Discipline Course – I
Semester - II
Paper: Fundamentals of Biochemistry
Lesson: Water

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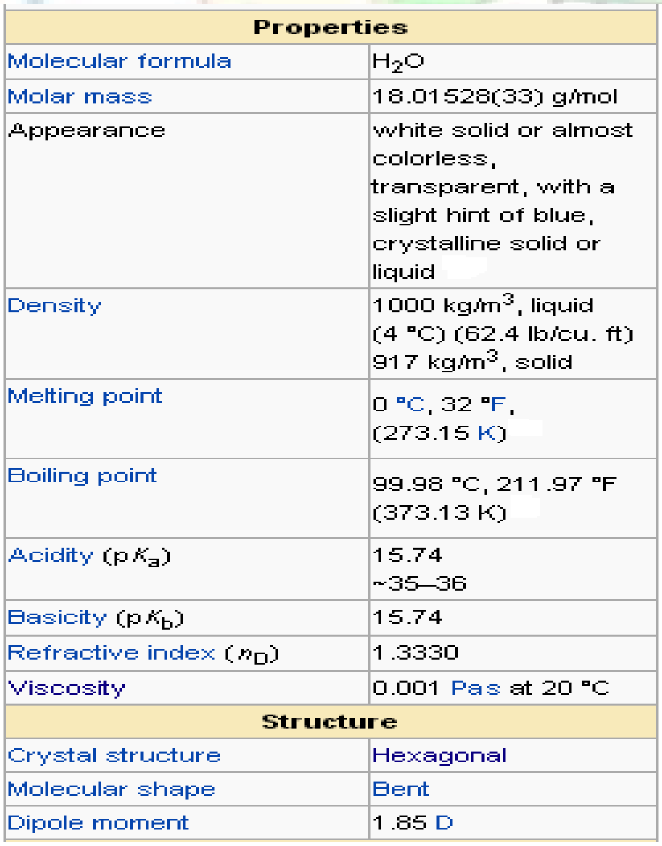
Table of Contents

Chapter: Water

Introduction

Water is the most essential element of human life. Humans cannot survive without water. It constitutes about 70% or more of the weight of most organisms. It exists in nature as solid, liquid and gaseous states. It is a tasteless and odorless liquid. Water is a known as **universal solvent** as it is able to dissolve many substances in it. The attractive forces between water molecules are important for the structure and function of all biomolecules universally present in cells. Water has high melting point, boiling point, heat of vaporization and surface tension. These properties are anomalously high for a substance of this molecular weight. These physical properties suggest that there is high intermolecular force of attraction between the water molecules leading to high internal cohesion of this substance. It has high dielectric constant. The solid form of water i.e. ice floats on water as its density is lower than the density of water which is opposite to the property of any solid form of a substances which is of higher density than its liquid form. The explanation of these unique properties lies in the structure of water.



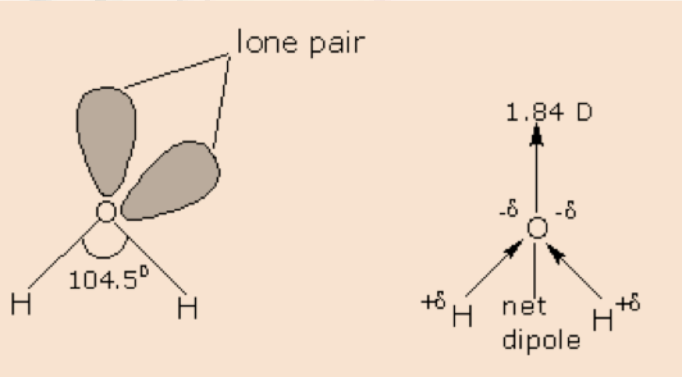
Properties	
Molecular formula	H_2O
Molar mass	18.01528(33) g/mol
Appearance	white solid or almost colorless, transparent, with a slight hint of blue, crystalline solid or liquid
Density	1000 kg/m^3, liquid (4 °C) (62.4 lb/cu. ft) 917 kg/m^3, solid
Melting point	0 °C, 32 °F, (273.15 K)
Boiling point	99.98 °C, 211.97 °F (373.13 K)
Acidity (pK_a)	15.74 ~35–36
Basicity (pK_b)	15.74
Refractive index (n_D)	1.3330
Viscosity	0.001 Pas at 20 °C
Structure	
Crystal structure	Hexagonal
Molecular shape	Bent
Dipole moment	1.85 D

Table: Properties of water

Source: https://www.boundless.com/image/the-properties-of-water/ (CC)

Chemical Structure of Water

The chemical formula of water is H_2O, in which each of the two hydrogen nucleus is bound to central oxygen atom by a covalent chemical bond. Only two out of six outer shell electrons of central oxygen atom is bound to the each hydrogen atoms. These four electrons (lone pairs) are arranged into two non-bonding pairs and are far apart from each other to minimize repulsion between the clouds of negative charge. This would lead to a nearly tetrahedron arrangement comprising of H-O-H bond angle of 104° instead of 109.5° which is present in molecules such as methane (CH_4) arranged in a perfect tetrahedron geometry. These outer electron orbital of oxygen atom dictates the shape of the molecule which is similar to sp^3 bonding orbital of carbon.



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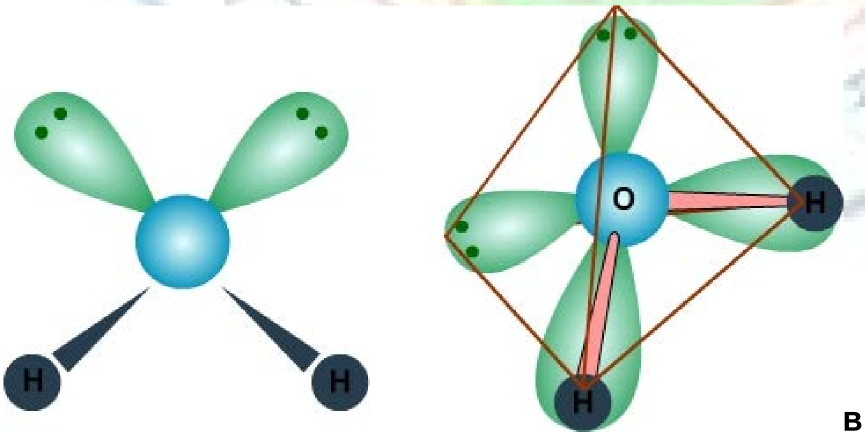

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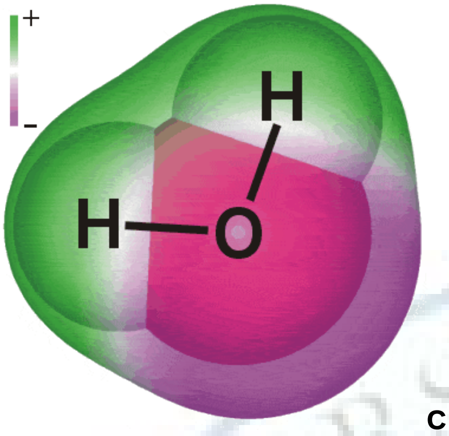


Figure: A. Polar structure of water molecule showing O as partially negative and H as partially positive creating a dipole. **B-C.** Three dimensional structure of water showing tetrahedron shape comprising of two nonbonding orbitals of oxygen and two orbitals of hydrogen .

Source: **A,B.** Author; **C.** http://www1.lsbu.ac.uk/water/images/molecul2.gif

The oxygen atom is more electronegative than hydrogen nucleus resulting in unequal electron sharing there by creating two dipoles in the water molecule one along each of the H-O bonds. In Greek language polarity is represented by letter sigma superscripted with a negative and a positive sign to indicate a partial charge. The two hydrogen atoms have a localized partial positive charges ($\delta+$) and the oxygen atom has a partial negative charge ($\delta-$). Because of electrostatic attraction between oxygen atom of one water molecule and the hydrogen of another, a **hydrogen bond** is formed between two neighboring water molecules. Electrical attraction between water molecules due to this **dipole** pulls individual molecules closer together making it more difficult to separate the molecules and therefore raising the boiling point. This electrical attraction is known as the hydrogen bonding. Because of this bond, water has high **boiling point** as it takes more heat energy to overcome these bonds and turn the liquid of H_2O into a gas.

Water can be viewed as hydrides of oxygen. Other hyrides of closely related elements are HF (hydrogen fluoride), hydrogen sulfide (H_2S) and ammonia (NH_3). They all have lower boiling point than water. The low boiling point of these substances arose from difference in their electronegativities and molecular geometry. Though, Fluorine (4.0) has higher electronegativity than Oxygen (3.5) but HF has lower boiling point than H_2O. HF and NH_3 form limited intermolecular hydrogen bonding forms as compared to extensive one as observed between water molecules. Similarly though oxygen and sulfur are in the same column of periodic table, but there is little difference in the electronegativity of H and S and so S-H bond is insufficiently nonpolar. Thus many peculiar properties of water results from electronegative difference in its structure and geometry of its hydrogen bonded interactions.

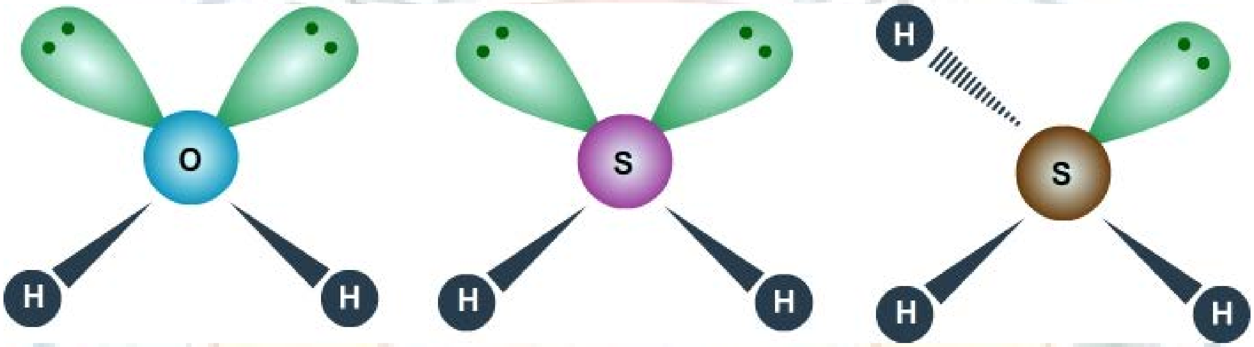


Figure: Three dimensional structure represented by Sp^3 hybridization of hydrides of atoms such as N and F are similar to O.

Source:Author

Did you know
Water's composition (two parts hydrogen to one part oxygen) was discovered by the London scientist Henry Cavendish (1731-1810) in about 1781. He reported his findings in terms of phlogiston (later the gas he made was proven to be hydrogen) and dephlogisticated air (later this was proven to be oxygen). Cavendish died (1810) in his Laboratory just 30 minutes' walk from the present site of London South Bank University.

