Module 3 - WATER

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Earth

↓

Metals

↓

Water

↓

Energy

note : some pictures and graphs could not be reproduced here for copyright reasons - references to visual resources are given

Module 3 - WATER

Overall content of this module

- Water as a solvent
- Physical properties of water
- Molecular structure and intermolecular forces : relationship with physical properties
- Comparison of water with the ‘normal’ behaviour of other small molecules (NH_3, H_2S)
- Formation of aqueous solutions; ionisation; diffusion
- Molarity and other measures of concentration
- Heat capacity; calorimetry
- ***Special role of water as a solvent and especially in biology***

Water : General Chemistry Concepts

- solutions and solubility - explained at a molecular level
- using Lewis structures to understand the shapes of small molecules
- polarity of molecules - related to structure and bonding
- intermolecular forces - explaining physical (macro) properties based on interactions between molecules
- concentrations; molarity

Water - Relationship to Other Modules

- Water uses the following concepts from the Earth and Metals Modules

EARTH

- Introduction to bonding and Lewis dot structures
- ionic and covalent bonds; ionic and covalent lattices
- physical vs chemical change, including boiling (and presumably other changes of state)

METALS

- organisation of the periodic table
- the mole
- electronegativity

Water - Relationship to Other Modules

- Concepts from the Water Module used in the fourth Energy module
  - intermolecular forces (for hydrocarbons)
  - distillation (fractional distillation of petroleum)
  - endothermic and exothermic reactions

Relationship with the Old Syllabus

- Some of the content of the Water module was contained in the Core 8 Structure and Bonding section of the old syllabus
  - intermolecular forces and polarity
  - physical properties of molecules related to structure and bonding
  - solubility; solvent polarity
- Environmental chemistry becomes core - includes significant parts of the elective from the old syllabus
  - initially in the preliminary WATER module and later in the chemical monitoring section of the year 12 syllabus

General perspective on WATER as a context

- Successful for many core chemistry ideas such as solubility, concentration, polarity, molecular basis of physical properties,

- For some concepts, the very uniqueness of water tends to dominate : the behaviour of other ‘less unusual’ molecules may get too little attention
  - eg intermolecular forces

1. Water is distributed on earth as a solid, liquid and gas

- water as a solvent (recall solute, solvent, solution)

- distribution of water in the biosphere, lithosphere, hydrosphere, atmosphere (links to pt. 1 of EARTH module)

- water on earth
  - in living cells
  - a solvent and raw material in metabolism
  - a habitat
  - an agent of weathering
  - a natural resource

Why is water important / interesting ?

- Life *developed in* and *relies on* water

- This essential role played by water is a consequence of its unique properties

  - Water is the only naturally occurring inorganic liquid on earth
  - Water is the most abundant molecule on earth
  - Water is the only compound that occurs naturally on earth in its solid, liquid and vapour forms - sometimes simultaneously
  - Solid water is less dense than its liquid
  - Water has unique properties as a solvent
  - Water has an unusually high heat capacity (for a small molecule)

Distribution of Water on Earth

- Biosphere (living organisms on earth)
  - water is the solvent within living cells
  - water is involved in photosynthesis and respiration
- Lithosphere (the earth's outer mantle and crust)
  - the part of the earths crust accessible to water
  - water in soil and in minerals
- Hydrosphere (the earth's water)
  - 70% of the planet is covered by oceans (97% of the water)
  - Approx 2×10^{11} L of water for every person on earth
  - The majority of the world's freshwater is locked in the Antarctic ice cap
  - Lakes and rivers 0.01 %; groundwater
- Atmosphere (the gases above the earth's surface)
  - water vapour

Water is interchanged between all of the above spheres

Water in the atmosphere - example

- Water in the atmosphere can be present as gas (vapour), liquid (droplets) and solid (hail, snow)

relevant photos available from

Student Resources CD

Chemistry : Structure and Dynamics

JS Spencer, GM Bodner, LH Rickard

J. Wiley, 1999

other textbook resources - including CDs - are listed later

Water in Biology

- Living tissue is composed mostly of water
- Water is the solvent for biochemical reactions
- Water is also directly involved in the detailed processes of molecular biology being essential in determining the structure of biomolecules such as proteins
- Water is both a reactant and product in different biochemical reactions

