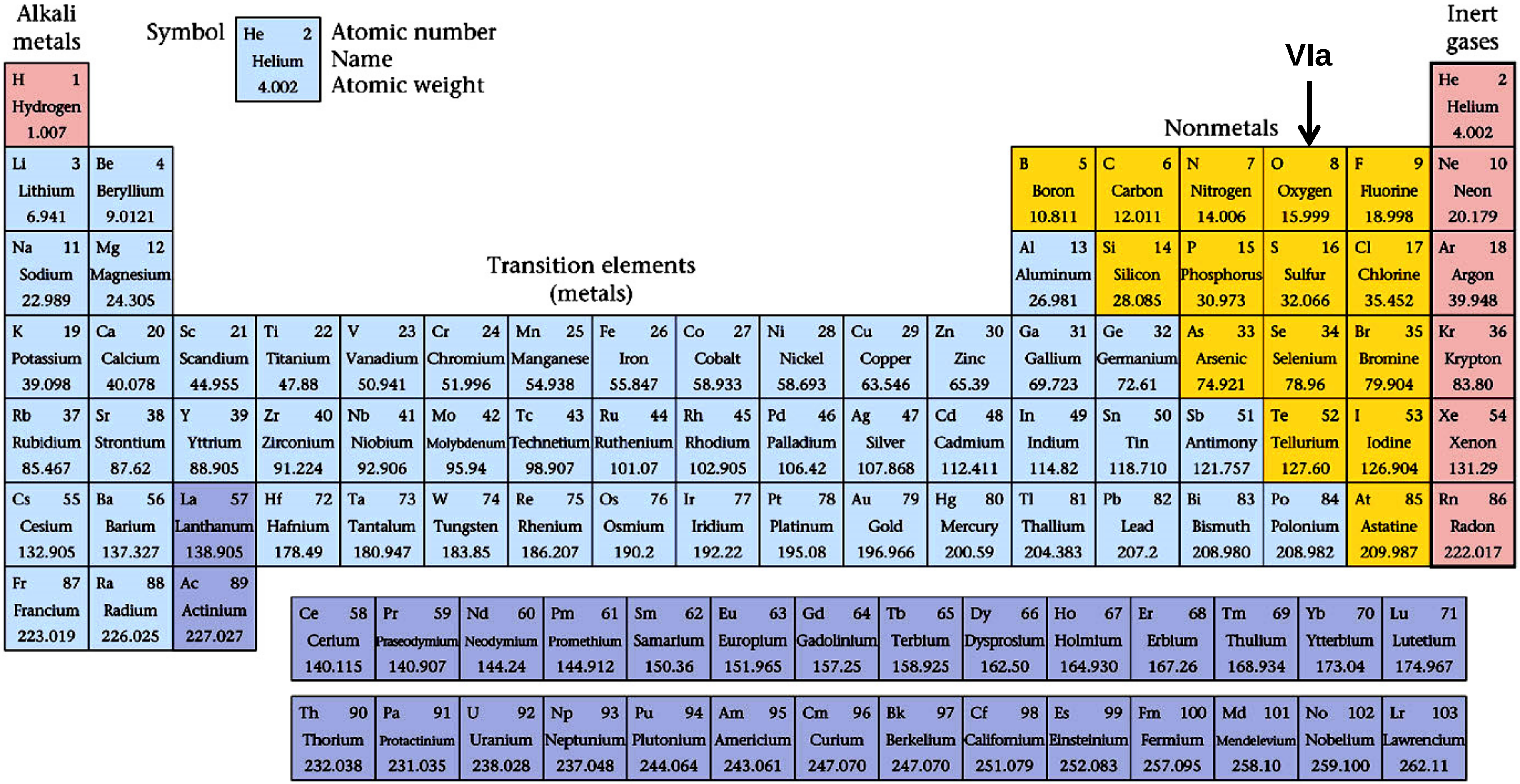


TABLE 2.11

Composition of Water with Respect to the Different Forms of Water

Water Molecule	Portion in Total Water	Portion in Heavy Water	Comparable Concentration
$^{1}H_{2}{}^{16}O$	99.73	—	—
$^{1}H_{2}{}^{18}O$	0.20	73.5	Mg = 0.0521 M
$^{1}H_{2}{}^{17}O$	0.04	14.7	Ca = 0.0103 M
$^{1}H_{2}H^{16}O$	0.032	11.8	K = 0.0100 M
$^{1}H_{2}H^{18}O$	6×10^{-5}	0.022	N
$^{1}H_{2}H^{17}O$	1×10^{-5}	0.003	Al
$^{2}D_{2}{}^{16}O$	3×10^{-6}	0.001	P
$^{2}D_{2}{}^{18}O$	6×10^{-9}	2×10^{-6}	Hg
$^{2}D_{2}{}^{17}O$	1×10^{-9}	3×10^{-7}	Au

Periodic table of the elements



Symbol

He 2 Helium 4.002

Atomic number
Name
Atomic weight

Alkali metals

Inert gases

VIa

Nonmetals

Transition elements (metals)

H 1 Hydrogen 1.007																	He 2 Helium 4.002
Li 3 Lithium 6.941	Be 4 Beryllium 9.0121											B 5 Boron 10.811	C 6 Carbon 12.011	N 7 Nitrogen 14.006	O 8 Oxygen 15.999	F 9 Fluorine 18.998	Ne 10 Neon 20.179
Na 11 Sodium 22.989	Mg 12 Magnesium 24.305											Al 13 Aluminum 26.981	Si 14 Silicon 28.085	P 15 Phosphorus 30.973	S 16 Sulfur 32.066	Cl 17 Chlorine 35.452	Ar 18 Argon 39.948
K 19 Potassium 39.098	Ca 20 Calcium 40.078	Sc 21 Scandium 44.955	Ti 22 Titanium 47.88	V 23 Vanadium 50.941	Cr 24 Chromium 51.996	Mn 25 Manganese 54.938	Fe 26 Iron 55.847	Co 27 Cobalt 58.933	Ni 28 Nickel 58.693	Cu 29 Copper 63.546	Zn 30 Zinc 65.39	Ga 31 Gallium 69.723	Ge 32 Germanium 72.61	As 33 Arsenic 74.921	Se 34 Selenium 78.96	Br 35 Bromine 79.904	Kr 36 Krypton 83.80
Rb 37 Rubidium 85.467	Sr 38 Strontium 87.62	Y 39 Yttrium 88.905	Zr 40 Zirconium 91.224	Nb 41 Niobium 92.906	Mo 42 Molybdenum 95.94	Tc 43 Technetium 98.907	Ru 44 Ruthenium 101.07	Rh 45 Rhodium 102.905	Pd 46 Palladium 106.42	Ag 47 Silver 107.868	Cd 48 Cadmium 112.411	In 49 Indium 114.82	Sn 50 Tin 118.710	Sb 51 Antimony 121.757	Te 52 Tellurium 127.60	I 53 Iodine 126.904	Xe 54 Xenon 131.29
Cs 55 Cesium 132.905	Ba 56 Barium 137.327	La 57 Lanthanum 138.905	Hf 72 Hafnium 178.49	Ta 73 Tantalum 180.947	W 74 Tungsten 183.85	Re 75 Rhenium 186.207	Os 76 Osmium 190.2	Ir 77 Iridium 192.22	Pt 78 Platinum 195.08	Au 79 Gold 196.966	Hg 80 Mercury 200.59	Tl 81 Thallium 204.383	Pb 82 Lead 207.2	Bi 83 Bismuth 208.980	Po 84 Polonium 208.982	At 85 Astatine 209.987	Rn 86 Radon 222.017
Fr 87 Francium 223.019	Ra 88 Radium 226.025	Ac 89 Actinium 227.027															

Ce 58 Cerium 140.115	Pr 59 Praseodymium 140.907	Nd 60 Neodymium 144.24	Pm 61 Promethium 144.912	Sm 62 Samarium 150.36	Eu 63 Europium 151.965	Gd 64 Gadolinium 157.25	Tb 65 Terbium 158.925	Dy 66 Dysprosium 162.50	Ho 67 Holmium 164.930	Er 68 Erbium 167.26	Tm 69 Thulium 168.934	Yb 70 Ytterbium 173.04	Lu 71 Lutetium 174.967
Th 90 Thorium 232.038	Pa 91 Protactinium 231.035	U 92 Uranium 238.028	Np 93 Neptunium 237.048	Pu 94 Plutonium 244.064	Am 95 Americium 243.061	Cm 96 Curium 247.070	Bk 97 Berkelium 247.070	Cf 98 Californium 251.079	Es 99 Einsteinium 252.083	Fm 100 Fermium 257.095	Md 101 Mendelevium 258.10	No 102 Nobelium 259.100	Lr 103 Lawrencium 262.11