Source: http://www1.lsbu.ac.uk/water/molecule.html (CC)

Hydrogen bond

Hydrogen bonds are weaker bonds than the covalent O-H bond and C-C bond as observed from it's the bond energy of 10 kJ/mol compared to bond energy of covalent O-H bond of 467kJ/mol. The tetrahedron shape of water molecule allows one water molecule to form hydrogen bonds with four neighboring water molecules.

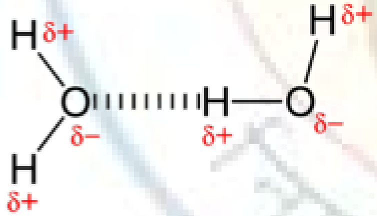


Figure: Intermolecular Hydrogen bond

Source: Author

At any given time, most of molecules in liquid water are hydrogen bonded. When water is heated, water molecules are disorganized and are in continuous motion so that when one hydrogen bond breaks it is replaced by a new hydrogen bond within 0.1ps. Because of this continuous motion of molecules/solute particles in water and changing their positions in the liquid crystal like structure,they are also referred to as **flickering crystal**. The lifetime of each hydrogen bond is about 1-20 picosecond. On the other hand, in ice each water molecule is hydrogen bonded to four other water molecules yielding a stable crystal lattice structure which attributes to high **melting point of water** as high thermal energy is required to destabilize this lattice.

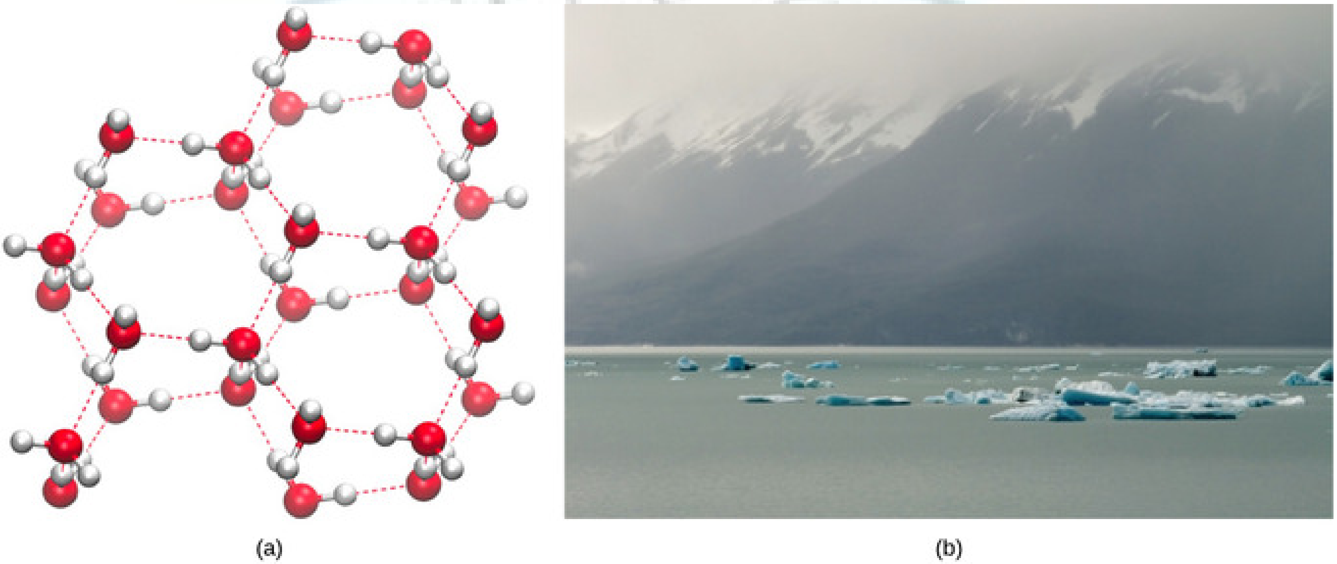
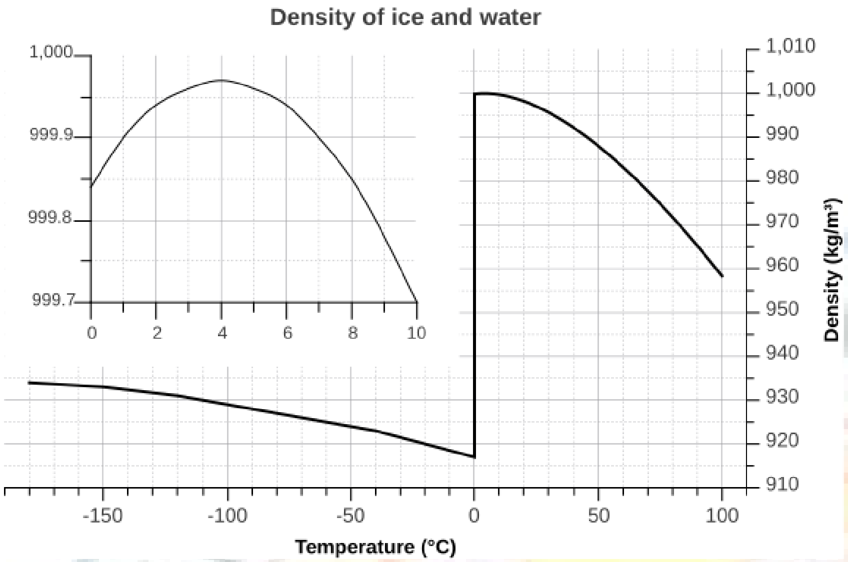


Figure: Hydrogen bonding makes ice less dense than liquid water. (a) The lattice structure of ice makes it less dense than the freely flowing molecules of liquid water, enabling it to (b) float on water.

Source: https://www.boundless.com/biology/the-chemical-foundation-of-life/water/water-s-states-gas-liquid-and-solid/ (CC)

For further details visit: http://www1.lsbu.ac.uk/water/hbond.html

Did you know water in its liquid form is denser than its solid form (Ice)
Molecules in solid form are generally denser than their liquid form. In solid state the molecules are close to each other and arrange themselves in a stable lattice structure. But when molecules in crystalline solid are heated to convert them back to their liquid state, there is increased motion between the molecules, the increased temperature force these molecules to move far away from each other, thereby decreasing density.



But when **ice** (the solid state of water) is melted, its density increases, reaching a maximum at 4°C. However, if the temperature is further increased, increased motion of water molecules leads to reduced density. Thus water has a maximum density at 4°C which explains **why ice floats on water**.

Source:http://upload.wikimedia.org/wikipedia/commons/thumb/8/8a/Density_of_ice_and_water_%28en%29.svg/573px-Density_of_ice_and_water_%28en%29.svg.png

Polar and ionic compounds dissolve in water

Ionic compounds are formed due to electrostatic interactions between oppositely charged ions. Water is a good solvent for many ionic compounds because of its polarity. For instance common salt such as sodium chloride is readily soluble in water owing to its dissociation in two charged species, Na^+ and Cl^- leading to disruption of the lattice structure due to the weakening of electrostatic interactions between the two ions. As the salt dissolves, the ions leaving the crystal lattice acquire far greater freedom of motion there by increasing the entropy (randomness) of the system.

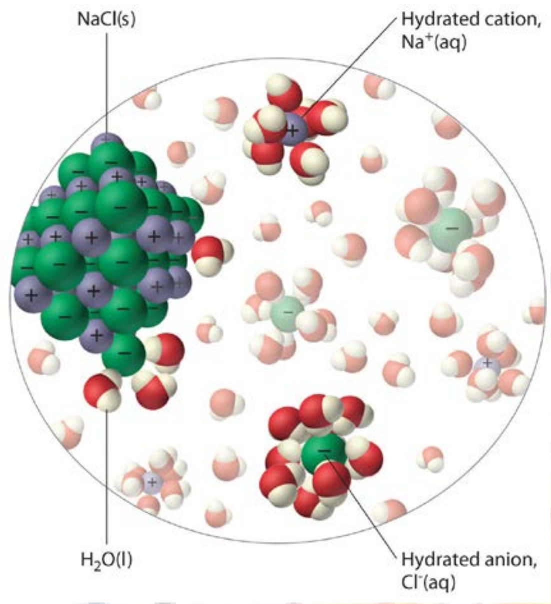


Figure: Water molecules dissolves sodium chloride by forming hydration shells around Na^+ and Cl^- ions separating the ions.

Source: http://2012books.lardbucket.org/books/general-chemistry-principles-patterns-and-applications-v1.0m/section_08/c8f8e3a5c9fe175b453731a869ea429c.jpg (CC)

The interaction between water molecules interacting with hydrating ions is much greater than the tendency of oppositely charged ions to interact with one another. Water can surround ions in dipole interactions. This diminishes their attraction for each other. This is a measure of its dielectric constant, D. Indeed ionization in solution depends on the dielectric constant of the solvent otherwise the strongly attracted positive and negative ions would unite to form neutral molecules. The strength of Dielectric constant is related to the force, F experienced between two ions of opposite charge separated by a distance r , as given in the relationship,

$F=e_1\, e_2/Dr^2$

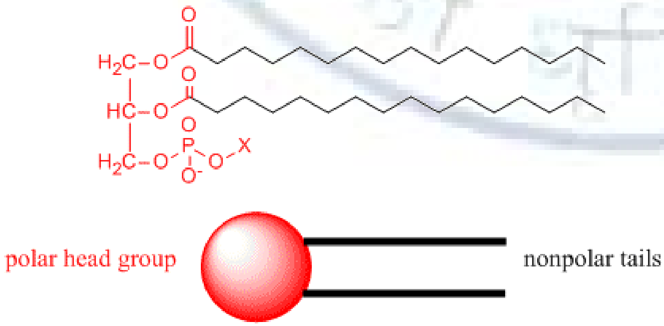
Thus the Dielectric constant of water is more than twice than of methanol and 40 times that of hexane.

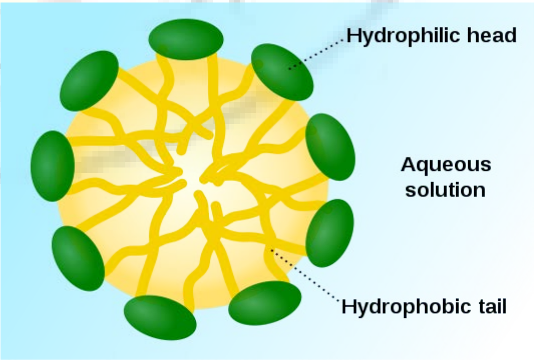
Many uncharged substances like alcohol, amines, amides, ketones, etc., dissolve readily in water as they bear polar functional groups which form favorable interactions with water. Polar and ionic compounds are called hydrophilic (water loving) as they can form hydrogen bonds with water molecules. Sugars like glucose which have many OH groups interact well with water by breaking hydrogen-hydrogen bonds and forming stable glucose-hydrogen bonds with the result glucose is very soluble in water. These polar interactions between solvent and solute are stronger than the intermolecular attractions between solute molecules caused by Van der Waals forces and weaker hydrogen bonding. Thus solute molecules dissolve readily in water.