Photosynthesis : $6CO_2 + 6H_2O \xrightarrow{\text{sunlight}} C_6H_{12}O_6 + 6O_2$

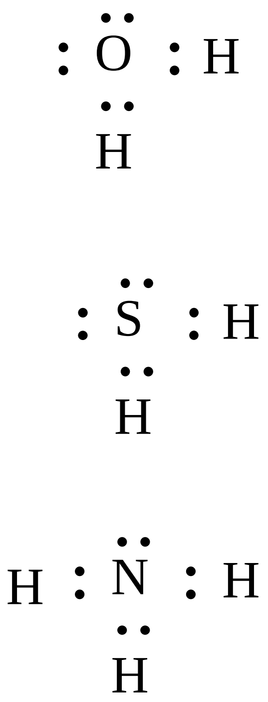
Respiration : $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

2. The wide distribution and importance of water ~ molecular structure

- Lewis electron dot structures of H_2O NH_3 H_2S
- Comparison of molecular structures, shapes and physical properties (melting and boiling points)
- Water as a polar molecule
- Dipole-dipole forces and hydrogen bonding
- Physical properties of water in terms of intermolecular forces

- The activities section implies extension of comparisons to 'other similar sized molecules' - to what extent are other types of intermolecular forces to be included here ? eg if comparing methane and water ... ?

Lewis Structures



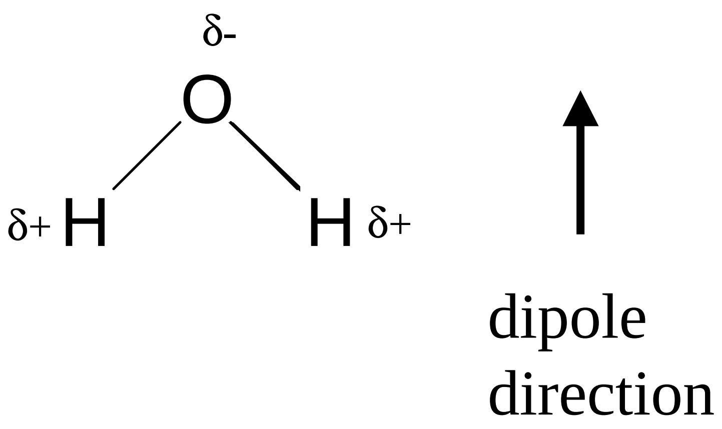
shape of water is required, but not the ability to work this out from the Lewis diagram

shapes of small molecules - lone pairs and bonding electron pairs each occupy a region of space

3-d models can be used to illustrate this and hence explain the bent shape of water - if desired

Water as a Polar Molecule

- Electronegativity - recall definition and periodic table relationships from metals module
  - Oxygen EN = **3.5**
  - Hydrogen EN = **2.1**



- Each -OH **bond** is polar
- The H_2O **molecule** is polar - due to its shape
- The H_2O molecule acts as a dipole (has a +ve and a -ve end)

*Note : the idea of a **dipole** is required in order to discuss dipole-dipole and later ion-dipole interactions*