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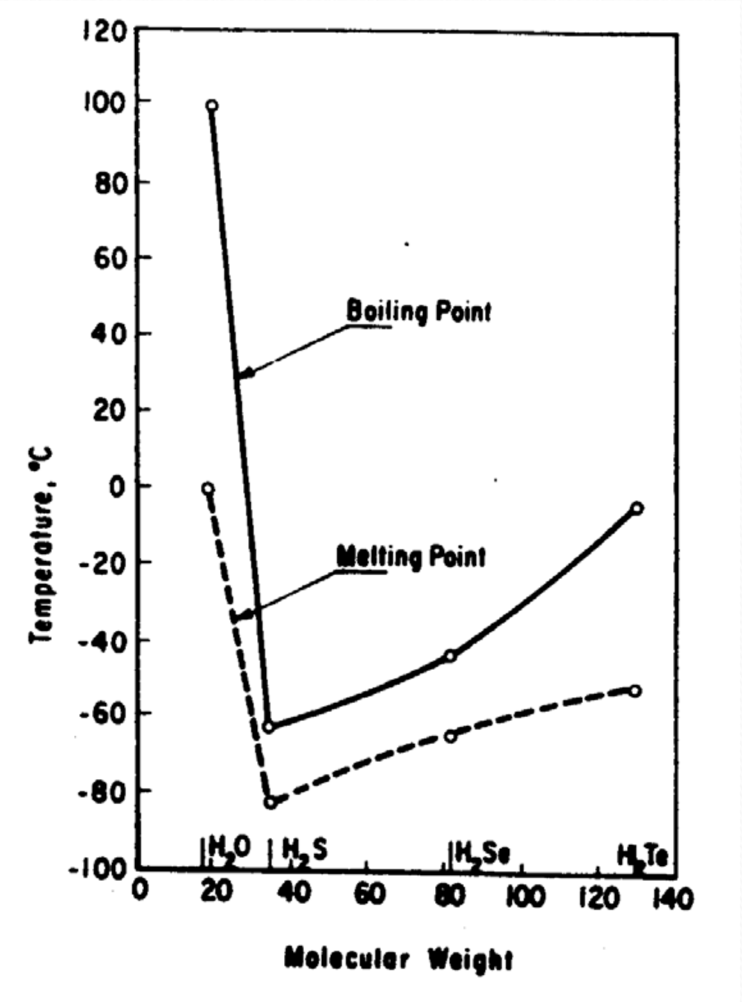
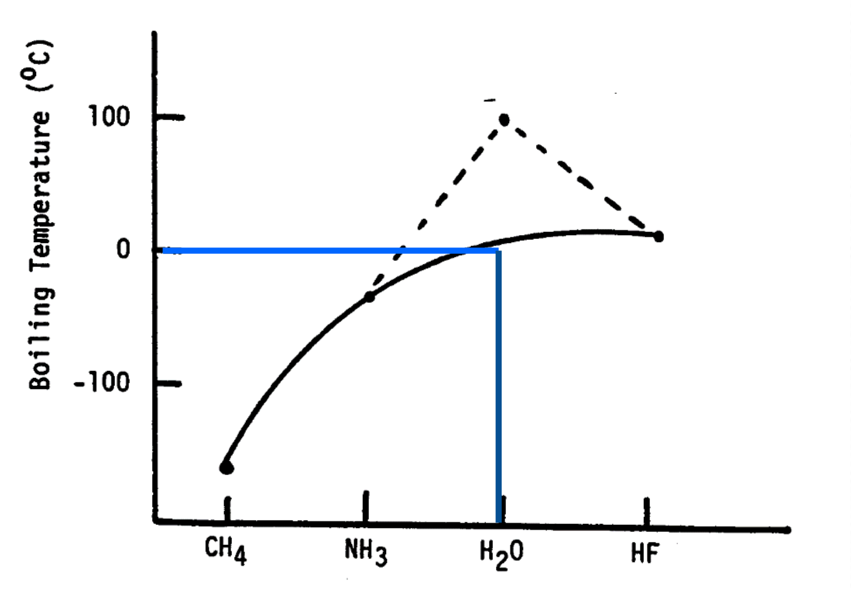
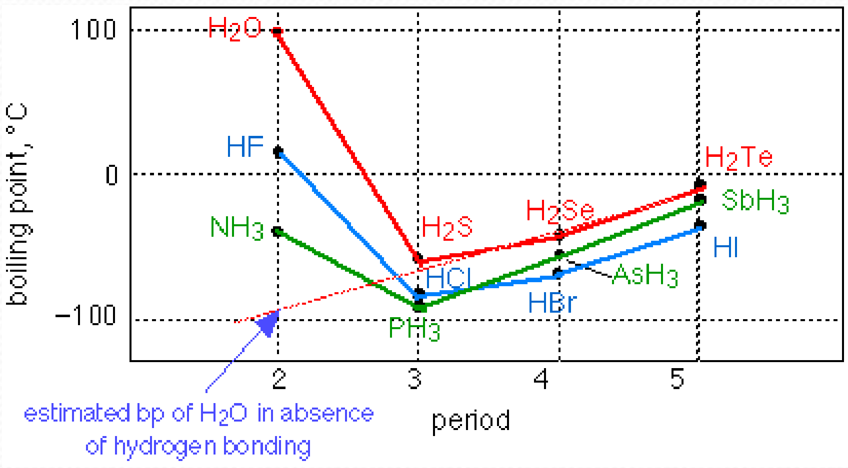
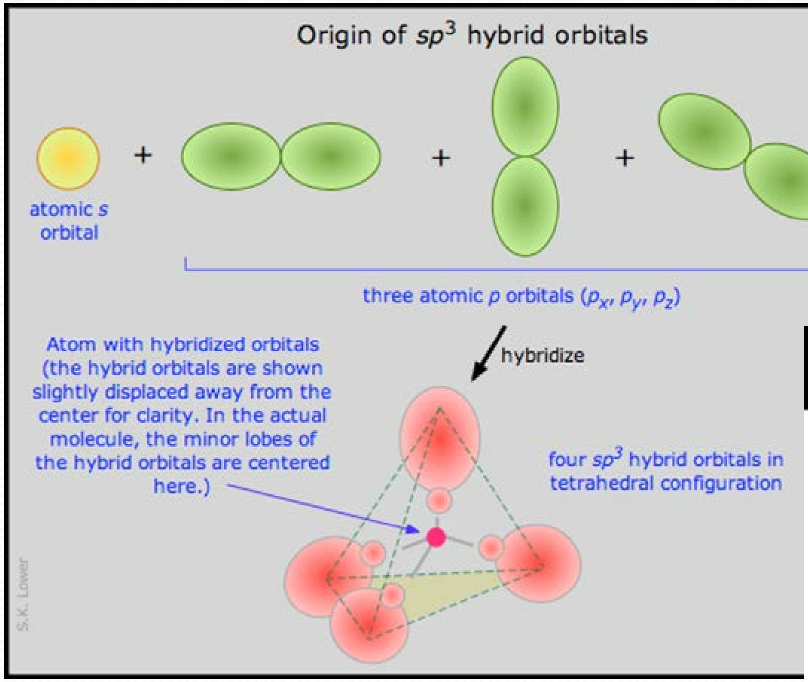


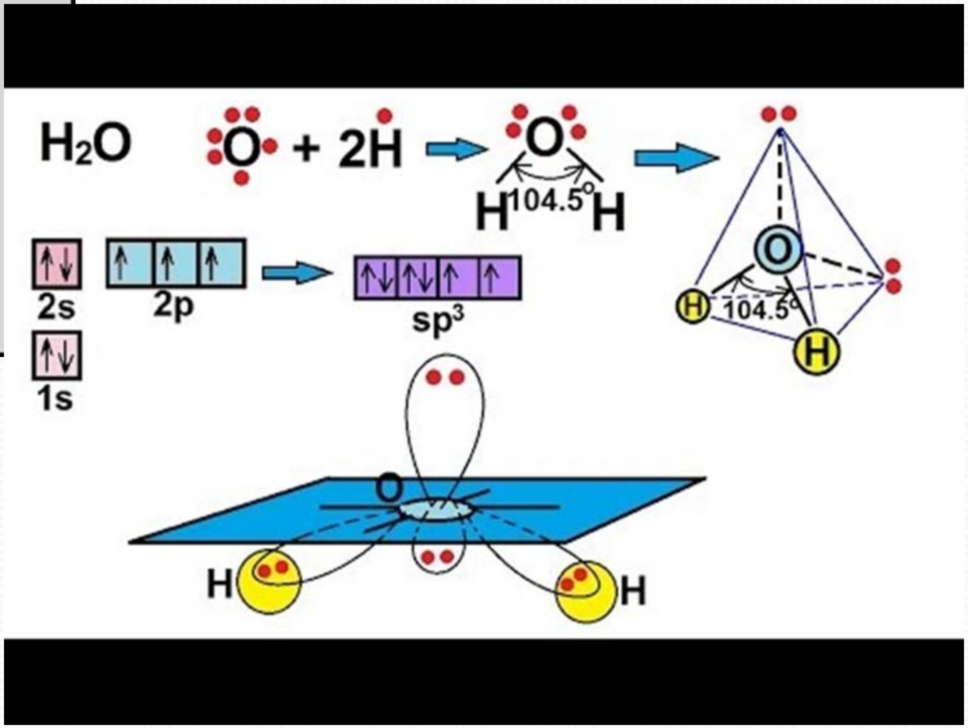




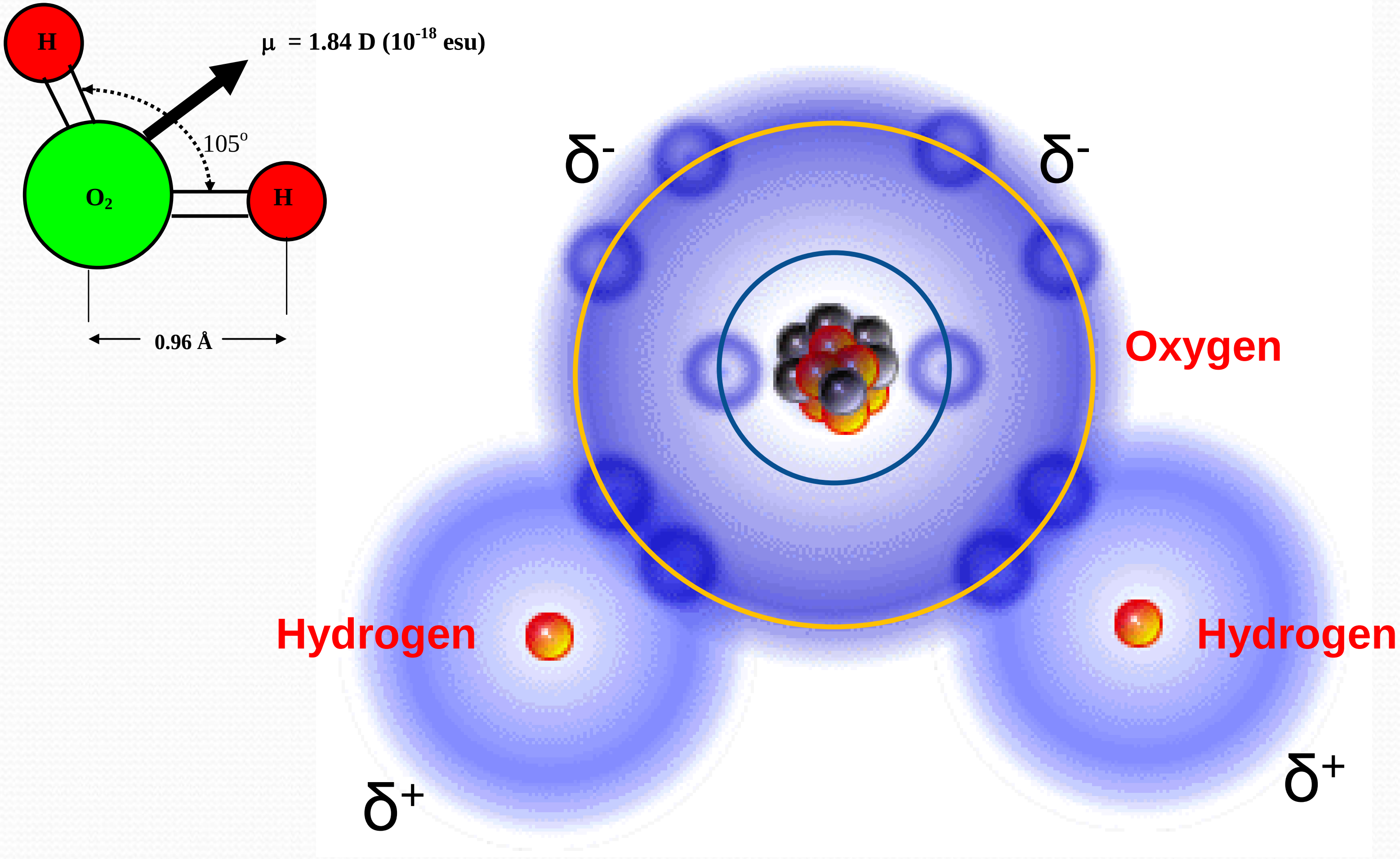
sp^3 hybridization and the formation of water


Origin of sp^3 hybrid orbitals

Atom with hybridized orbitals (the hybrid orbitals are shown slightly displaced away from the center for clarity. In the actual molecule, the minor lobes of the hybrid orbitals are centered here.)