Usually, nonpolar compounds are not water soluble since they do not contain any polar functional group. They are called hydrophobic (water fearing) as they escape any contact with water. Biologically important gases such as O_2, N_2 and CO_2 are poorly soluble in water because of their nonpolar nature followed by a decrease in entropy when they enter an aqueous solution.

Hydrocarbons are examples of such kinds of compounds. When a non polar compound is dissolved in water, some hydrogen-hydrogen bonds are broken to create a cavity for solute molecules. Each solute molecule is entrapped in a cage ice like structure known as "**hydrate**" formed by highly ordered water molecules held together by hydrogen bonds.

There are many compounds known as "Amphiphiles" or "Amphipathic" which have both simultaneously hydrophilic and hydrophobic characteristics in them such that polar head interact with water where as non polar tail escapes any contact with water. Fatty acids and phospholipids belong to this group of molecules. The long alkyl chains of fatty acid forms surface film on water with polar acid group of the molecule in water phase whereas the hydrophobic alkyl chain protrudes out in the air above the liquid surface. Upon entering wate, amphiphilic compounds form "**micelles**". These are spherical lipid molecules in which non polar chains cluster together by **hydrophobic interactions** in the interior and form the core of the micelles whereas polar hydrophilic head groups stay on the surface interacting with water.





A **B**

Figure: A) Lipid molecule is an amphipathic molecule having both polar head group and a nonpolar hydrophobic tails. B) Lipid molecules form another spherical lipid structures known as micelles when they are dissolved in water.

Source: http://employees.csbsju.edu/hjakubowski/classes/ch111/olsg-ch111/solutions/doublechainamp.gif,http://upload.wikimedia.org/wikipedia/commons/thumb/4/4d/Micelle_scheme-en.svg/532px-Micelle_scheme-en.svg.png

Many biomolecules such as proteins, pigments, certain vitamins and sterols are also amphiphiles. The structure of biological membranes formed from these biomolecules such as lipids and proteins interact with each other by hydrophobic interactions. The three dimensional structure of many proteins are also stabilized by hydrophobic interactions between the non polar amino acids.

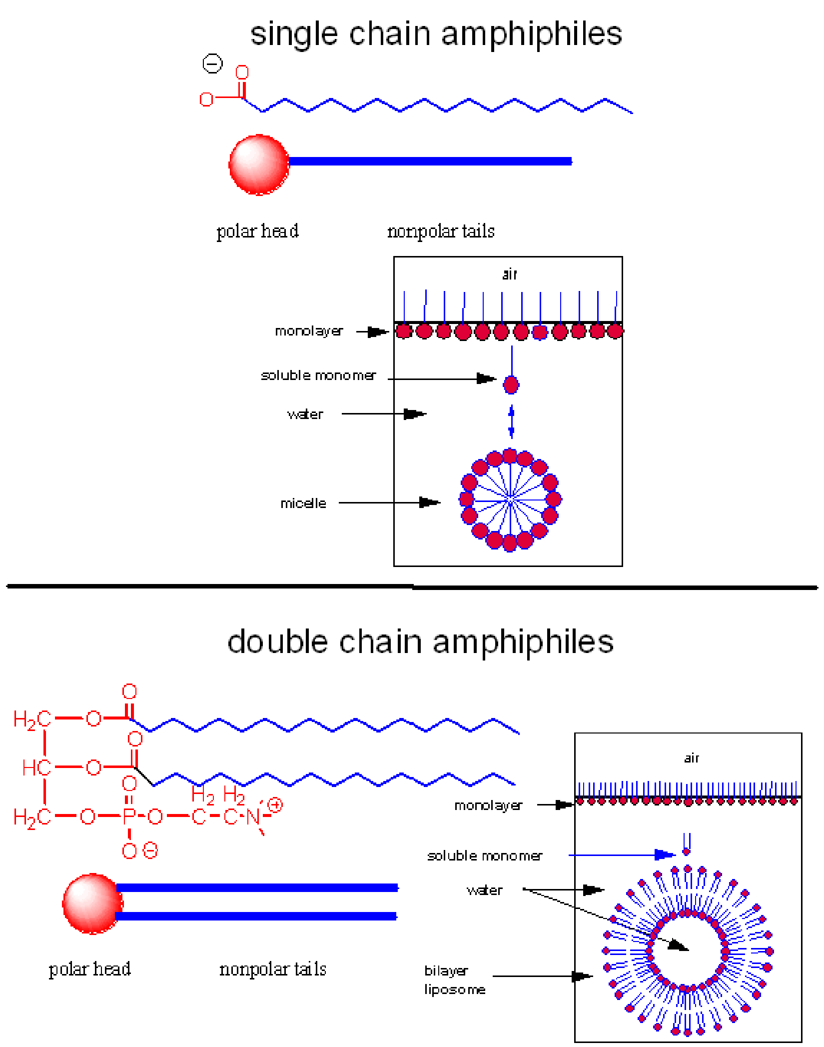


Figure: Single chain amphiphiles such as fatty acids form both monolayer on the surface of water and micelles inside the aqueous solution, whereas double chain amphiphiles like phospholipids forms bilayer instead of micelles.

Source:http://employees.csbsju.edu/hjakubowski/classes/ch331/lipidstruct/lipidsinwater.gif

Frequently asked questions

Water is considered a polar solvent. Which substances should dissolve in water?

1. methanol (CH_3OH)
2. sodium sulfate (Na_2SO_4)
3. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

1. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
2. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
3. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

Source: http://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological/s12-01-solutions.html (CC)

Water plays an important role for the formation of three dimensional structure and function of macromolecules

The strongest bonds that are present in biomolecules are the covalent bonds such as the bond that hold atoms together within the individual bases. A covalent bond is formed by sharing a pair of electrons between adjacent atoms. A typical C-C covalent bond has bond energy of 85 kcal mol^{-1} (365 kJ mol^{-1}). Hydrophobic interactions are much weaker than the covalent bonds. Chemical reactions entail breaking and forming of covalent bonds. The four non covalent molecular interactions viz., hydrogen bond, electrostatic, hydrophobic and Van der Waals interactions, play a significant role in replication of DNA, folding of proteins into complex three-dimensional form, specific recognition of substrate by enzyme, binding of hormone with their receptors and detection of molecular signals. Although these four non covalent interactions are weaker than the covalent ones, the structure and function of all the biological processes depends upon the interplay between non covalent interactions with the covalent ones. Further these bonds are further affected in different ways by the presence of Water. Water greatly reduces the electrostatic interactions. X-ray crystallography studies of proteins such as hemoglobin and nucleic acids (DNA or RNA) showed that water molecule is part of their crystal structure. The properties of these bound water molecules are different from those of the "bulk" water molecules present in the solvent. They do not exert osmotic pressure. These tight bound water molecules can also form an important part of the binding site of a protein for its ligand.

Colligative properties of a solution is greatly affected by different solute particles

The presence of polar solutes such as ions of salt (NaCl) which form hydration shells through interaction with water dipoles create a local order. Hydrophobic substances make different structures like micelles within water. Thus, the presence of solute molecules in water disturbs its ordered structure and diminish the dynamic interplay among H_2O molecules in pure water. This characteristic change in behavior of water due to the presence of solute are termed as colligative properties. The colligative properties of water like the vapor pressure, the boiling point, the freezing point and the osmotic pressure) depend entirely on the ratio of number of solute particles in a given solvent and not on the type of chemical species present. Colligative properties are mostly studied for dilute solutions which behave like an ideal solution. For example, 1mol of an ideal solute (1m or molal solution) dissolved in 1000g of water at 1 atm pressure depresses the freezing point by 1.86°C, raises the boiling point by 0.543°C, lowers the vapor pressure in a temperature dependent manner and yields a solution whose osmotic pressure relative to pure water is 22.4 atm (at 25°C).

Thus by imposing local order on the water molecule, solutes makes it more difficult for water molecules to assume its crystalline lattice (freeze) or escape into the atmosphere (boil or vaporize). Also when 1m solution is separated from a volume of pure water by a semi-permeable membrane, the solution draws water molecules across this barrier. The pure water molecules are moving from a region of higher effective concentration (pure water) to a region of lower effective concentrations (the solution). The osmotic force, exerted by each mole of solute is so strong that it requires the imposition of 22.4 atm of pressure to be negated. This osmotic pressure is directly related to the concentration of nonpermeant solute.

Osmotic pressure of solution is directly proportional to concentration of solvent, absolute temperature and concentration of solute particles.

$\Pi = i\,c\,R\,T$,

Where Π is osmotic pressure, R is gas constant, T is absolute temperature, i is van't Hoff factor which is a measure of the extent to which solutes dissociates into two or more ionic species. *ic* is osmolarity of a solution which is product of van't Hoff factor i and solute molar concentration c.

- For completely ionising solution like NaCl the i=2
- For non ionising solution i=1

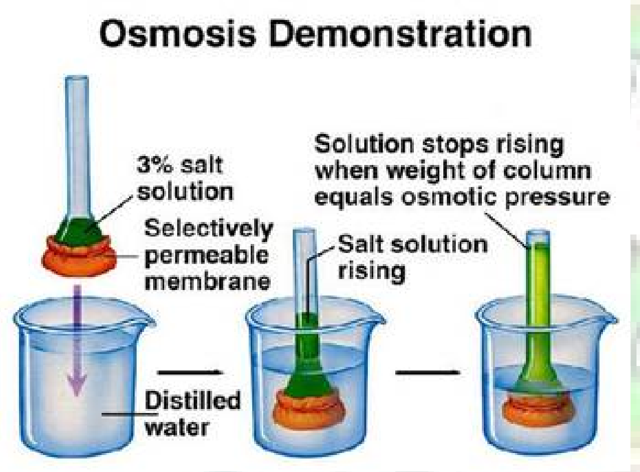


Figure: Osmosis and osmotic pressure.
Water molecules move across semi-permeable membrane from beaker (distilled water) towards the inside of thistle funnel (3% salt solution) which has lower water concentration. The level of solution rises in the funnel till hydrostatic pressure becomes equal to the osmotic pressure.
Source: http://tgesbiology.weebly.com/uploads/9/0/8/0/9080078/8062825.jpg?345

Solutions can have different types of osmolarities:

Isotonic - with same osmolarity as that of the cell's cytosol

Hypertonic – with osmolarity higher than that of cell's cytosol

Hypotonic – with osmolarity lower than that of cell's cytosol

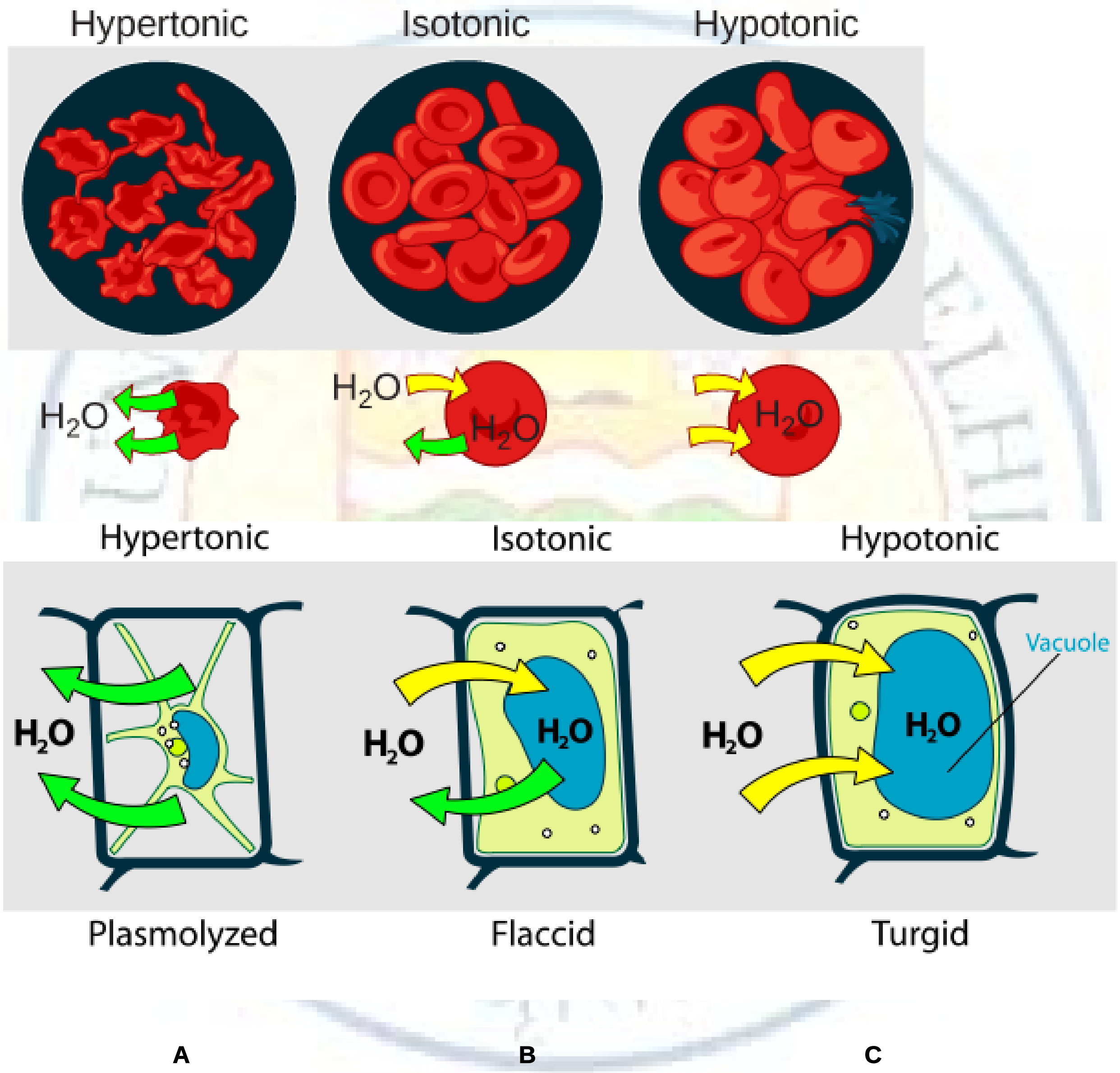


Figure: Effect of extracellular osmolarity on plasma membrane of plant and animal cell. A) When cell is in hypertonic solution, water moves out and cell shrinks.B) When cell is in isotonic solution, there is no net water movement. C) When cell is in hypotonic solution, water moves in, creating outward pressure, cell may eventually burst.

Source: https://www.boundless.com/physiology/cellular-structure-and-function--2/transport-across-membranes/water-balance/ (CC)

Osmotic pressure form high concentration of dissolved solutes is a serious problem for cells.

- Bacteria and plants have strong rigid cell wall to contain the osmotic pressure.
- Contractile vacuoles in some fresh water protists pumps water out of the cell that lives in highly hypotonic medium.
- In multicellular animals, blood plasma and extracellular fluid maintains high osmolarity due to presence of high concentration of proteins in the blood. Cells also actively pump out Na^+ and other ions into the interstitial fluid to stay in osmotic balance with their surroundings.
- Also to minimize osmotic pressure created by contents of their cytosol, cells tend to store substances such as amino acids and sugars in polymeric form. For example a molecule of glycogen or starch containing 1000 glucose units exerts only 1/1000 the osmotic pressure that 1000 free glucose molecules would.

Dialysis

The main function of the kidneys is to filter the blood to remove wastes and extra water, which are then expelled from the body as urine. Some diseases rob the kidneys of their ability to perform this function, causing a buildup of waste materials in the bloodstream. If a kidney transplant is not available or desirable, a procedure called dialysis can be used to remove waste materials and excess water from the blood.

In one form of dialysis, called *hemodialysis*, a patient's blood is passed though a length of tubing that travels through an *artificial kidney machine* (also called a *dialysis machine*). A section of tubing composed of a semipermeable membrane is immersed in a solution of sterile water, glucose, amino acids, and certain electrolytes. The osmotic pressure of the blood forces waste molecules and excess water through the membrane into the sterile solution. Red and white blood cells are too large to pass through the membrane, so they remain in the blood. After being cleansed in this way, the blood is returned to the body.

Dialysis is a continuous process, as the osmosis of waste materials and excess water takes time. Typically, 5–10 lb of waste-containing fluid is removed in each dialysis session, which can last 2–8 hours and must be performed several times a week. Although some patients have been on dialysis for 30 or more years, dialysis is always a temporary solution because waste materials are constantly building up in the bloodstream. A more permanent solution is a kidney transplant.

Source: http://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological/s12-04-properties-of-solutions.html

Ionization of Water and relation of K_{eq} with K_w

Water undergoes self ionization, where two water molecules interact to form a hydronium (H_3O^+) ion and a hydroxide ion (OH^-).

$H_2O + H_2O \Leftrightarrow H_3O^+ + OH^-$

This tendency is demonstrated by electrical conductivity of pure water, a property that establish the presence of charged species (ions).When an electric current is passed through the ionic solution the ions migrate towards an electrode of opposite polarity at a rate proportional to the electric field and inversely proportional to the frictional drag experienced by the ion as it moves through the solution. Ionic mobility of both H_3O^+ and OH^- are anomalously large as compared to other ions such as Na^+, K^+, H^+ and Cl^-. This high ionic mobility results from **"proton hopping".** It is process where series of protons hops between hydrogen bonded water molecules which help protons to cover long distances in a remarkably short time.

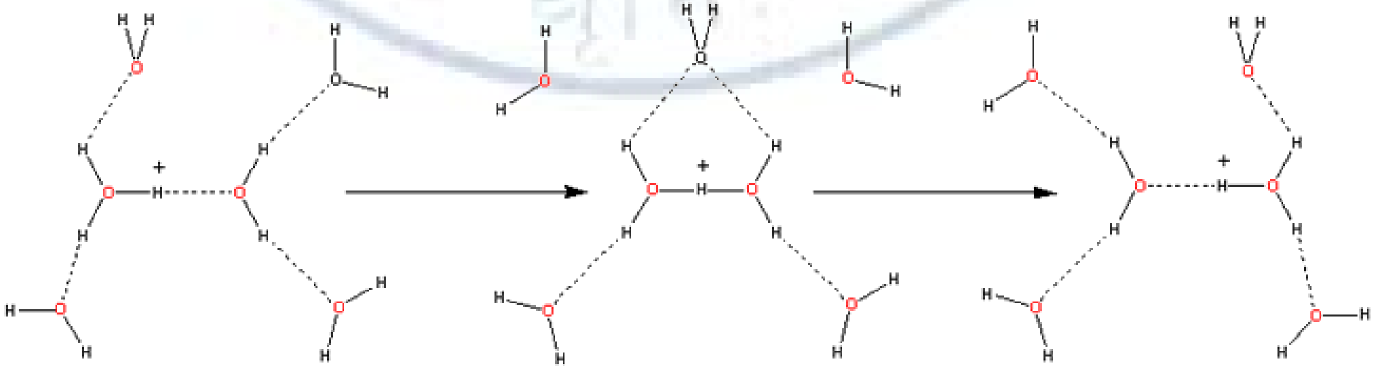


Figure: Proton hopping. Proton hops between series of hydrogen bonded water when one hydronium ion gives up a proton, a water molecule some distance away acquires one, becoming a hydronium ion, this result in extremely fast movement of proton over a long distance in a very short time.

Source: http://www1.lsbu.ac.uk/water/grotthuss.html

Pure water ionizes slightly into hydrogen and hydroxide ions and its ionisation is expressed by an **equilibrium constant, K_{eq}**

$H_2O \Leftrightarrow H+ + OH-$

$$K_{eq} = [H^+]\ [OH^-] \ / \ [H_2O]$$

where bracket denote concentration in moles per liter. The amount of H_3O^+ or OH^- in 1L of pure water at 25°C is $1x10^{-7}$ mol; the concentrations are equal and are stoichiometric.

Because the concentration of H_2O in 1L of pure water is equal to the number of grams in a liter divided by gram molecular weight of H_2O or 1000/18, the molar concentration of water is 55M.

$$(55.5\ M)\ (k_{eq}) = [H^+][OH^-] = K_w$$

The value for K_{eq} for water at 25°C is 1.8×10^{-16}. By substituting the value of K_{eq} in the above equation, the ion product of water, $\mathbf{K_w}$ is

$$\mathbf{K_w} = [H^+][OH^-] = (55.5M)\ (1.8 \times 10^{-16} M)$$

$$= 1.0 \times 10^{-14}\ M^2$$

Thus the product $[H^+][OH^-]$ in aqueous solutions at 25°C is always equal to $1.0 \times 10^{-14}\ M^2$ and is essentially constant. By taking square root of $1.0 \times 10^{-14}\ M^2$ the concentration of H^+ and OH^- was found to be 10^{-7}. When other molecules which have the ability to accept or donate H^+ are dissolved in water, the concentrations of H^+ and OH^- can change. If the concentration of H^+ is increased it is counterbalanced by a decrease in the concentrations of OH^- and the equilibrium is maintained.

When the concentrations of H^+ and OH^- in the solution are equal it is said to be at **neutral pH**. At this pH, concentrations of H^+ and OH^- are 10^{-7} M. From the ion product of water we can calculate concentration of hydrogen ion [H^+] if we know [OH^-] and vice versa. Strong acids and bases

The ion product of water, $K_{w,}$ is the basis for pH scale. pH is defined as ,

pH $=\log 1 / [H^+] = -\log [H^+]$

The symbol **p** denotes –“negative logarithm of”. Low pH values represent the highest H^+ concentrations and lowest OH^- concentrations as K_w specifies.