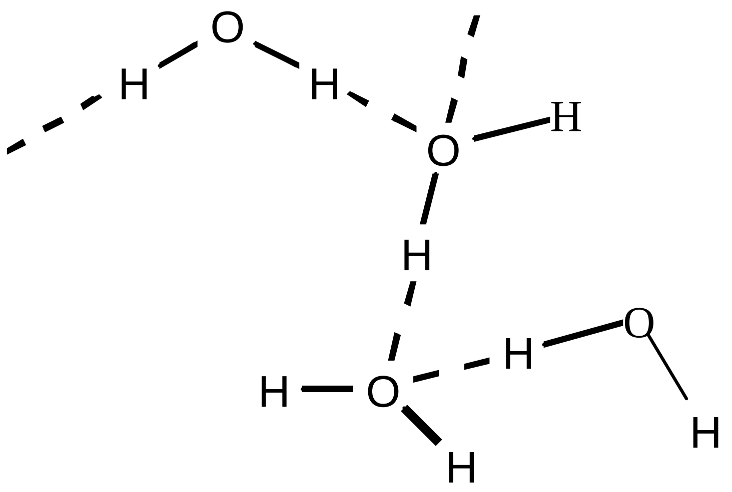
Intermolecular Forces

- Dipole-dipole interactions

  electrostatic attractions between + and
  - ends of polar molecules

- Hydrogen bonding
  - O-H bonds are very polar and hydrogen only has the shared pair of electrons - electron deficient
  - extra strong dipole-dipole interactions --> hydrogen bonding
  - Hydrogen bonding requires H attached to a very electronegative element

  F (4.0) O (3.5) N(3.0)



Hydrogen Bonding in Water

- Each O has 2 lone pairs of electrons - 2 H-bonds to oxygen can be formed
- Hydrogen-bonding network formed in liquid water - responsible for the special properties of water
- Ice forms a crystalline lattice, held together by H-bonds
- compare **H_2O** and **NH_3**
  - electronegativity difference is less for N-H vs O-H and
  - only one lone pair on N - overall effect of H-bonding is less

Boiling Point of water - comparisons

- Differences in boiling point between
  H_2O and NH_3 *or*
  H_2O and H_2S
  can be rationalised using hydrogen bonding arguments only

- but this is a simplification and once the comparison is extended to (say) CH_4 or H_2Se, then dispersion forces are needed too.

- the separation of intermolecular forces between modules (water and energy) may also lead to confusion over where different types of intermolecular forces are present. So, for example, there are dispersion forces between water molecules in addition to hydrogen bonding.

Physical Properties of Water

- A molecular-level description of the following physical properties **of water**

surface tension

adhesion

cohesion

viscosity

boiling and melting

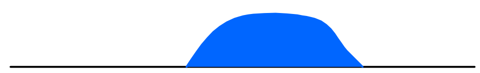
hardness and brittleness

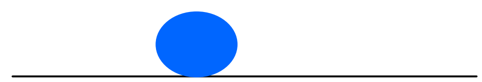
Surface Tension

- **Cohesion** - forces between like molecules in the liquid ie intermolecular forces. For water these are dominated by hydrogen bonding.
- Bulk liquid has uniform cohesion in all directions
- Surface molecules experience a cohesive force tending to pull them into the bulk and to minimise surface area --> SURFACE TENSION

Adhesion

- Liquids interact with solid surfaces. If the adhesive forces are strong, the liquid ‘wets’ the solid surface.
- the shapes of droplets reflect the balance between adhesion and surface tension
- Water forms a film on glass, with which it has strong adhesive forces (Si-OH surface groups on silicate glass)
- Water ‘beads’ or forms droplets of low surface area on hydrophobic (or non-polar) surfaces - eg raindrops on waxed car surface
- Adhesion and surface tension effects are also seen in meniscus shapes and capillary rise - see activities/experiments section





Viscosity

- Viscosity is the resistance to flow. High viscosity is associated with strong intermolecular forces - harder for molecules to 'slide past each other'

- water > octane
- paraffin oil > octane > pentane
- (but ethanol > water ...!)
  - The viscosity of water is fairly high - but not as high as might be expected based on the intermolecular forces argument

- Viscosity decreases with increasing temperature (for small molecules)

Hardness and Brittleness of Ice

- Hardness depends on the strength of the bonds holding the lattice together.
  - Water is not as hard as metals (see module 2) or covalent crystals : hydrogen bonds are about 1/10 the strength of normal covalent bonds.
  - hardness depends on the strength of the weakest links in the lattice
  - ice can be scratched by metals or glass ...
  - but ice is harder than typical soft materials like wax

- Brittleness is the tendency to fracture (opposite of toughness)
  - brittle materials are not very resistant to mechanical shock
  - ice is fairly brittle - it fractures - cracks in ice - chunks break off icebergs etc
  - once again, brittleness is a complex property - and especially for ice (ice has some elastic/plastic behaviour too !)

physical properties of ice are complex and not fully understood ...