Quadrapole moment of water



Quadrapole moment of water and hydrogen bonding

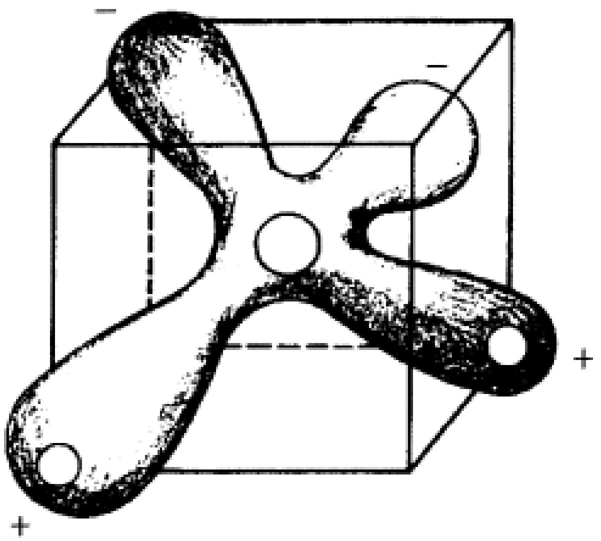
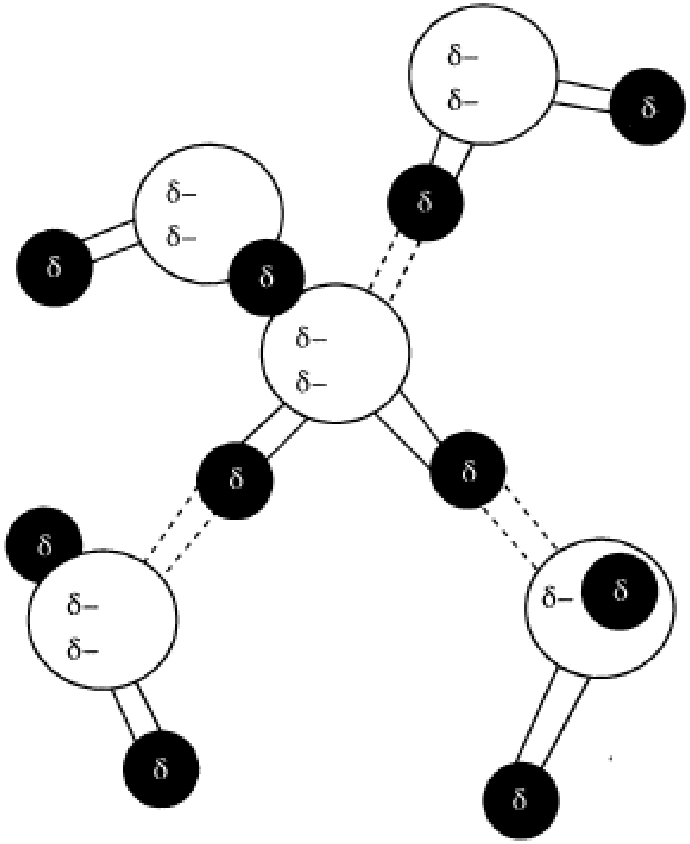
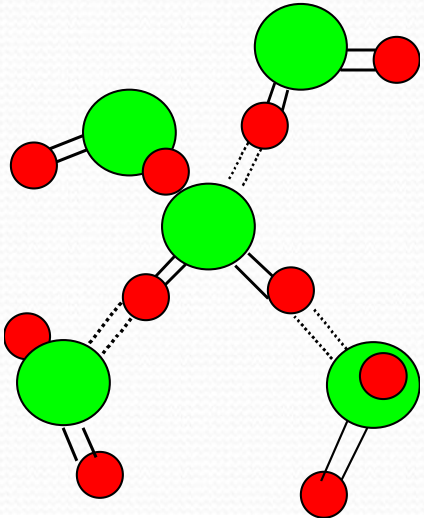


FIGURE 4.4
The three-dimensional structure of the water molecule.

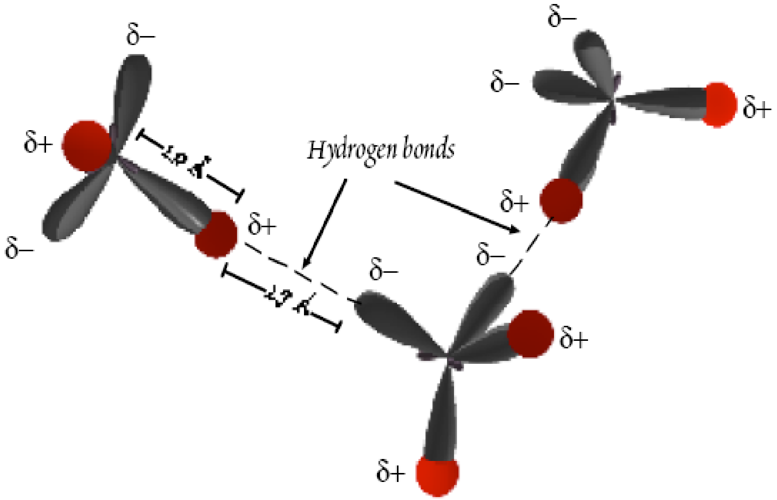


WATER

The hydrogen bond



ΔE = 19 kJ/mol



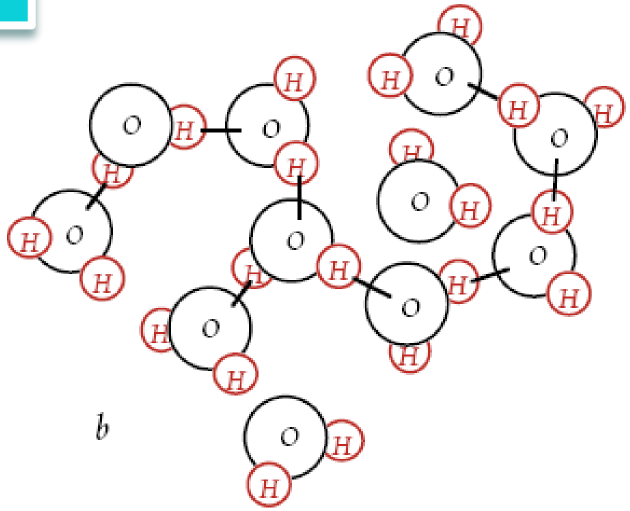


Figure 3.9. (a.) Structure of the water molecule. Bond angle in the liquid phase is 108°, 105° in the gas. The hydrogens retain a partial positive charge and the oxygen retains a partial positive charge. (b.) Partial structure present in liquid water. Lines connecting adjacent molecules illustrate hydrogen bonds.

Anomalous Properties of Water

- Maximum Density - $\rho_{solid} < \rho_{liquid}$
- High Heat Capacity
- High Heat of Fusion and Evaporation
- High Surface Tension and Viscosity
- High Dielectric Constant
- High Transparency
- High Thermal Expansion
- High Heat Conduction

Anomalous Properties of Water

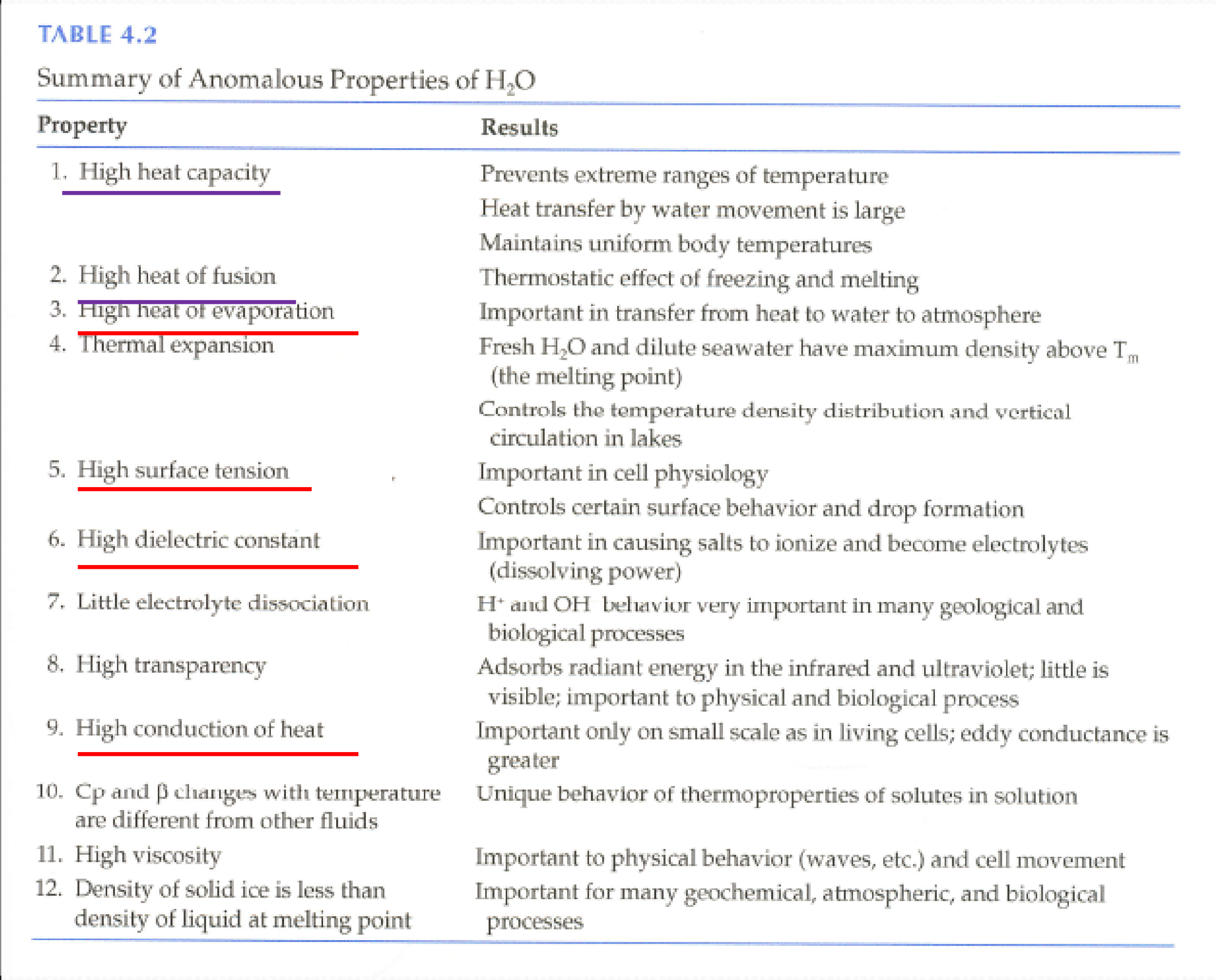
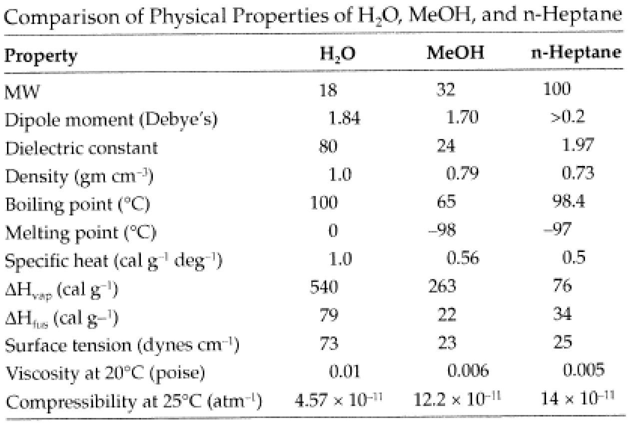