Also,

$K_w = pH + pOH = 14$

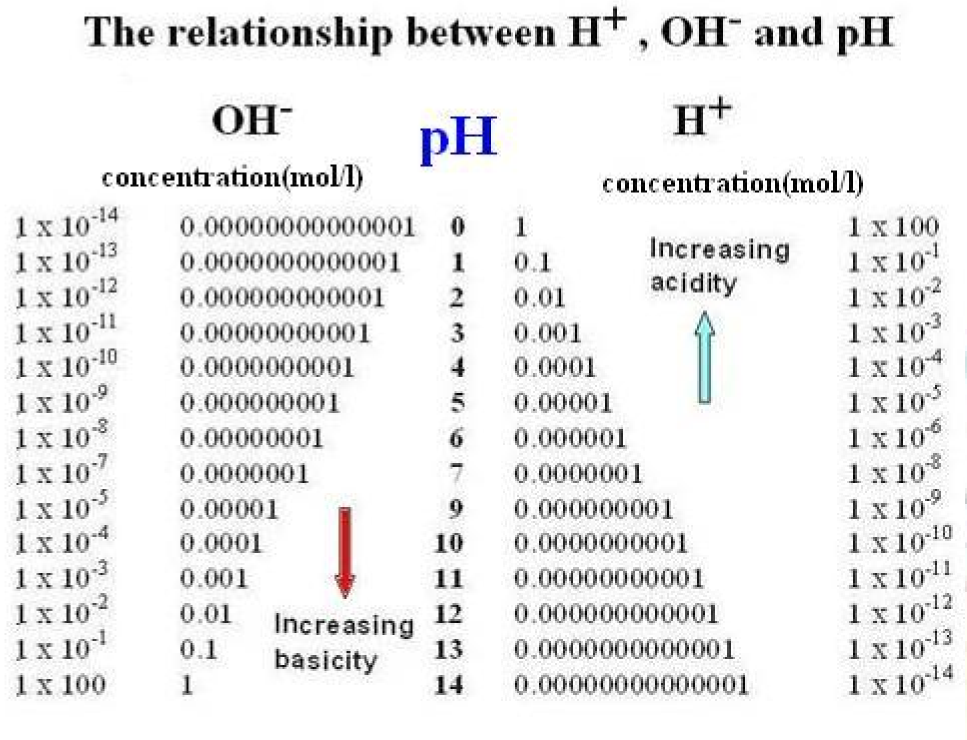
The value of K_w is 14 at 25°C and is a constant but it changes with temperatures.

For a neutral solution at 25°C in which concentration of hydrogen ions is 1.0×10^{-7}M,

The pH can be calculated as

$pH = \log 1/(1.x10^{-7}) = 7.0$

The concentration of H^+ must be expressed in molar (M) terms. Thus value of pH gives us the absolute value of the exponent of hydrogen ion concentration.



The relationship between H^+ , OH^- and pH

OH^- concentration(mol/l)		pH	H^+ concentration(mol/l)	
1×10^{-14}	0.00000000000001	0	1	1×100
1×10^{-13}	0.0000000000001	1	0.1	1×10^{-1}
1×10^{-12}	0.000000000001	2	0.01	1×10^{-2}
1×10^{-11}	0.00000000001	3	0.001	1×10^{-3}
1×10^{-10}	0.0000000001	4	0.0001	1×10^{-4}
1×10^{-9}	0.000000001	5	0.00001	1×10^{-5}
1×10^{-8}	0.00000001	6	0.000001	1×10^{-6}
1×10^{-7}	0.0000001	7	0.0000001	1×10^{-8}
1×10^{-5}	0.00001	9	0.000000001	1×10^{-9}
1×10^{-4}	0.0001	10	0.0000000001	1×10^{-10}
1×10^{-3}	0.001	11	0.00000000001	1×10^{-11}
1×10^{-2}	0.01	12	0.000000000001	1×10^{-12}
1×10^{-1}	0.1	13	0.0000000000001	1×10^{-13}
1×100	1	14	0.00000000000001	1×10^{-14}

Source: http://oxygensupercharger.com/blog/neutral-ph-balance-importance-stabilized-oxygen/

This figure reveals the relation of H^+, pH and OH^-. pH scale tells us approximately how many zeroes are present in the value or how many places we have to move the decimal point to get to our concentration. Notice how at a pH of 1 the concentration of the H+ is $1x\ 10^{-1}$, Notice that a a pH of 14 the concentration is much smaller value, $1x10^{-14}$. The reason that more acidic solution has the smaller pH value is because the pH is really measuring the negative exponent. The more negative the value becomes, the smaller the concentrations. Notice how for every change in 1 pH value means that the negtaive exponent increases by 1 or decimal gets bigger by 1 place or a factor of 10 (e.g. when you change pH from 3 to pH 4, $[H^+]$ change from $1x10^{-3}$ to $1x\ 10^{-4}$).

pH calculations

If you want the pH of a solution all you have to do is take negative logarithm of the $[H^+]$

$[H^+]$	pH
$1x\ 10^{-5}$	$-\log(1x10^{-5}) = 5$

If you know pH and want to calculate $[H^+]$, then you have to perform antilog

$[H^+] = 10^{-pH}$

pH	$[H^+]$
3.6	$1 \times 10^{-3.6} = 2.51 \times 10^{-4}$

pH measure how acidic a solution is but water has two parts to it, H^+ and OH^-. pOH is the exact the opposite of pH. As for the pOH goes down, the solution becomes more basic, as pOH goes up, the solution becomes more acidic. We already know that

$$pH + pOH = 14$$

Thus if know pH we can calculate pOH of solution.

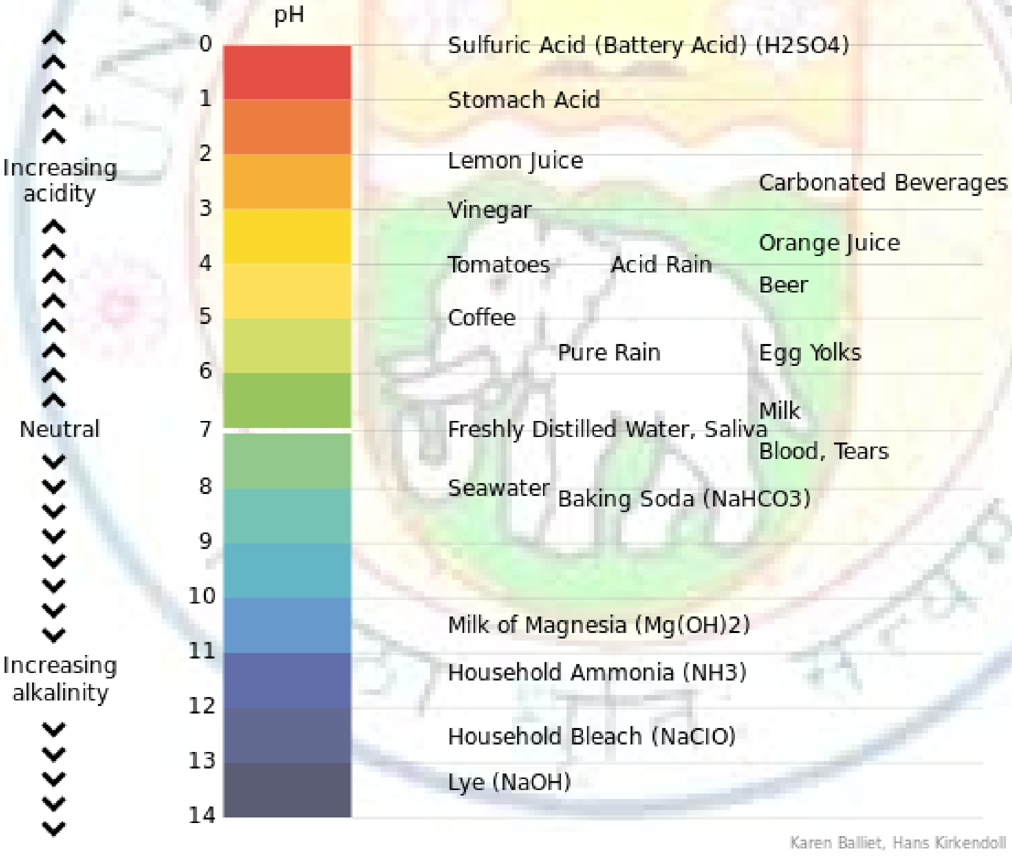


Figure: pH of some biologically important substances

Source:http://commons.wikimedia.org/wiki/File:Power_of_Hydrogen_%28pH%29_chart.svg pH scale is **logarithmic**. If two solutions differ in pH by 1pH unit it means that solution1 has ten times the H^+ concentration present in solution 2. On the pH scale, 7 is considered to be neutral and $[H^+] = [0H^-]$. Solutions having pH greater than 7 are basic and $[H^+] < [0H^-]$ whereas solutions having pH less than 7 are acidic and $[H^+] > [0H^-]$.

Most living organisms can survive within narrow pH range. Normal physiological pH of the blood is **7.4**. An organism can even die if the pH of the blood falls below 6.8 or above 7.8.Overabundance of acid or CO_2 in blood leads to **acidosis** whereas **alkalosis** occur when there is loss of hydrogen ions due to prolonged vomiting or there is increased bicarbonate in the blood. Thus body tries to maintain a stable, constant condition known as **homeostasis**. pH measurement of blood and urine are commonly used in medical diagnosis.

Acid dissociation constant of weak acids and bases

Strong acids such as HCl, HNO_3 or H_2SO_4 and bases like NaOH and KOH ionize completely in dilute aqueous solution but weak acids and bases which do not ionize completely are of prime importance in regulation of metabolism of cells. Weak acid such as acetic acid partially dissociate into acetate and hydrogen ions.

Reaction of acid is generalized in the form $HA \Leftrightarrow H^+ + A^-$, where HA represent the acid and A^- is the conjugate base. Acid dissociation constant, K_a is a quantitative measurement of the strength of an acid in solution. It is usually written as a quotient of equilibrium concentrations in (mol/l):

$K_a = [H^+][A^-]/ [HA]$

The K_a is expressed by using pK_a which is equal to $-\log_{10} K_a$. The larger the value of pK_a, the smaller the extent of dissociation of protons. Weak acid has pK_a value in the range of -2 to 12 in water, whereas strong acids have pK_a values of less than -2. While K_a measures strength of an acid compound, the strength of an aqueous acid solution is measured by pH.

Acids can be further classified into monoprotic and polyprotic acid. Monoprotic acid are those acids which can donate one proton per acid molecule during process of dissociation for e.g. HCl, HNO_3, CH_3COOH, C_6H_5COOH etc. Polyprotic acids also known as polybasic acids are able to donate more than one proton per acid molecule. Diprotic acid is symbolized as H_2A releases two protons whereas triprotic acids (H_3A) can donate three protons depending on the pH. Sulfuric acid and carbonic acid are examples of diprotic acid. Each dissociation has its own dissociation constant K_{a1} and K_{a2}.