3. Water as a solvent in biological systems

- explain at a molecular level
  - the interaction of water with ionic and covalent substances (soluble and insoluble)
  - the relationship between solubility and bonding type
  - the relationship between solubility and the polar nature of water
  - ionisation in water leading to the production of acidic and basic solutions
  - diffusion and osmosis (esp. in living systems)

Hydration of Ions ~ important in solubility of ionic compounds

- Cations interact with the negative ‘end’ of the water molecule : $O^{\delta-}$
- Anions interact with the positive ‘end’ : $H^{\delta+}$
- These strong ion-dipole interactions (hydration / solvation) are responsible for the high solubility of many ionic compounds in water.
- Q. Why are some ionic compounds NOT very soluble in water ?

Solvent-solute interactions - covalent solutes

Sucrose - polar, hydrogen bonds to water (related examples: alcohols)

I_2 O_2 - non-polar molecules - weak intermolecular interactions with water (dipole-induced dipole ...included ??)

HCl - polar molecule - fully ionised in water - very soluble

(note : HCl is molecular, but ionises in water, so is *not* in the same category as I_2 and O_2)

Si, SiO_2 - covalent networks - insoluble

Polymers : cellulose, polyethene (or poly(ethene) *not (poly)ethene !)*

Plenty of polymers ***are*** *soluble in water : if they contain polar , H-bonding or ionisable groups and are not cross-linked; size is not the only determining issue (though generally larger polymeric molecules have a lower driving force to enter solution than smaller ones).*

Cellulose .... more detailed background info.

- To explain why cellulose is water-insoluble requires more advanced concepts than those included in this module ...
- The stereochemistry of the glucose-glucose linkage is such that cellulose forms ‘flat’ chains which can easily H-bond between chains - a type of cross-linking
- Starch - a glucose polymer with the opposite linkage stereochemistry is quite water soluble. The chains form helices with intramolecular H-bonding. Inter-chain H-bonding is much reduced.

- **Simple argument : cellulose is insoluble becasue there are ‘many hydrogen-bonds’ holding the chains together**

- Cellulose is indigestible (by humans); starch is digestible
- *Cellulose is the most abundant organic compound on earth*

Solubility in Water ~ Bonding type ~ Polarity of water

- This section links in closely with part 5, which looks more explicitly at the energy changes associated with forming a solution
- Bonding type
  - solute-solute interactions are broken when the substance dissolves
- Polarity of Water
  - solute-solvent interactions form when the substance dissolves
  - solvent-solvent interactions (ie H-bonds in water) are partially disrupted when a solution forms
- Solubility is determined by the result of all of these factors (+ entropy....)
  - be careful of simple correlations between bond-type and solubility

Ionisation of Molecules in Water

Examples

- HCl (see earlier)
- CH_3COOH
- NH_3
- CO_2

- At this stage, distinguish between strong and weak acids or bases ? corresponding to complete or incomplete ionisation in water

Diffusion

- Diffusion
  - Translational movement of molecules in liquids (and gases) is called diffusion.
  - Diffusion tends to randomise the distribution of molecules in a mixture (eg add ink to water; put soluble crystals in the bottom of a beaker of water).

  or

  - Diffusion is the mixing of molecules of one substance with those of another by random motion of the molecules. For example, this results in net diffusion of solute from concentrated to dilute regions of solution and of solvent in the other direction.