TABLE 4.2

Summary of Anomalous Properties of H_2O

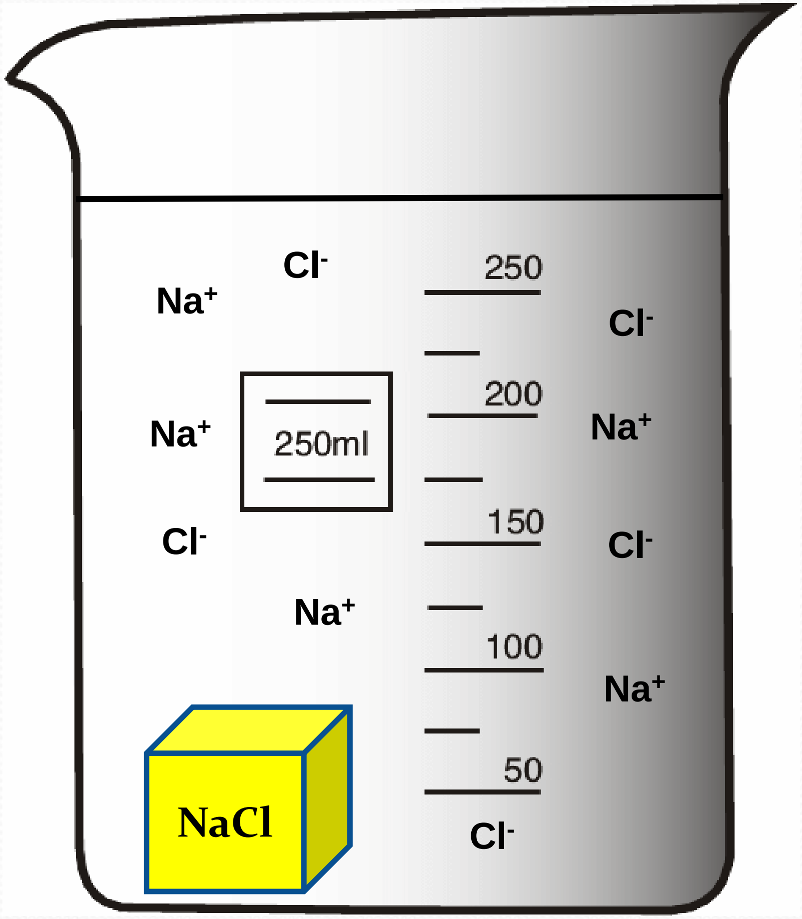
Property	Results
1. High heat capacity	Prevents extreme ranges of temperature Heat transfer by water movement is large Maintains uniform body temperatures
2. High heat of fusion	Thermostatic effect of freezing and melting
3. High heat of evaporation	Important in transfer from heat to water to atmosphere
4. Thermal expansion	Fresh H_2O and dilute seawater have maximum density above T_m (the melting point) Controls the temperature density distribution and vertical circulation in lakes
5. High surface tension	Important in cell physiology Controls certain surface behavior and drop formation
6. High dielectric constant	Important in causing salts to ionize and become electrolytes (dissolving power)
7. Little electrolyte dissociation	H^+ and OH^- behavior very important in many geological and biological processes
8. High transparency	Adsorbs radiant energy in the infrared and ultraviolet; little is visible; important to physical and biological process
9. High conduction of heat	Important only on small scale as in living cells; eddy conductance is greater
10. Cp and β changes with temperature are different from other fluids	Unique behavior of thermoproperties of solutes in solution
11. High viscosity	Important to physical behavior (waves, etc.) and cell movement
12. Density of solid ice is less than density of liquid at melting point	Important for many geochemical, atmospheric, and biological processes



Comparison of Physical Properties of H_2O, MeOH, and n-Heptane

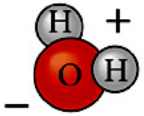
Property	H_2O	MeOH	n-Heptane
MW	18	32	100
Dipole moment (Debye's)	1.84	1.70	>0.2
Dielectric constant	80	24	1.97
Density (gm cm^{-3})	1.0	0.79	0.73
Boiling point (°C)	100	65	98.4
Melting point (°C)	0	−98	−97
Specific heat (cal g^{-1} deg^{-1})	1.0	0.56	0.5
ΔH_{vap} (cal g^{-1})	540	263	76
ΔH_{fus} (cal g^{-1})	79	22	34
Surface tension (dynes cm^{-1})	73	23	25
Viscosity at 20°C (poise)	0.01	0.006	0.005
Compressibility at 25°C (atm^{-1})	4.57×10^{-11}	12.2×10^{-11}	14×10^{-11}

Addition of an electrolyte to water

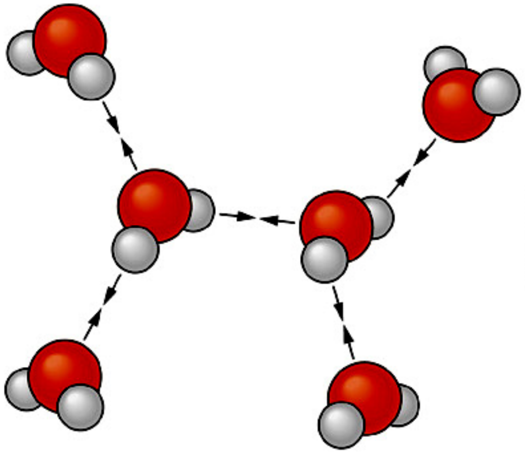


Bonds resulting from the polarity of molecules

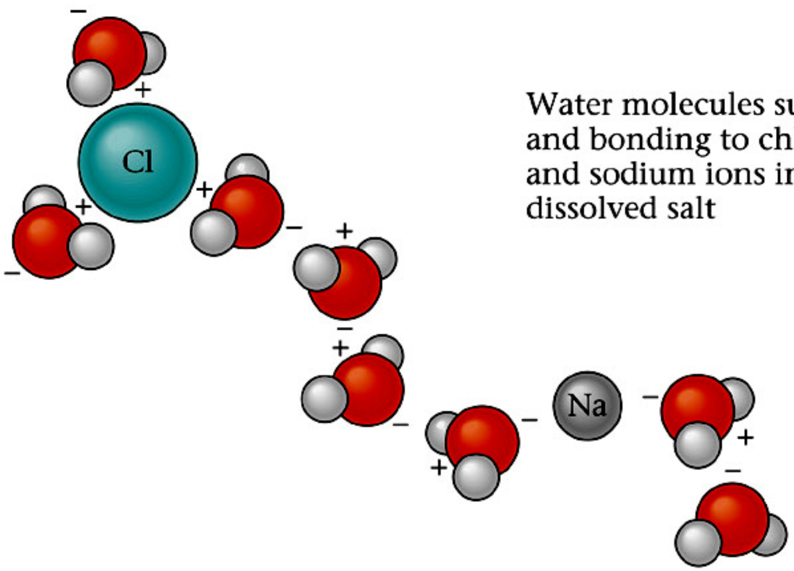
Water is a very good solvent



A polar water molecule

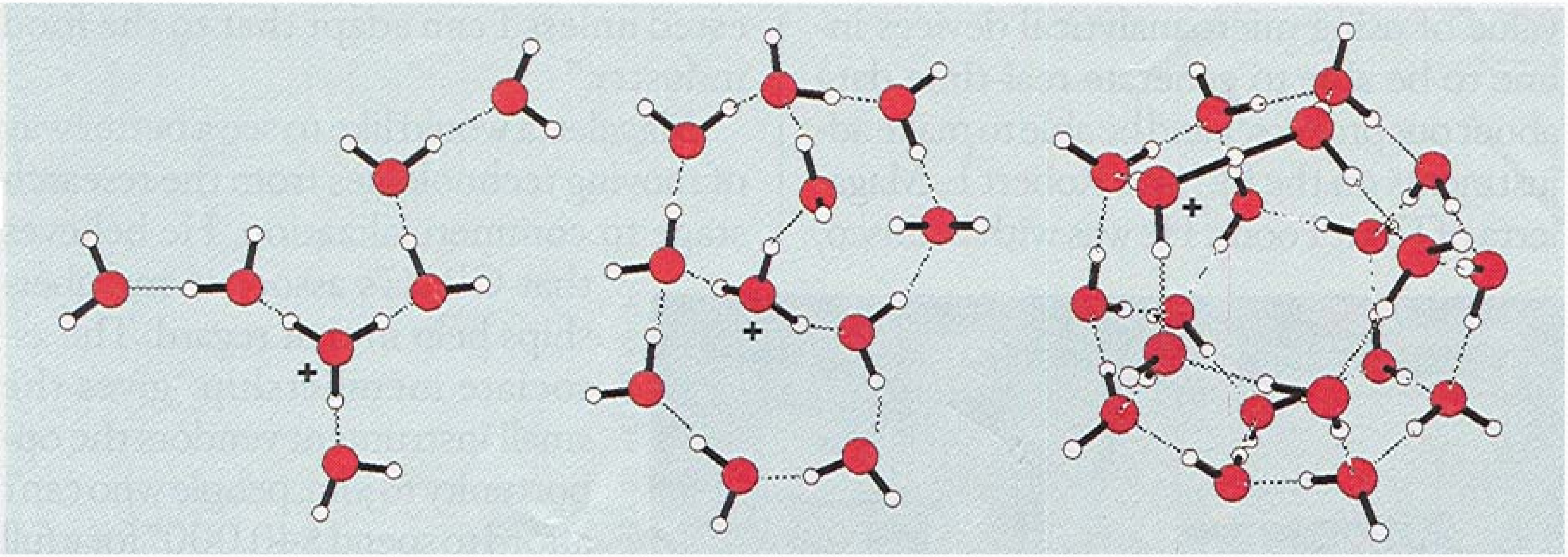


Hydrogen bonding
in water
(→← = hydrogen bond)

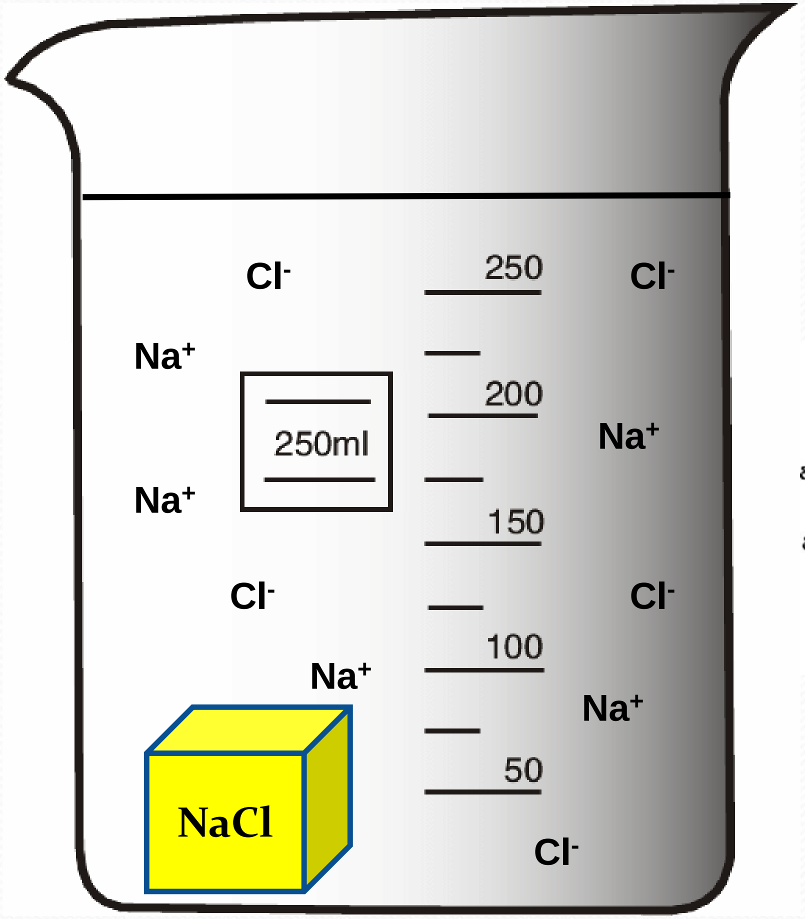


Water molecules surrounding
and bonding to chlorine
and sodium ions in
dissolved salt

Interaction of water with H^+ (H_3O^+)