H_2A (aq) + H_2O (l) $\Leftrightarrow H_3O^+$ (aq) + HA^- (aq) K_{a1}

HA^- (aq) + H_2O (l) $\Leftrightarrow H_3O^+$ (aq) + A^{2-} (aq) K_{a2}

The first dissociation constant is usually greater than the second i.e. $K_{a1} > K_{a2}$.

For example sulfuric acid (H_2SO_4) can donate one proton to form bisulfate anion (HSO_4^-) and then it can donate second proton to form sulfate anion (SO_4^{2-}). In a similar manner weak carbonic acid can lose one proton to form bicarbonate (HCO_3^-) and second proton to form carbonate anion (CO_3^{2-}).

A triprotic acid in a similar way can lose one, two or three protons during ionization process and has three dissociation pathways.

H_3A (aq) + H_2O (l) $\Leftrightarrow H_3O^+$ (aq) + H_2A^- (aq) K_{a1}

H_2A (aq) + H_2O (l) $\Leftrightarrow H_3O^+$ (aq) + HA^- (aq) K_{a2}

HA^- (aq) + H_2O (l) $\Leftrightarrow H_3O^+$ (aq) + A^{2-} (aq) K_{a3}

Phosphoric acid is an example of triprotic acid which loses three protons to yield H_2PO_4, HPO_4^{2-} and finally PO_4^{3-}. Citric acid is another example of triprotic acid. Amino acids are weak polyprotic acids for example aspartic acids and tyrosine are triprotic acids. All amino acids contain an acidic carboxylic group and a basic amino group attached to α-carbon and they also contain ionizable groups in their side chains that act as weak acids or bases when the pH of the solution is added. The strong positive charge on amino group induces the tendency for carboxylic acid to lose a proton so amino acids are considered to be **strong acids**. All amino acids exist as zwitter ion at neutral pH and are amphoteric molecules that can be titrated with both acid and alkali. At **isoelectric point (pI)**, the net charge on amino acids has zero charge. Isoelectric point is the pH of amino acid in aqueous solution when the net charge on the molecule is zero i.e. positively charged groups exactly balanced by the negatively charged groups.

Thus, acids play important role in human body. Hydrochloric acid present in stomach aids in digestion by breaking down large complex food. Amino acids which are building blocks of proteins and fatty acids are required for growth and repair of body tissues. Nucleic acids (DNA and RNA) are responsible for storage of genetic information. Carbonic acid is required for maintenance of blood pH equilibrium in body.

Interesting Fact
The dissociation of soluble ionic compounds gives solutions of these compounds an interesting property: they conduct electricity. Because of this property, soluble ionic compounds are referred to as electrolytes. Many ionic compounds dissociate completely and are therefore called strong electrolytes. Sodium chloride is an example of a strong electrolyte. Some compounds dissolve but dissociate only partially, and solutions of such solutes may conduct electricity only weakly. These solutes are called weak electrolytes. Acetic acid (CH_3COOH), the compound in vinegar, is a weak electrolyte. Solutes that dissolve into individual neutral molecules without dissociation do not impart additional electrical conductivity to their solutions and are called nonelectrolytes. Table sugar ($C_{12}H_{22}O_{11}$) is an example of a nonelectrolyte.
Source: http://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological/s12-03-the-dissolution-process.html

Titration curves of biologically important acids

Titration is a technique used to determine concentration of unknown acids or bases. A plot of pH of acid solution plotted against the amount of base added during a titration is known as titration curve. Initially when small amounts of strong base is added to the acid solution which has low pH, pH increases sharply till it reaches a point where all of the H^+ ions are neutralized.

1. $HAc \leftrightarrow H^+ + Ac^-$
2. $H^+ + OH^- \leftrightarrow H_2O$

As the titration begins, mostly HAc is present, plus some amounts of H^+ and Ac^- in the solution. Addition of NaOH to the solution, allows OH^- ions to neutralize any H^+ ion present. As reaction 2 is strongly favored, as H^+ is neutralized more HAc dissociates to H^+ and Ac^-. The stoichiometry of titration is 1:1, for each increment of OH^- added an equal amount of weak acid HAc is titrated. As additional NaOH is added, the pH gradually increases as Ac- accumulates at the expense of diminishing HAc and the neutralization of H^+. At the point where half of HAc has been neutralized (that is where 0.5 equivalents of OH^- has been added), the concentration of HAc and Ac^- are equal and $pH=pK_a$ for HAc. After all of the acid has been neutralized (that is one equilavent of base has been added),the pH rises exponentially. Thus, we have experimental method to determine pK_a values of weak electrolytes. These pK_a lies in the midpoint of their titration curves. Titration curves of all weak electrolytes follow same basic shape. The pK_a values are directly related to dissociation constant of the substance, or tells relative affinities of conjugate bases for protons e.g. NH_3^+ has affinity for proton compared to Ac^- that is why NH_4^+ ion is a weaker acid than acetic acid.

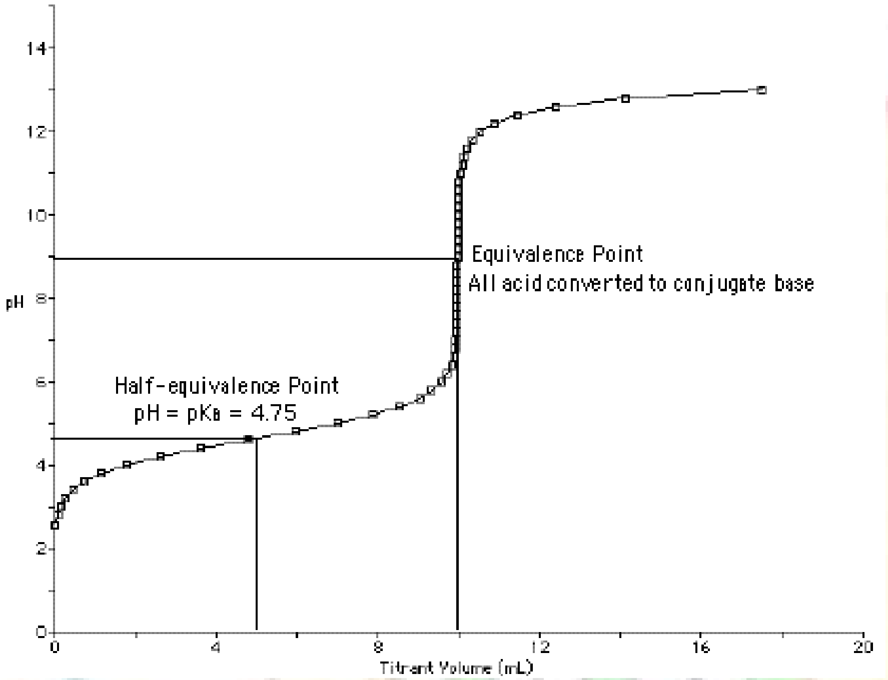


Figure: Titration curve of acetic acid

Source:http://www.dartmouth.edu/~chemlab/chem3-5/acid1/graphics/chemistry/chem3.gif

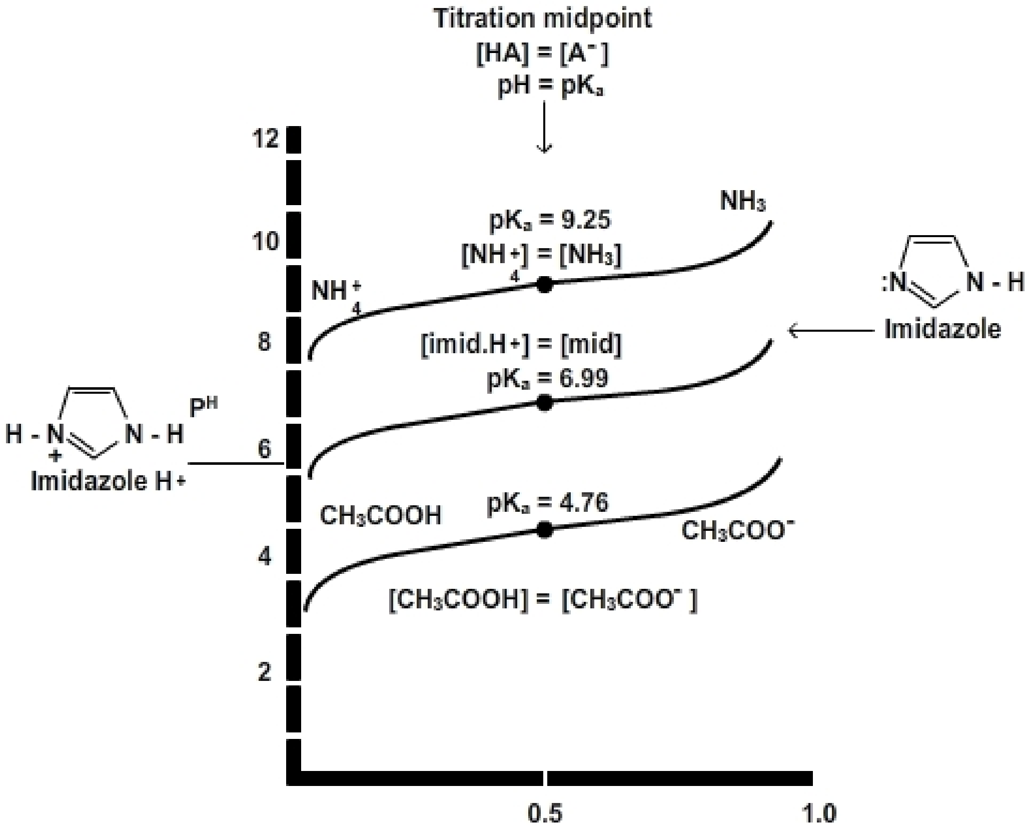


Figure: Titration curves of weak acid and bases such as acetic acid, imidazole and ammonium have the same shape.

Source: Author

Buffers play important role in biological system

Buffers are substances that minimize changes in concentration of H^+ ions or OH^- ions. Buffer solution is a solution that resists changes in pH when small quantities of either strong acids (H^+) or a strong base (OH^-) is added. It is a mixture of weak acid and its conjugate base. For example, mixture of equal concentration acetic acid and acetate ion found in the midpoint of the titration curve is a *buffer* system. Here CH_3COOH is represented as HAc and CH_3COO^- as Ac^-. In this region ($pH=pK_a$) the titration curve is relatively flat. Addition of H^+ then has little effect because it is absorbed by the following reaction:

$H^+ + Ac^- \leftrightarrow HAc$

Similarly increase in $[OH^-]$ is offset by the process

$OH^- + HAc \leftrightarrow Ac^- + H_2O$

Thus pH remains relatively constant. It is at the *pK_a* that buffer system shows its greatest *buffering capacity*. At pH values more than 1pH unit from the pK_a, a buffer system becomes ineffective because the concentration of one of the component becomes too low to absorb the influx of H^+ and OH^- ions. The molarity of a buffer is sum of the concentration of the acid and conjugate base forms. Each conjugate acid-base pair has characteristic pH zone in which it is an effective buffer for e.g. H_2PO_4 /HPO_4 pair has a pK_a of 6.86 and serve as an effective buffering system between pH 5.9 and pH 7.9.