- *Note : in real water samples, convection currents are responsible for much of the mixing*

Osmosis

- Osmosis - due to selective diffusion of the solvent
  - Osmosis is caused by diffusion of water through cell walls (through semi-permeable membranes generally). Solvent can diffuse through but not solute.
  - Net diffusion *of water* from the dilute to the concentrated side of the cell wall results
  - Cells swell if placed in water or dilute solutions; collapse if places in very concentrated solutions.
  - Osmosis is mainly responsible for the transport of water up through plants (transpiration from the leaves maintains the concentration gradient)

4. Concentrations of Salts in Water

- Recall qualitative descriptions of reactions and products in precipitation reactions
- Use solubility data to identify combinations of solutions which produce precipitates
- Model for movement of ions when solution and precipitation occur; dynamic nature of solubility equilibrium in a saturated solution
- example of a reversible reaction (equilibrium) *not* involving solubility
- molarity $c = n/V$
- why different measures of conc. are important (what others are required ? ... ‘volume-to-volume’ and ‘mass-to-volume’ ....)

- *Comment : the activities section is a bit unclear in defining exactly what types of calculations involving concs. and precipitation are required of students*

Use solubility data to identify combinations of solutions which produce precipitates

- Solubility data
  - presumably this refers to solubility rules; does it include solubility information (eg in g L^{-1}) ?
- Identify combinations of solutions producing precipitates
  - this is dealt with in detail in the ‘experiments’ section
- Includes
  - gather and process information to calculate mass and concentration relationships in precipitation reactions as they are encountered.

Dynamic nature of solubility equilibrium in a saturated solution

- Model for movement of ions when solution and precipitation occur; dynamic nature of solubility equilibrium in a saturated solution
  - ions at the surface of the solid interact with the water molecules (ion-dipole interactions)
  - ions are ‘pulled’ off into solution

  - idea of a saturated solution
  - solid is in equilibrium with solution
  - ions move on and off the surface of the solid - at equilibrium the concentrations of ions in solution remain constant

Different measures of concentration

Molarity

- For chemical calculations

eg involving working out yields of reactions, titrations etc

Mass/volume g / L   mg / L

- Where the bulk quantity is required

eg extracting gold from ore : want to know how many g / L

- when measuring pollutants

often at low concentrations so use **ppm = mg / L**

be careful to specify the substance so ppm (of what) or mg (of what) per litre

so ppm sodium   *ppm sodium chloride*

Volume / Volume % by volume

- mixtures of liquids

Pollution and Monitoring of Heavy Metals

- Recall pollution as contamination by unwanted substances

- Why monitor of mercury and other heavy metals in waterways (Pb, Cd etc)

  - toxicity issue (toxic to people, fish, plants ...?)
  - low levels are concentrated up the food chain
  - environmental pollution examples - Minimata (Hg)
  - effect of lead on children (behaviour, IQ)

- Sources of information

  - NSW State of the Environment 1997; Chemistry in the Marketplace; Environment Australia website, ABC ‘the lab’ website. (details given at end)

5. Water has a higher heat capacity than many other liquids

- Note : distinguish here between between heat capacity and specific heat
- It seems that comparisons of data and calculations require **specific heat**, while the more general term **heat capacity** is used generally throughout this section of the water module

- Specific heat
- Changes in temperature - calorimetry
- Exothermic and endothermic dissolutions
- Significance of water's high heat capacity / specific heat

Heat Capacity and Specific Heat

- Definition : Heat Capacity

  Heat capacity is a measure of the temperature rise when a substance is heated

  (molar heat capacity - heat required to raise the temperature of 1 mol of a substance by 1 ^{0}C **or 1 K**)

- Definition : Specific Heat

Specific heat is the heat required to raise the temperature of 1 g of substance by 1 ^{0}C **(or 1 K - see note on units, next slide)**

$$\Delta H = mC\Delta T$$

m = mass/g, C = specific heat/J K^{-1} g^{-1}, $\Delta T = T_{final} - T_{initial}$ /^{o}C

strictly only applies at constant pressure (eg open container)