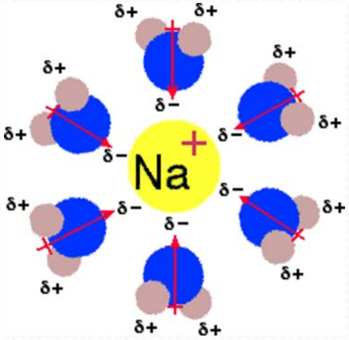
Addition of an electrolyte to water

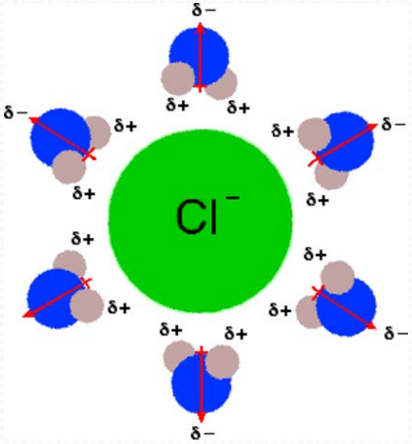


$NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$

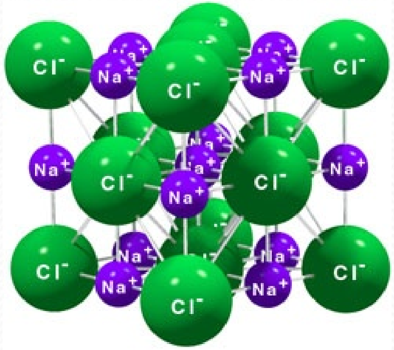
$\Delta H_{rx} = + 2.5$ kJ/mole

(endothermic reaction)

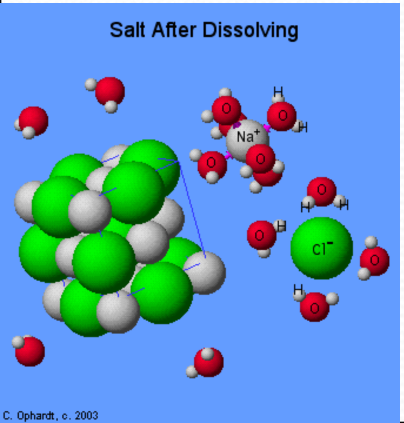




Addition of an electrolyte to water



$$\begin{tikzcd}
Na^+_{(g)} + Cl^-_{(g)} \arrow[r, "\Delta H_1"] \arrow[d, "\Delta H_3"'] & NaCl_{(solid)} \arrow[dl, "\Delta H_2 = +2.5\ \text{kJ/mole}"] \\
Na^+_{(aq)} + Cl^-_{(aq)} &
\end{tikzcd}$$



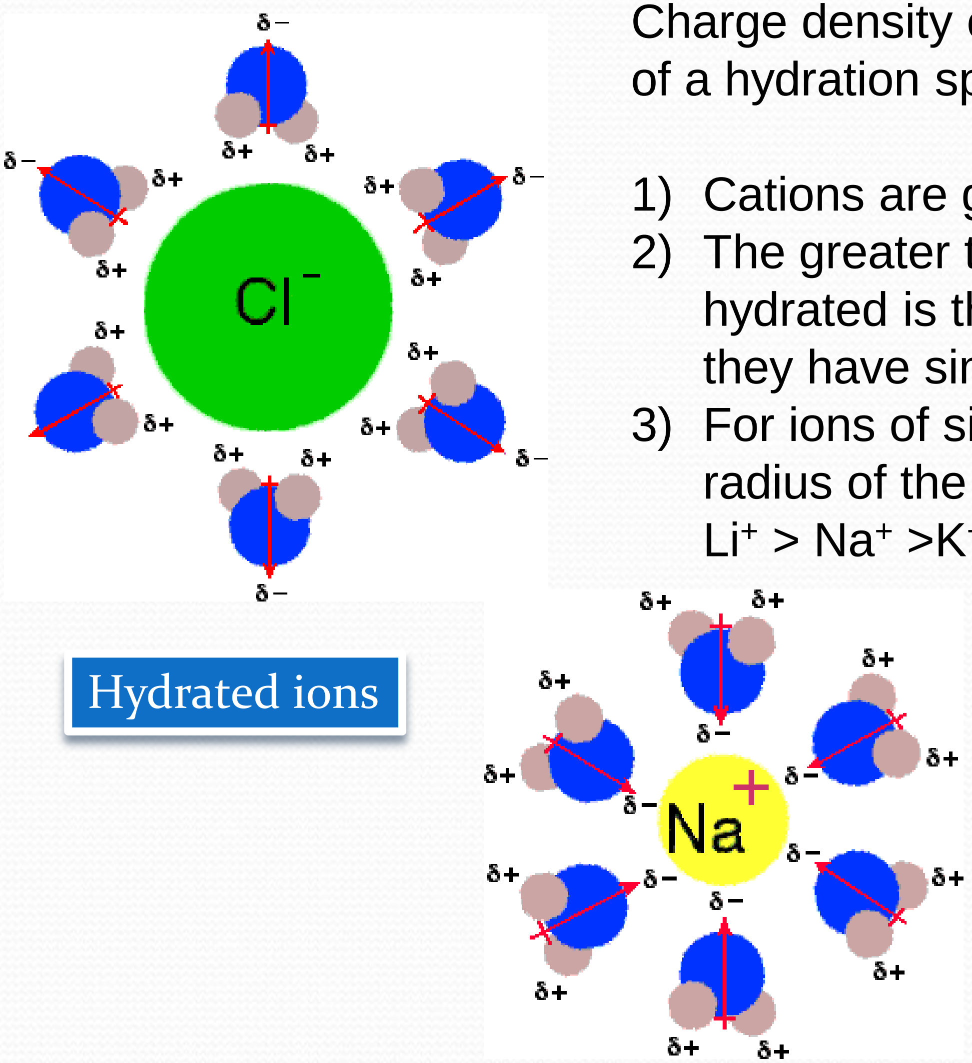
ΔH_1 = lattice heat = -757.3 kJ/mole

ΔH_3 = heat of hydration = $\Delta H_1 + \Delta H_2$ = -754.8 kJ/mole

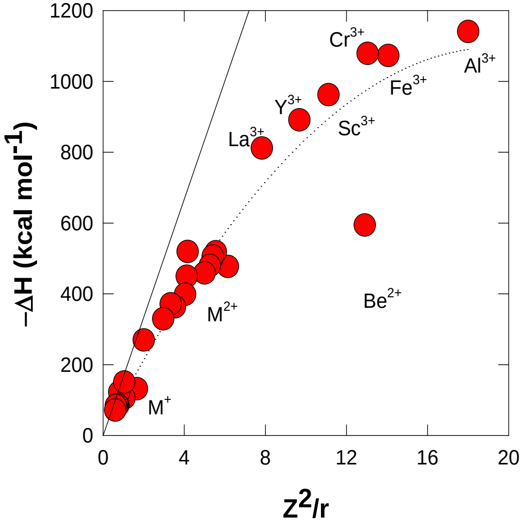
Solvated ions by water

Charge density of an ion (Zé/volume) and the formation of a hydration sphere:

1) Cations are generally more hydrated than anions.
2) The greater the charge of the ion, the more heavily hydrated is the ions (ex: $Mg^{2+} > Li^{+}$, even though they have similar ionic radii).
3) For ions of similar charge, the smaller the ionic radius of the ion, the more heavily hydrated it is (ex: $Li^{+} > Na^{+} > K^{+}$).



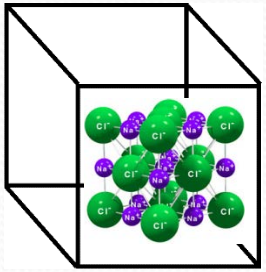
Hydrated ions



Hydration Numbers

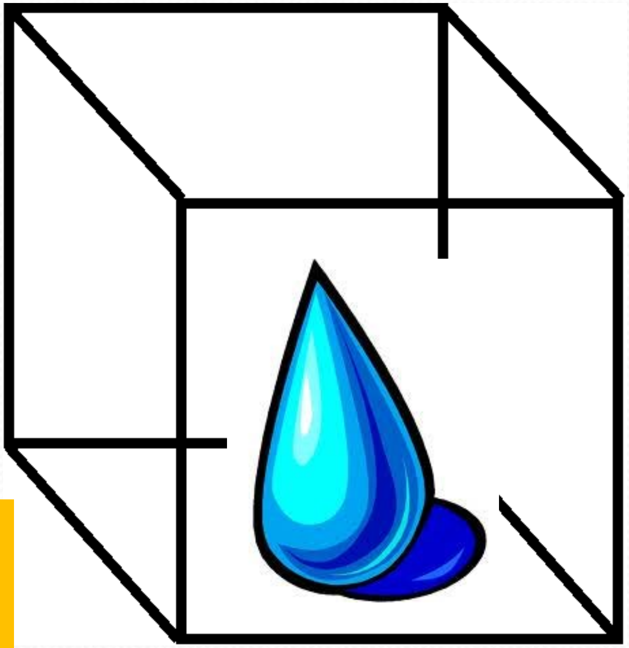
Ion	n_h	Ion	n_h
Li^+	2.8	F^-	5.6
Na^+	3.7	Cl^-	2.0
K^+	2.9	Br^-	1.2
Mg^{2+}	7.8	I^-	0.1
Ca^{2+}	6.5	OH^-	6.4
Cu^{2+}	7.6	SO_4^{2-}	8.6
La^{3+}	14.7	CO_3^{2-}	12.8

Electrostriction



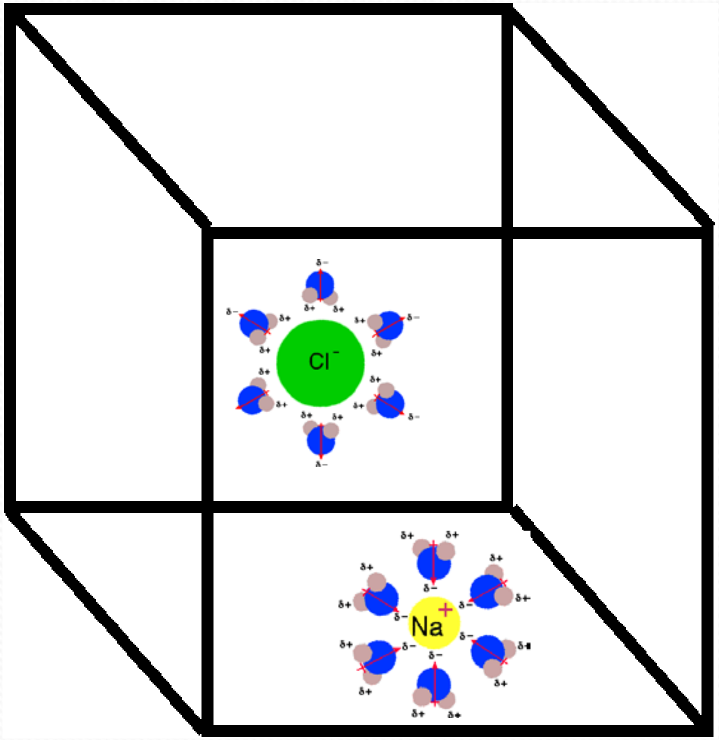
0.5 mole NaCl
= 29.22 g
$\rho = 2.165\ \mathrm{g/cm^3}$
→13.5 $\mathrm{cm^3}$