The above equation is described by the equilibrium constant K_{eq} or K_a

$K_a = [H^+]\ [Ac^-] / [HAc]$ (A)

Taking long of both the sides of above equation yields

$\log K_a = \log [H^+] + \log [Ac^-] / [HAc]$ (D)

We already know that pH= $-\log [H^+]$ (B)

And $pK_a = -\log k_a$ (C)

Using the definitions of pH and pK_a and rearranging equation D produces Henderson-Hasselbach equation:

$pH = pK_a + \log [Ac^-] /[HAc]$

The **Henderson-Hasselbalch** equation relates pH, pK_a and buffer concentration. The Henderson Hasselbalch equation is written as **$pH=pK_a + \log [A^-]/[HA]$**. Thus the pH of a solution can be calculated, provided K_a and the concentration of the weak acid HA and its conjugated base A^- are known. Note particularly that when $[HA] = [A^-]$, $pH=pK_a$.

Maintenance of pH is vital to all cells. Metabolism of all living cells depend on activities of various enzymes, in turn enzyme activity is markedly influenced by pH. Organism have variety of mechanism to keep the pH of extracellular and intracellular fluids constant but the primary protection against harmful pH changes is provided by buffer systems. The buffer system selected reflects both the need for pKa value near pH 7 and the compatibility of the buffer components with the metabolic machinery of cells. Two buffer systems which act to maintain intracellular pH constant are phosphate system and histidine system. The pH of extracellular fluid that bathes the cells and tissue of animals is maintained by bicarbonate/carbonic acid system.

Phosphate buffer systems maintains intracellular pH of the cell

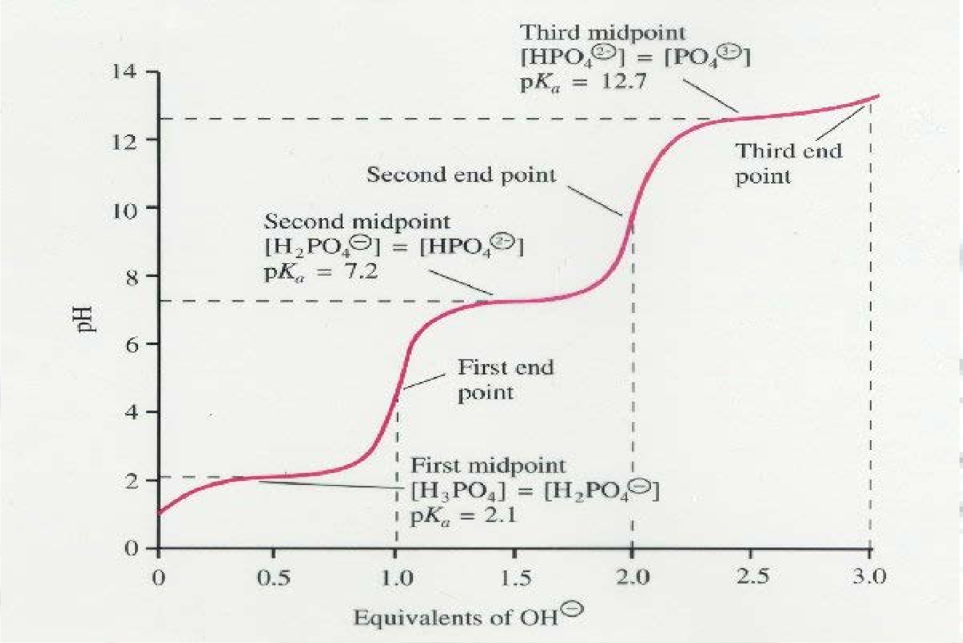


Figure: Titration curve of polyprotic Phosphoric acid

Source:http://web.campbell.edu/faculty/nemecz/323_lect/acid_base/images/titration2.png

This buffer is present in internal fluid of all cells. It is a mixture of dihydrogen phosphate ions ($H_2PO_4^-$) which acts as weak acid and its conjugate base, hydrogen phosphate ions (HPO_4^-).

$H_2PO_4^- \leftrightarrow H^+ + HPO_4^-$

If an additional hydrogen ion enters the fluid, they are consumed by HPO_4^-, and equilibrium shift towards left. If any hydroxide ions enter the fluid they react with $H_2PO_4^-$ producing HPO_4^- and shifting the equilibrium towards right. This buffer is maximally effective at pH close to its pK_a of 6.86 and thus tends to resist pH changes in range between 5.9 and 6.9. In absence of phosphate buffer from cytoplasm of the cell, sharp changes in the pH of cellular fluid may cause cell death or leads to improper functioning of cell organelles and different proteins present in the cell.

pK_a of Histidine–Imidazole system is closest to physiological pH

Histidine is one of the twenty standard amino acids commonly found in proteins. In cells it is present in either free amino acid or as constituent of proteins such as Hemoglobin and as part of some dipeptides in combination with some other amino acids. Its structure comprise of an imidazole group, a five membered heterocylic ring possessing two nitrogen atoms. The pK_a for dissociation of the imidazole hydrogen of histidine is 6.04.

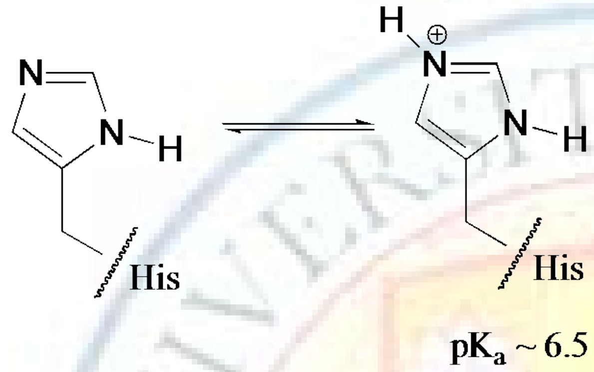


Figure: How histidine acts as buffer at physiological pH.

Source: Author

In a dipeptide such as anserine, which consist of β-alanine and histidine, the pK_a of imidazole histidine is 7.04. Thus, this pK_a is near physiological pH and some histidine peptides are well suited for buffering at physiological pH.

Bicarbonate buffer system regulates pH of Blood

Bicarbonate buffer system which comprise of carbonic acid ($H_2CO_3^-$) and hydrogen bicarbonate (HCO_3^-) plays an important role in maintaining pH of the blood around 7.4. In this system, $H_2CO_3^-$ is a weak acid and HCO_3^- is its conjugate base. It is represented by the equations

1. $CO_2\,(g) \leftrightarrow CO_2\,(d)$

2. $CO_2 + H_2O \leftrightarrow H_2CO_3$

3. $H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

4. $H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^-$

By combining equation 2 and 4 we get equation 5

5. $CO_2 + H_2O \leftrightarrow H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^-$

Under normal circumstances there is much more bicarbonate present than carbonic acid (the ratio is approximately 20:1). As normal metabolism of cell produce more acids than bases, this is consistent with the body need and would probably lead to lowering of pH. But to counteract this effect, blood maintains high concentration of base which is able to neutralize the metabolic acids produced. Since relatively small amounts of metabolic bases are produced, the carbonic acid concentration in the blood can be lower.

Since carbonic acid is not stable in aqueous solutions some of it decomposes to form CO_2 and H_2O. The respiratory system is than responsible for removing this CO_2 (equation 5) by exhalation and the normal blood pH is maintained.

The bicarbonate buffer system works well because the critical concentration of H_2CO_3 is maintained relatively constant through the equilibrium with dissolved CO_2 produced in tissues and available as a gaseous CO_2 reservoir in the lungs (equation 1). Gaseous CO_2 from lungs and tissues is dissolved in blood plasma, symbolized as CO_2 (d) is hydrated to H_2CO_3 by an enzyme carbonic anhydrase which facilitates the equilibrium by rapidly catalyzing the reaction (equation 2).

Consider the production of lactic acid in muscles. When lactic acid enters the blood it donates proton to water to form H_3O^+. This increase H_3O^+ concentration. In order to restore the H_3O^+concentration to normal the equilibrium of equation 4 shifts to left. This shift results in production of H_2CO_3. In order to reduce H_2CO_3 concentration, the equilibrium of equation 5 shifts to left as well. This shift result in production of CO_2 which is exhaled by lungs and the blood pH is maintained.

In the absence of this buffer in the blood the pH may fall below the normal value (pH 7.4) leading to condition known as acidosis and or the pH may rise above the normal value leading to alkalosis.

Anomalous properties of water give it a unique role in environment

Water is a universal and a powerful solvent, as it can dissolves many different substances compared to any other chemically inert solvent. Hydrophobic interaction of non polar substances in water is also important for evolution of cell as through hydrophobic interactions, lipids coalesce, membrane forms, boundaries are created delimiting compartments and cellular nature of life is established. Because of its high dielectric constant, H_2O is a medium of ionization. Water ionizes and allows easy proton exchange between molecules. The large heat capacity of water maintains uniform body temperature by preventing extreme temperature fluctuations. High latent heat of evaporation helps human to use this heat to evaporate their sweat and provide cooling. Low density of ice than that of liquid water leads to formation of ice on the surface of water bodies forming an insulating layer protecting the marine life dwelling in the bottom layers of liquid water underneath. High surface tension of water plus its expansion and freezing properties encourage erosion of rock to provide soil for our agriculture. High degree of internal cohesion between water molecules helps plants to transport their nutrients from roots to leaves by capillary movement of water. Also osmosis which relates to bulk movement of water from dilute solutions to a more concentrated one across a semi- permeable membrane determine its shape and form of living things.

Summary

- Water molecule is a highly polar molecule which can form hydrogen bonds with its molecules and with solutes in the solution. Water is a good solvent for polar (hydrophilic) molecules. It interacts with charged solutes electrostatically.
- Non polar (hydrophobic) molecules dissolve poorly in water. To minimize the surface exposed to water, nonpolar compounds like lipids form micelles. Micelles are organised amphipathic molecules.
- Weak non covalent forces help folding of macromolecules such as proteins and nucleic acids in such a way that the hydrophilic molecules interact with water and hydrophobic molecules hide from water.
- When hypotonic and hypertonic solution is separated by semipermeable membrane water moves depending on the osmotic pressure created.
- Pure water ionizes slightly, forming equal number of hydrogen and hydroxide ions. The extent of ionization is described by an equilibrium constant $K_{eq.}$
- pH of an aqueous solution is logarithmic value of the concentration of hydrogen ions: $pH=log1/[H^+] = -log [H^+]$.
- pK_a is logarithmic of dissociation weak acid: $pK_a =log1/K_a = -log K_a$.
- Buffer is a mixture of weak acid (or base) and its salt which can resist changes in pH caused by the addition of H^+ and OH^-.
- Henderson-Hasselbalch equation: $pH = pk_a + log [A]/[HA^-]$ gives pH of the buffer solution.