Heat Capacity of Water

- **Specific Heat of Water (liquid)**

water C = 4.184 J K^{-1} g^{-1}

- **Compare with other liquids**

ethanol C = 2.42 J K^{-1} g^{-1}

CCl_4 C = 0.86 J K^{-1} g^{-1}

Quite a few textbooks use J ($^{o}C^{-}$)$^{-1}$ g^{-1} as the units for specific heat, although the SI units are J K^{-1} g^{-1}

(values are numerically the same)

- **Why is the heat capacity of water higher than expected for a small molecule ?**

Hydrogen bonding network in water can store more energy than a liquid with less extensive intermolecular forces; more energy is required to get the molecules to rotate in the liquid; as the liquid is heated it expands (at least above 4 ^{0}C) and energy is required to ‘pull apart’ the hydrogen bonds

Calorimetry

- To find ΔH for a reaction, set up an experiment to measure ΔT in an insulated system - this is the basis of **calorimetry**
- Assume we choose examples consisting of a reaction in aqueous solution, then the temperature change of the liquid phase is the experimental measurement
- Then, if no heat is lost to the surroundings, the total enthalpy change is zero so

$$\Delta H_{reaction} + \Delta H_{cal} + \Delta H_{soln} = 0$$

or

$$\Delta H_{reaction} = - (\Delta H_{cal} + \Delta H_{soln})$$

Exothermic and Endothermic dissolutions

- Endothermic $NH_4Cl(s)$ $KCl(s)$ $NH_4NO_3(s)$
- Exothermic $NaOH(s)$ $CaCl_2(s)$ $H_2SO_4(l)$ $HCl(g)$
- What energy changes are involved when a compound dissolves in water ?
  - solute-solute break bonds or intermolecular forces (costs energy)
  - solvent-solvent disrupt the intermolecular forces (H-bonding) in pure water

    offset against
  - solute-solvent interactions of dissolved ions or molecules with water (solvation or hydration)

If solute-solvent interactions are stronger then **$\Delta H < 0$ exothermic**

If solute-solvent interactions are weaker then **$\Delta H > 0$ endothermic**

Heat Capacity of Water - Implications in Biology

The effect on climate; aquatic organisms

- lakes and oceans are slow to freeze - must lose a lot of energy for the temperature to fall
- oceans (and other large bodies of water) moderate the climate by acting as a thermal reservoir
  - extremes of temperature are less on the coast than inland (cf Sydney weather forecast on any typical day)
- ocean currents (cold and warm) strongly influence climate in various parts of the world
- temperature variations in the water itself are not so extreme - aquatic life survives climate fluctuations
- heat capacity (combined with density) means that waterways generally don't freeze solid - aquatic life remains viable under the ice

- eg **sea-ice** - information on sea ice and its effect on climate www.antcrc.utas.edu.au/aspect/seaice.html

Thermal Pollution

- Unwanted change in temperature (usually of waterways) due to human activity

- eg release of warm water from a power plant into a river or lake
  - rapid change in temperature can have a detrimental effect on aquatic organisms
  - solubility of oxygen decreases with increasing temperature - if below 5 ppm O_2, then fish survival is threatened

List of Resources for Water Module

- NSW State of the Environment Report 1997
  - available as a book and on-line (www.epa.nsw.gov.au); book version highly recommended - online difficult to navigate if you don't know what is available
- Chemistry in the Marketplace, Ben Selinger, Harcourt Brace, 4th Ed. 1994
  - lots of chemistry-in-context ideas and activities; Australian examples
- Environment Australia website www.environment.gov.au
  - links to education resources; info. on streamwatch.
- P. Atkins and L. Jones : 2 textbooks. (i) Chemistry : Molecules, Matter and Change (ii) Chemical Principles (more advanced). Freeman (McMillan).
  - good CD-ROMS. both books have good graphics and case studies to draw on
  - Most new first year university level texts now come with fairly sophisticated CD-ROMs, including molecular models, simulations, video clips etc.
- ABC website : abc.net.au/science/
  - links to environmental info.; teachers resources etc.

- *Note : resources quoted for other sections are relevant in this module too (and vice versa)*