+



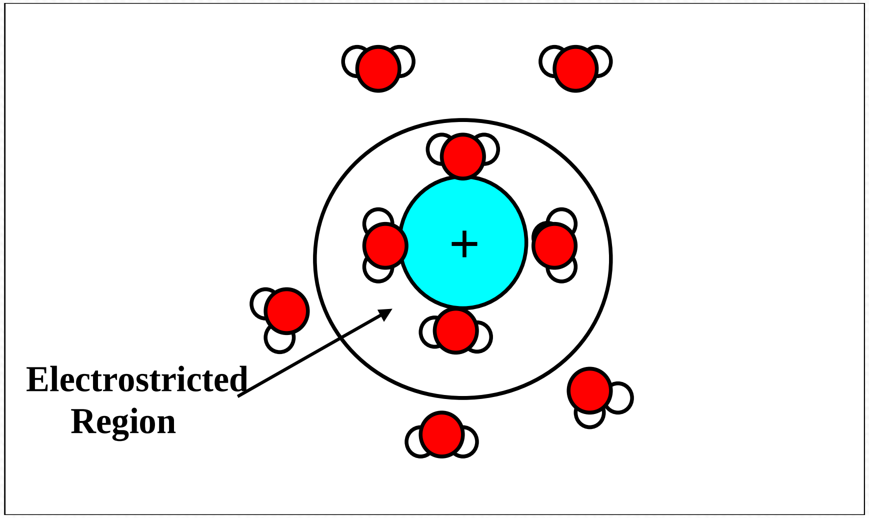
970.78 g of water
$\rho = 0.997\ \mathrm{g/cm^3}$
→973.7 $\mathrm{cm^3}$

=



1000 g of solution
$V \neq 13.5 + 973.7 = 987.2\ \mathrm{cm^3}$
but ~ 982.5 $\mathrm{cm^3}$

Electrostriction



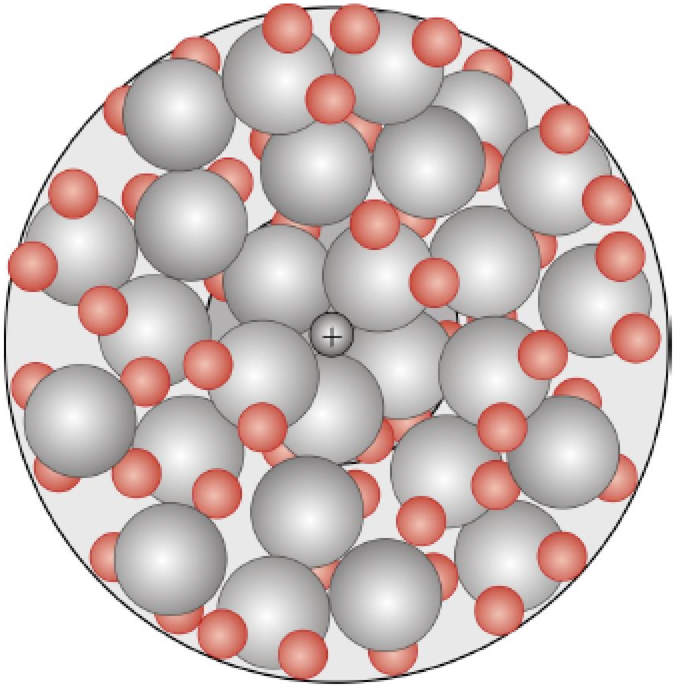


Figure 3.10. Solvation of a cation in aqueous solution. In the first solvation shell, water molecules are bound to the cation and oriented so that the partial negative charge on the oxygen faces the cation. In the second solvation shell molecules are only loosely bound and partially oriented.

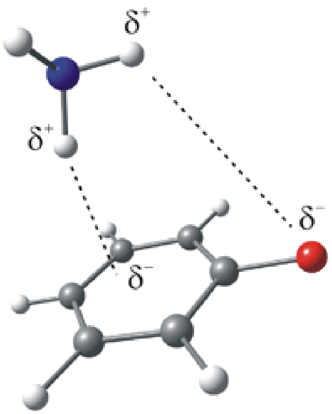
The amount of electrostriction is dependent upon the concentration and nature of the salt. It is related to the partial molal volume ($\bar{V}$) of the constituent ions.

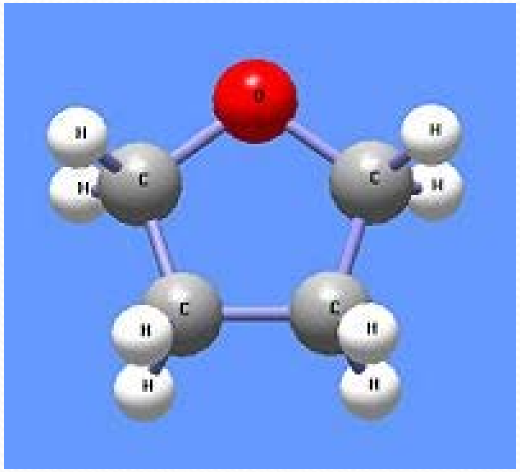
$(d\mu_i/dP)_T = \bar{V}_i$ = partial molal volume

where $\mu_i = \mu_i^\circ + RT \ln a_i$ = chemical potential
a_i = activity of species i

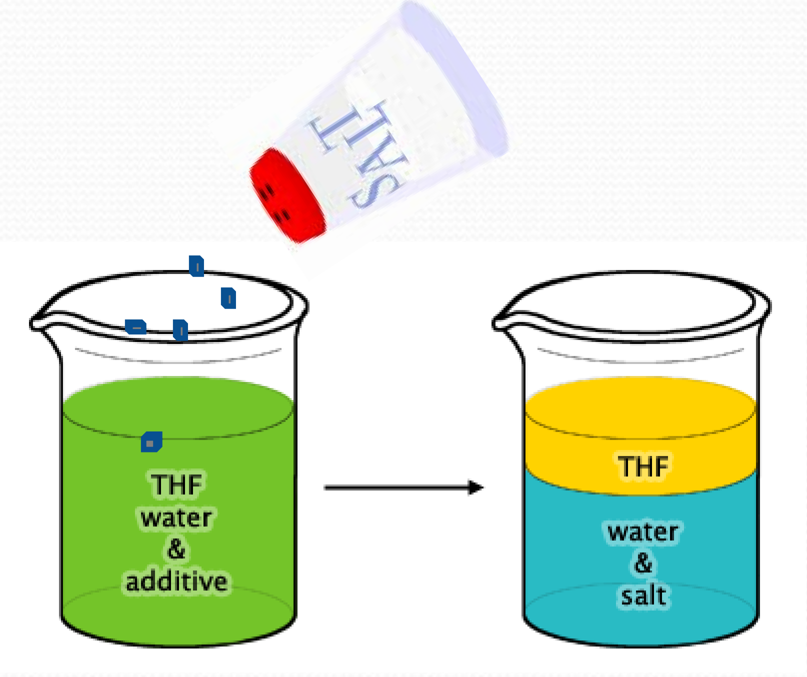
Non-electrolyte in water

Non-electrolytes are held in solution by weak Van der Waals or dipole-dipole interactions with water.





THF - tetrahydrofurane



Salting-out

Salting-out

FIZZZZZZ …

Salting-out

Number of available water molecules in 1 liter (or ~1 kg) $= (1000\text{g l}^{-1})/(18\text{g mol}^{-1})$
$= 55.55$ moles l^{-1}

Upon the addition of an electrolyte (salt), the number of water molecules (per liter of water) available to dissolve a non-electrolyte is given by:

$$55.55 - \Sigma\, c_i n_h$$

c_i = ion concentration in mole l^{-1}
n_h = hydration number of the ion

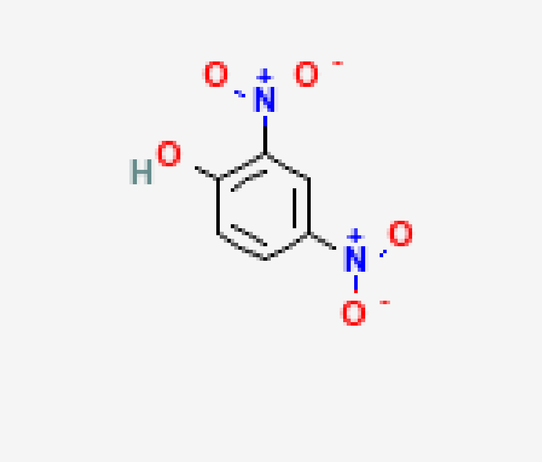
Assuming that the solubility of a non-electrolyte in water is simply proportional to the number of water molecules outside the first hydration layer of the ions, then:

$$S/S_o = (55.55 - \Sigma\, c_i n_h)/55.55$$

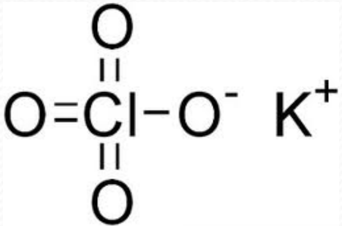
S_o = solubility of the non-electrolyte in pure water
S = solubility of the non-electrolyte after the addition of an electrolyte

Salting-out

2, 4 dinitrophenol



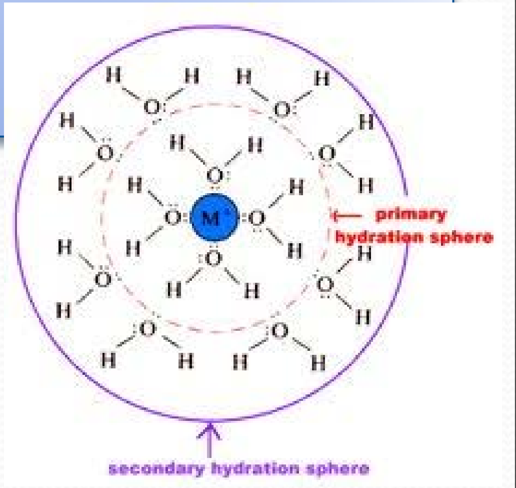
1 mole $KClO_4$ (potassium perchlorate)

+ 
$O{=}\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{Cl}}{-}O^- \; K^+$