- In cells and tissues, phosphate and bicarbonate buffer systems help to maintain physiological pH 7. Proteins maintain their optimal conformation at this pH.
- Any change in pH like in acidosis or alkalosis can disturb the internal milieu of cell.
- Water can act as solvent as well as reactant in many metabolic reactions.

Exercises

Q1. Explain why ethanol is more soluble in water than is ethane?

Q2. What is the structure of water molecule and how does it react with polar and non polar solutes?

Q3. Define osmosis and osmotic pressure?

Q4. What is Proton hopping?

Q5. If the concentration of H^+ in a solution is 10^{-3} M, what will the concentration of OH^- be in the same solution at 25° C?

Q6. Convert the following pH values to $[H^+]$: 6.37; 4.83?

Q7. Convert the following pOH values to $[H^+]$: 3.28; 9.86?

Q8. Convert the following molar hydrogen ion concentrations to pH values: 0.0139; 2.07×10^{-5}?

Q9. Calculate the pH of each of the following systems:

a. 40 ml of a solution containing 1.00 g of nitric acid.

b. 0.180 M benzoic acid solution

c. 0.120 M chloroacetic acid solution

d. a solution of 0.500 g of o-phthalic acid in 125 ml of water

Q10. Calculate the equilibrium concentration of H^+, $C_2H_5COO^-$, and C_2H_5COOH in a solution of 0.040 moles of propionic acid in 150 ml of water.

Q11. A 2% solution of a monoprotic acid, $pK_a = 5.2$, had a pH of 3.5. What is the molecular weight of the acid?

Q12. A 0.01 M solution of phenol is 0.05% ionized at 25^0C. What is the pK_a of the acid?

Q13. What strength of formic acid ($K_a = 1.76 \times 10^{-4}$) solution should be prepared to give a pH of 3.8?

Glossary

Acid dissociation constant (k_a): The dissociation constant of an acid which gives the rate at which acid dissociates into its conjugate base and proton.

Acidosis: It is the condition of body when normal physiological pH falls less than 7.4 e.g. 6.

Alkalosis: It is the condition of body when normal physiological pH increases more than 7.4 e.g. 8.

Amphipathic: Molecules containing polar or nonpolar domains.

Buffer: It is a solution which can resist change in pH. It is made up of conjugate base and acid or conjugate acid and base.

Equilibrium constant (k_{eq}): It is a rate constant of a reaction which gives specific concentrations of reactants and products at equilibrium at given temperature and pressure.

Henderson-Hasselbalch equation: An equation relating the pH, and pK_a and the ratio of the concentrations of proton-acceptor (A^-) and proton-donor (HA) species in a solution:

$pH = pk_a + \log [A]/[HA^-]$

Hydrogen bond: A weak electrostatic attraction between one electronegative atom (such as oxygen or nitrogen) and a hydrogen atom covalently linked to a second electronegative atom.

Hydrolysis: Cleavage of bond by addition of the elements of water yielding two or more products e.g. peptide bond breaks to form amino acid.

Hydrophilic: Molecules which has high affinity for water. They dissolve easily in water e.g polar and charged molecules.

Hydrophobic: Molecules or groups that have low affinity for water. They are insoluble in water e.g. nonpolar molecules.

Hydrophobic interactions: The interaction of nonpolar molecules so that they can escape interacting with surrounding water.

Ion product of Water (K_w): The product of the concentration of H^+ and OH^- in pure water: $K_w = [H^+] \times [OH^-] = 1 \times 10^{-14}$ at 25°C.

Micelle: The circular arrangement of amphipathic molecules in water. In this arrangement their nonpolar portions are in the inner side. Polar portions at the outer side and are exposed to water.

Osmosis: It is flow of water through a semi permeable membrane from hypotonic solution to hypertonic solution.

Osmotic pressure: It is the pressure generated on hypotonic solution across the semi-permeable membrane by the osmotic molecules present in hypertonic solution.

pH: The hydrogen ion concentration given in the negative logarithm of an aqueous solution.

pk_a: The negative logarithm of dissociation constant of an acid e.g pKa of acetic acid is 4.6

Titration curve: A plot of pH versus the amount of acid or base added to neutralize the solution.

Van der waals interactions: Weak intermolecular forces between molecules as a result of each inducing polarization in the other.

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Solutions to numerical problems

Ans 5. Relation between H^+ and OH^- concentrations at 25° C

In aqueous solutions at 25° C, the product of the H^+ and OH^- concentrations is always 10^{-14}, as expressed in this equation:

$$[H^{+}]\,[OH^{-}] = 10^{-14}$$

This allows calculation of the OH^{-} concentration if the H^{+} concentration is known.

$$[OH^{-}] = 10^{-14} / [H^{+}]$$

$$[OH^{-}] = 10^{-14} / 10^{-3} = 10^{-11}$$

This calculation is used when the solution in question is not pure water, but contains some mixture of acids and bases.

Ans 6. $pH = -\log[H^{+}]$

$-pH = \log[H^{+}] = -6.37 = 0.63 - 7.00$

$[H^{+}] = 4.27 \times 10^{-7}$

$pH = -\log[H^{+}]$

$-pH = \log[H^{+}] = -4.83 = 0.17 - 5.00$

$[H+] = 1.48 \times 10^{-5}$

Ans7. $pH + pOH = 14$

$pH + 3.28 = 14$, $pH = 10.72$

$-\log[H^{+}] = 10.72$

$\log[H^{+}] = -10.72 = 0.28 - 11.00$

$[H^{+}] = 1.91 \times 10\text{-}11$

Ans8. $0.0139\ M = 1.39 \times 10^{-2}$ moles/liter

$-\log(1.39 \times 10^{-2}) = -(-2+ 0.14) = 1.86$

2.07×10^{-5} moles/liter

$-\log (2.07 \times 10^{-5}) = -(-5 + 0.32) = 4.68$

Ans9. Since nitric acid is a strong acid, it is completely dissociated in aqueous solution, hence $[H^+]$ = molarity.

Molarity = moles/liter = [(1 gram)/(63 grams per mole)]/0.040 liter = 0.40 M

$[H^+] = 4.0 \times 10^{-1}$

$pH = -\log (4.0 \times 10^{-1})$

$pH = -\log 4.0 - \log(10^{-1})$

$pH = -0.60 - (-1) = -0.6 + 1.0 = 0.4$

$pH = 0.40$

Ans10. $CH_3CH_2COOH \leftrightarrow CH_3CH_2COO- + H+$

Since propionic acid is a weak acid, we assume its dissociation is negligible. Therefore,

$[CH_3CH_2COOH] \approx 0.04$ moles/0.15 liter = 0.267 M

$Ka = ([CH_3CH_2COO^-][H^+])/[CH_3CH_2COOH]$

Since $[CH_3CH_2COO^-] = [H^+]$. Then

$[H^+]^2 = K_a[CH_3CH_2COOH]$

$[H^+]^2 = (10^{-4.87})(0.267)$

$[H^+]^2 = 3.6 \times 10^{-6}$

$[H^+] = [CH_3CH_2COO^-] =$ ☐ $3.6 \times 10^{-6} = 1.89 \times 10^{-3}$

Ans 11. From the Henderson-Hasselbach equation

$pH = pK_a + \log([A^-]/[HA])$

$3.5 = 5.2 + \log([A^-]/[HA])$

$\log([A^-]/[HA]) = -1.7$

Since pH = 3.5, $[H^+] = 10^{-3.5} = 3.2 \times 10^{-4} M = [A^-]$

$\mathrm{Log}([HA]/[A^-]) = 1.7$

$[HA]/[A^-] = 50.0$

$[HA] = (50.0)(3.2 \times 10^{-4}) = 0.016M$

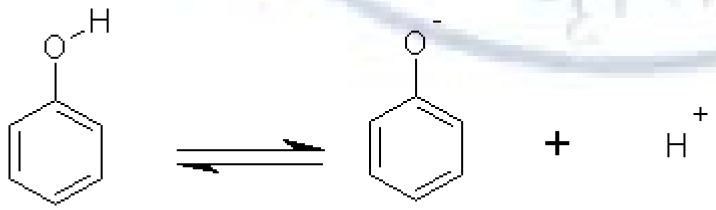
$[HA]_{total} = [HA] + [H^+] = 0.016 + 0.00032$ ☐ 1.63×10^{-2} moles/liter

Since the solution is 2% by weight, this means that it must contain 20 grams/liter of the unknown acid.

Dividing the grams/liter by the molarity (moles/liter) will give the desired molecular weight result in grams/mole,

(20 grams/liter0/1.63 x 10-2 moles.liter) = 1227 grams/ mole

Ans12.



$[\text{phenolate}^-]/[\text{phenol}] = \%$ ionized $= 0.0005$

$[\text{phenolate}^-] \approx (0.0005)(0.01) = [H^+]$

$[H^+] = 5.0 \times 10^{-6}$, therefore pH = 5.3

From the Henderson-Hasselbach equation

$pH = pK_a + \log([A^-]/[HA])$

$pK_a = pH - \log([A^-]/[HA])$

$pK_a = 5.3 - \log\{(5.0 \times 10^{-6})/0.01\} = 5.3 - \log(5.0 \times 10^{-4})$

$pK_a = 5.3 - (-3.3) = 8.6$

The actual pK_a for phenol is 9.89, so some of the assumptions inherent in this calculation are not totally correct.

Ans13. $HCOOH \leftrightarrow HCOO^- + H^+$

$F_{HCOOH} = [H^+] + [HCOOH]$

Since $pH = 3.8 = -\log[H^+]$,

$[H^+] = 10^{-3.8} = [HCOO^-] = 1.58 \times 10^{-4}$ M

From the Henderson-Hasselbach equation

$pH = pK_a = \log([A^-]/[HA])$

$3.8 = 3.75 = \log(1.58 \times 10^{-4}/[HCOOH])$

$0.05 = \log(1.58 \times 10^{-4}/[HCOOH])$

Taking the antilog of both sides,

$1.12 = (1.58 \times 10^{-4}/[HCOOH])$

$[HCOOH] = 1.41 \times 10^{-4}$ M

$F_{HCOOH} = [H^+] + \{HCOOH] = 1.58 \times 10^{-4}\ M + 1.41 \times 10^{-4}\ M$

$F_{HCOOH} = 2.99 \times 10^{-4}\ M$

Web Links

http://www1.lsbu.ac.uk/water/index2.html

http://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological/index.html

http://www.sumanasinc.com/webcontent/animations/content/propertiesofwater/water.html
http://tgesbiology.weebly.com/2-plant-water-relations.html