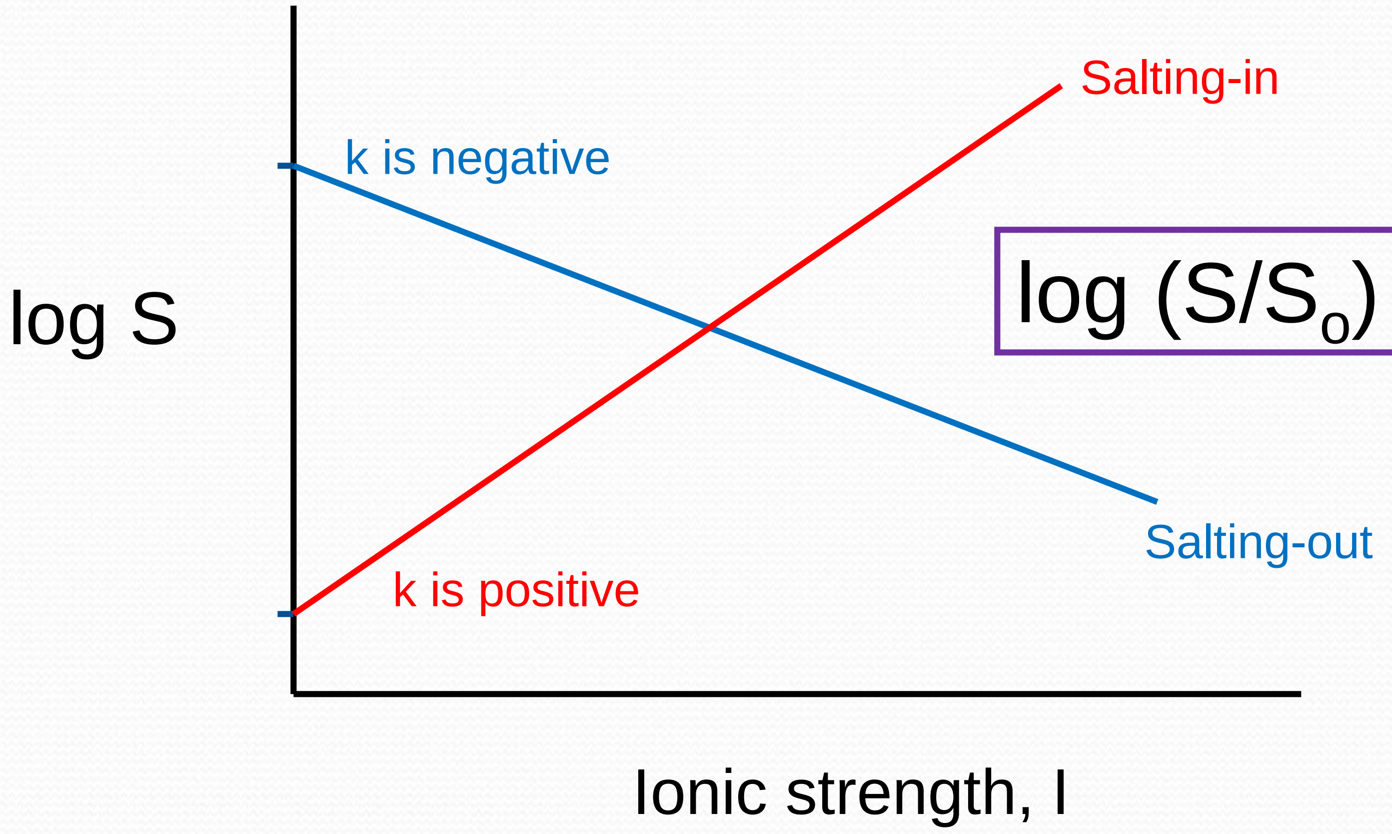
$\boxed{nK^+ = 2.9 \text{ and } nClO_4^- = 6}$

$$\begin{aligned} S/S_o &= (55.55 - (1 * 2.9 + 1 * 6))/55.55 \\ &= (55.55 - 8.9)/55.55 \\ &= 46.65/55.55 \\ &= 0.84 \end{aligned}$$

$$(S/S_o)_{Exp} = 0.7$$



Salting-in and Salting-out



$$\boxed{\log (S/S_o) = k\,I}$$

Ion-ion interactions
The non-ideal behaviour of solutes

The deviation from ideality is given by the activity coefficient (γ):

a_i = activity or "effective or thermodynamic concentration" = γ_i [i]

$\gamma_i = 1$ when $\Sigma[i] = 0$.

or, in terms of free energy or chemical potential,

$$\mu_i = \mu^o_i + RT \ln a_i = \mu^o_i + RT \ln \gamma_i + RT \ln [i]$$

In nearly pure water (infinite dilution solutions), where all solute ions or molecules contact only water molecules, $a_i = [i]$ and the activity coefficients of all solutes are equal to one. Given the definition of the standard state, the solute-water interactions are accounted for.

As salt concentrations increase, individual aqueous species interact with each other – electrostatic or coulombic interactions.

Ionic Strength

Coulombic interactions are proportional to the charge concentration of the ions involved. The charge concentration is given by the ionic strength (I):

$$I = \tfrac{1}{2}\,\Sigma([i] \bullet Z^2{}_i) \;\approx 0.7 \text{ m in seawater}$$

where [i] is in molal units (mole of ions/kg H_2O) and Z_i is the charge of the ion i. The ionic strength is summed for all charged species in solution, **assuming that all electrolytes are present as free ions in solution**.

I ~ 2 x 10^{-5} x TDS or ~0.8 x 10^{-5} x SpC for a NaCl solution
I ~ 2.5 x 10^{-5} x TDS or ~1.7 x 10^{-5} x SpC for typical surface waters
I ~ 2.8 x 10^{-5} x TDS or ~1.9 x 10^{-5} x SpC for $Ca(HCO_3)_2$ solutions

Debye-Hückel Theory

In dilute solutions, the interactions among ions are mostly due to long-range electrostatic forces: attraction of ions of opposite charge and repulsion of ions of like charge. As a result of these forces, the distribution of ions in solution is not uniform. The separation of charges at the molecular scale leads to local variations in the electrical potential of the solution which decreases the total free energy of the system.

Assuming that the only interactions not accounted for by chemical reactions are due to their electrical charge, strictly electrostatic interactions, Debye and Hückel evaluated the relevant electrostatic energy and included it in the expression of the free energy of the ions.

From electrostatic theory, we know that the work necessary to bring a charge 'c' from an electrical potential ψ to a potential ψ' is:

$$W = c\,[\,\psi' - \psi] = Z_i\,F\,[\,\psi' - \psi]$$

Debye-Hückel Theory

Given that the charge of an ion is equal to Z_iF, then:

$$W = Z_iF\,[\,\psi' - \psi^\circ]$$

$$(dG/dn_i)_{T,P} = \mu_i = \mu^\circ_i + RT\ln[i] + Z_iF\,\psi'$$

Assuming that the ions behave as point charges (finite dimension) in a continuous medium of uniform dielectric constant, Debye and Hückel derived the following expression of ψ':

$$\psi' = -\,A\,(RT/F)\,Zi\,(I^{1/2}/(1 + Ba\,I^{1/2})$$

$$\mu_i = \mu^\circ_i + RT\ln[i] - A\,RT\,Z_i^2\,(I^{1/2}/(1 + Ba\,I^{1/2})$$

Hence, electrostatic interactions among ions results in a decrease of their molal free energies.

Debye-Hückel Theory

$$\log \gamma_i = -AZ^2_i \; I^{1/2}/(1 + a_i \, BI^{1/2})$$

where A and B are constants that depend only on the temperature and dielectric constant of the system.

For water at 25°C and 1 atm total pressure:

$A = 1.824928 \times 10^6 (\varepsilon T)^{2/3} = 0.5085 \text{ mol}^{-1/2} \text{ l}^{1/2}$ and
$B = 50.29 \times 10^8/(\varepsilon T)^{1/2} = 0.3281 \times 10^8 \text{ cm}^{-1} \text{ mol}^{-1/2} \text{ l}^{1/2}$

ε is the dielectric constant of water (a measure of its capacity to hold charges in solution). Pure water has the highest dielectric constant of all liquids.

a_i = adjustable size parameter (in angstroms or 10^{-8} cm) which corresponds roughly to the distance of closest approach between the centre of adjacent ions or the radius of the hydrated ion.

Single ion activity coefficients calculated from the Debye-Hückel Equation

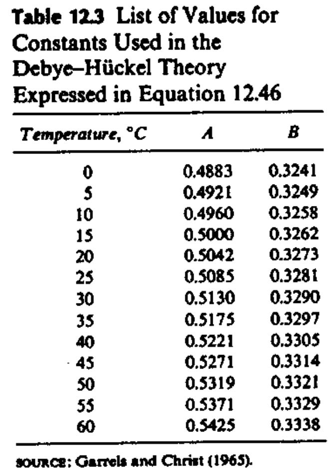


Table 12.3 List of Values for Constants Used in the Debye–Hückel Theory Expressed in Equation 12.46

Temperature, °C	*A*	*B*
0	0.4883	0.3241
5	0.4921	0.3249
10	0.4960	0.3258
15	0.5000	0.3262
20	0.5042	0.3273
25	0.5085	0.3281
30	0.5130	0.3290
35	0.5175	0.3297
40	0.5221	0.3305
45	0.5271	0.3314
50	0.5319	0.3321
55	0.5371	0.3329
60	0.5425	0.3338

SOURCE: Garrels and Christ (1965).

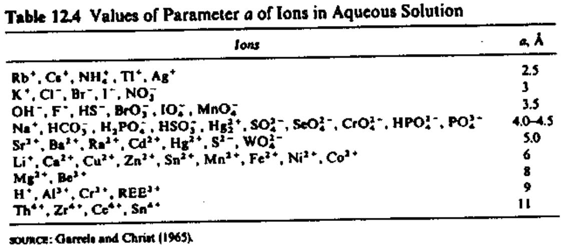


Table 12.4 Values of Parameter *a* of Ions in Aqueous Solution

Ions	*a*, Å
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	2.5
K^+, Cl^-, Br^-, I^-, NO_3^-	3
OH^-, F^-, HS^-, BrO_3^-, IO_4^-, MnO_4^-	3.5
Na^+, HCO_3^-, $H_2PO_4^-$, HSO_3^-, Hg_2^{2+}, SO_4^{2-}, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}, PO_4^{3-}	4.0–4.5
Sr^{2+}, Ba^{2+}, Ra^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, WO_4^{2-}	5.0
Li^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}	6
Mg^{2+}, Be^{2+}	8
H^+, Al^{3+}, Cr^{3+}, REE^{3+}	9
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	11

SOURCE: Garrels and Christ (1965).

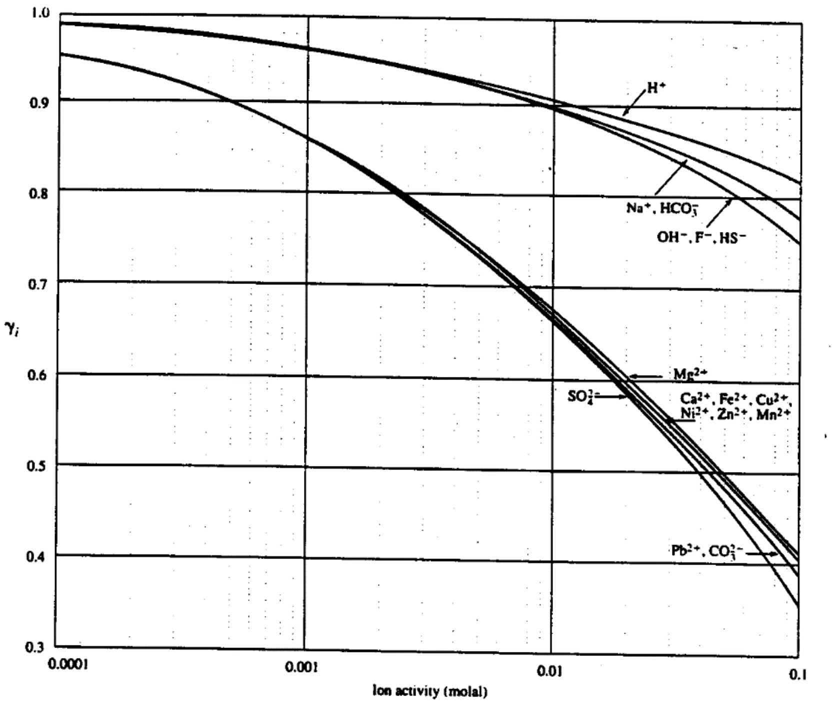


Figure 4.3 Some individual ion activity coefficients calculated using the extended Debye-Hückel equation.

The Debye-Hückel equation predicts that activity coefficients decrease continuously with ionic strength. The model is reasonably accurate to an ionic strength of 0.1 m.

Davies Equation

For higher ionic strengths, the Debye-Hückel equation was modified by adding a term which takes into account non-coulombic interactions and the increase of γ with I.

$$\log \gamma_i = -AZ^2_i \; (I^{1/2}/1+BaI^{1/2}) + bI$$

where b is a general constant (0.2-0.3) or a specific constant for each individual ion i. This expression is known as the ***Davies equation***. This equation yields reasonably accurate estimates of the individual ion activity coefficients for solutions of ionic strengths up to 0.5 m but is not suitable for seawater or solutions of higher ionic strength. … (PHREEQE, WATEQ, MINEQL, …)

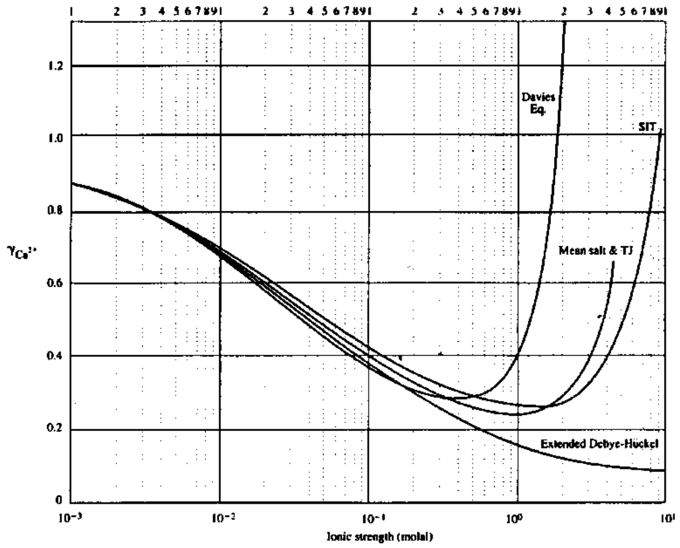
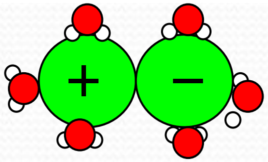


Figure 4.4 Comparison of the ion activity coefficient of Ca^{2+} as computed using different approaches. These include: (1) the Davies equation; (2) the mean salt approach using the MacInnes convention, and Truesdell-Jones equation (curve labeled Mean salt & TJ); (3) the specific ion interaction (SIT) equation; and (4) the extended Debye-Hückel equation.

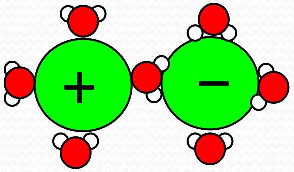
Associated electrolytes
(ion-pairs)

Ion-pairs result from purely electrostatic attraction between oppositely charged ions.

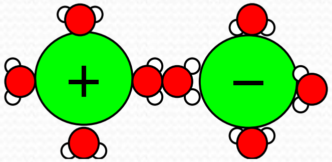
ex: $Cd^{2+} + Cl^{-} \leftarrow\rightarrow CdCl^{+}$ (positive ion pair)
$Hg^{2+} + 3Cl^{-} \leftarrow\rightarrow HgCl_3^{-}$ (negative ion pair)
$Mg^{2+} + SO_4^{2-} \leftarrow\rightarrow MgSO_4^{o}$ (neutral ion pair)



Contact ion-pair



Solvent-shared ion-pair

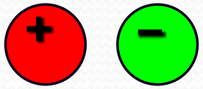


Solvent-separated ion-pair

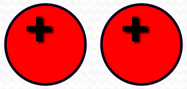
Specific Interaction or Pitzer Equation

$$\ln \gamma_M = \text{D.H.} + \sum \text{M-X} + \sum \text{M-N} + \sum \text{M-N-X}$$

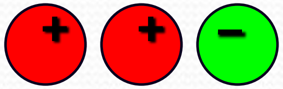
$$\sum \text{MX} = \sum \text{M-Cl} + \text{M-SO}_4 + \sum \text{M-HCO}_3$$



$$\sum \text{M-N} = \text{M-Na, M-Mg, M-Ca} \ldots$$



$$\sum \text{M-N-X} = \text{M-Na-Cl, M-Na-SO}_4\text{, } \ldots$$



Specific Interaction or Pitzer Equation

$$\begin{aligned}\ln \gamma_C = {} & z_C^2 f^\gamma + \sum_a m_a \left\{ 2B_{Ca} + \left(2 \sum_c m_c z_c \right) C_{Ca} \right\} \\ & + \sum_c m_c \left(2\Theta_{Cc} + \sum_a m_a \psi_{Cca} \right) + \sum_c \sum_a m_c m_a (z_C^2 B'_{ca} + |z_C| C_{ca}) \\ & + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \psi_{Caa'} + 2 \sum_n m_n \lambda_{Cn} + 3 \sum_i \sum_j m_i m_j \mu_{Cij}\end{aligned}$$

The first term on the right is a modified Debye-Hückel term which takes into account long range electrostatic interactions:

$$f^\gamma = -0.392\ [(I^{1/2}/1+1.2I^{1/2}) + (2/1.2)\ \ln\ (1 + 1.2I^{1/2})]$$

B terms describe the interactions of species of opposite sign and are functions of the ionic strength, much like the ion-pairing stability constants. Interactions between species of like charges (θ terms) are assumed independent of I. Ternary interaction terms (Ψ) in the Pitzer equation are not generally needed for I<3.5 mol/kg, they take into account interactions between two-like charged and a third unlike-charged species. They are also assumed to be independent of ionic strength.

*wwwbrr.cr.usgs.gov/projects/GWC_coupled/**phreeqc**/*
*www.ndsu.nodak.edu/**webphreeq**/*

Single ion activity coefficients

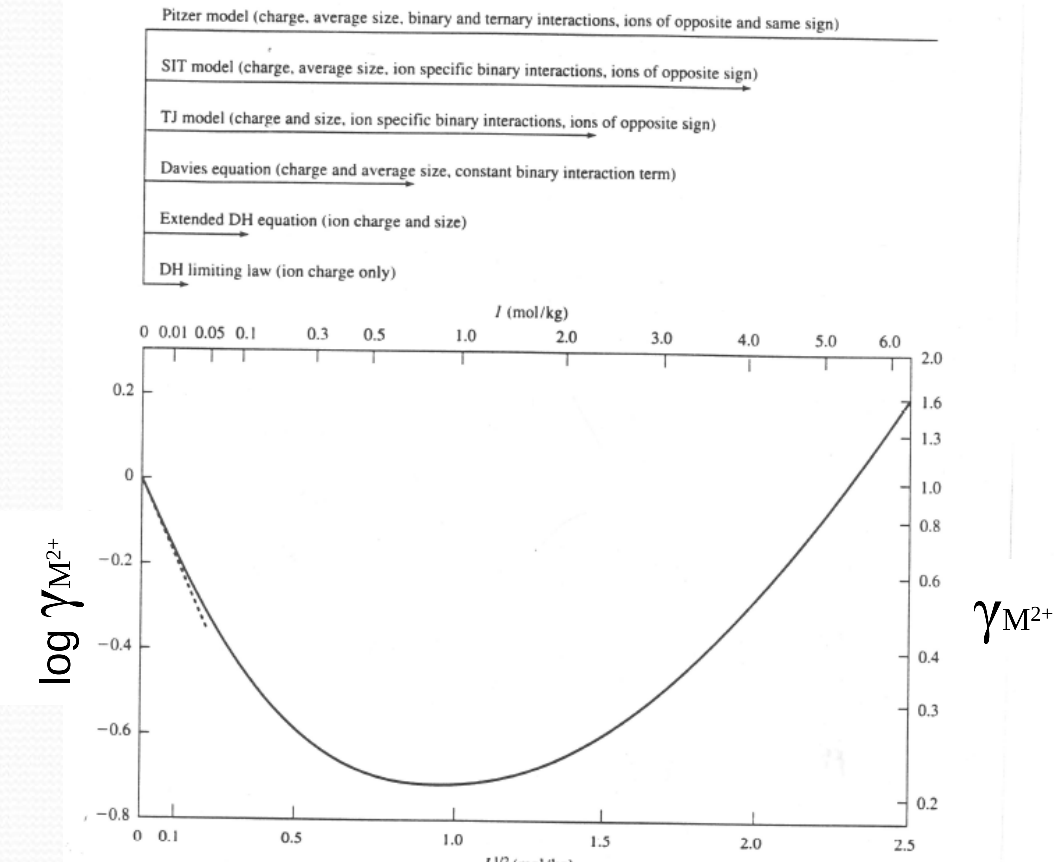


Figure 4.5 Schematic plot showing the general applicability of different activity coefficient models as a function of ionic strength for a divalent cation. The dashed tangent to the curve at its origin is a plot of the Debye-Hückel limiting law for the ion.

Activity coefficients of Neutral Species

Given that non-ideality for ions arises primarily as a result of electrostatic interactions with each other, one would expect that neutral species should behave differently since, with no charge, the electrostatic interactions should be negligible. In general, activity coefficients of uncharged species are near unity in dilute solutions and often rise above unity in concentrated solutions because more water is tied up in the hydration of ions and less water is available to interact with the uncharged species (i.e., salting-out). Irrespective of the behaviour of individual neutral solutes, most of the recent studies indicate that log γ_i is proportional to the ionic strength and can be represented by the Setchenow equation:

$$\log \gamma_i = K_i I$$

Activity coefficients of Neutral Species

(the Setchenow (salting-out) equation)

$$\log \gamma_i = K_i I$$

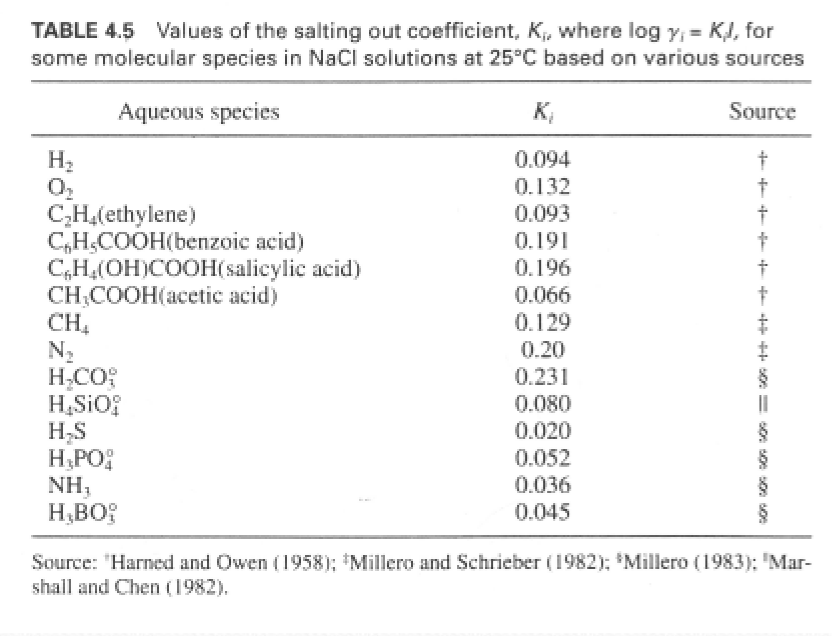


TABLE 4.5 Values of the salting out coefficient, K_i, where $\log \gamma_i = K_i I$, for some molecular species in NaCl solutions at 25°C based on various sources

Aqueous species	K_i	Source
H_2	0.094	†
O_2	0.132	†
C_2H_4(ethylene)	0.093	†
C_6H_5COOH(benzoic acid)	0.191	†
$C_6H_4(OH)COOH$(salicylic acid)	0.196	†
CH_3COOH(acetic acid)	0.066	†
CH_4	0.129	‡
N_2	0.20	‡
$H_2CO_3^\circ$	0.231	§
$H_4SiO_4^\circ$	0.080	‖
H_2S	0.020	§
$H_3PO_4^\circ$	0.052	§
NH_3	0.036	§
$H_3BO_3^\circ$	0.045	§

Source: [†]Harned and Owen (1958); [‡]Millero and Schrieber (1982); [§]Millero (1983); [‖]Marshall and Chen (1982).