TOPIC 13.
WATER, ACIDS AND BASES - pH calculations.

Water and hydrogen bonding.
Apart from its ability as a suitable solvent for dissolving ionic solids, water has other important properties due to the polar O–H bonds which arise from the unequal charge distribution within its molecule and the small volume occupied by the lone pairs of electrons on the O atom. [See Topics 4 and 6]. One of these properties results from the ability of water molecules to interact with other water molecules through the attractions between O atoms of one molecule and H atoms of another. This attraction is electrostatic in nature and is due to the very concentrated charge on the O atoms in water molecules and the resultant deficit of negative charge on the H atoms. The attraction is not limited to just one pair of water molecules, but extends throughout the medium so that at any instant many molecules are linked in this way. Because the electron deficient H atoms form a bridge between electron rich O atoms, the name "HYDROGEN BONDING" is used to describe this phenomenon. Although a significant force between molecules, hydrogen bonding is considerably weaker than normal ionic or covalent bonds. The atoms of the elements adjacent to oxygen in the Periodic Table, nitrogen and fluorine, also have lone pairs of electrons in their valence level and small atomic radii, so they too can participate in hydrogen bonding just like oxygen. Any molecules containing O–H, N–H or F–H bonds can interact in the same way as water. However, atoms of the elements immediately below N, O and F in the Periodic Table are much larger and the greater volume of their lone pairs prevents these atoms from participating significantly in hydrogen bonding with other atoms. The following diagrams represent water molecules interacting through hydrogen bonding and ethanol hydrogen bonding with water.

Hydrogen bonding between water molecules

The dashed lines represent the hydrogen bonds between water molecules.

Arrows in the diagram on the right represent the hydrogen bonds.
Molecules which can interact with water molecules in this manner tend to be soluble in water – e.g. acetic acid (vinegar), ammonia and sugar. The ability to hydrogen bond gives water some unusual properties. Because it requires energy to break down the network of hydrogen bonding, water has a very much higher melting and boiling point than it should have based just on its molecular weight. Consider the following table of boiling points for the compounds of hydrogen (hydrides) with the elements of Group 16 of the Periodic Table.

<table>
<thead>
<tr>
<th>hydride</th>
<th>bp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>100</td>
</tr>
<tr>
<td>H₂S</td>
<td>-60</td>
</tr>
<tr>
<td>H₂Se</td>
<td>-41</td>
</tr>
<tr>
<td>H₂Te</td>
<td>-2</td>
</tr>
</tbody>
</table>

From this table, water would be a gas at well below room temperature if it were not for hydrogen bonding, and life on earth as we know it could not exist.

Another example of how hydrogen bonding gives water unusual properties is seen in the fact that ice is less dense than liquid water, evidenced by observing that ice cubes float in a drink. In ice, water molecules are completely hydrogen bonded in a tetrahedral arrangement which leaves a lot of empty space in the ice structure. When ice melts, some of the hydrogen bonds break and the structure collapses, allowing more water molecules to occupy the same volume. Hence liquid water is more dense than ice. Water has its maximum density at 4°C. All other substances are more dense...
in the solid phase than in the liquid phase. If ice were more dense than liquid water, lakes would freeze from the bottom up and fish could not survive cold winters. Instead, the ice insulates the top of the frozen lake, preventing further heat loss.

**Hydrogen bonding in molecules other than water.**

Hydrogen bonding is partly responsible for proteins holding their shape and thus being able to function as enzymes. Hydrogen bonding in proteins can be disrupted by adding an acid or by boiling in water. This is termed "DENATURATION" of the protein, and is observed when egg white is boiled. Proteins are very large **MACROMOLECULES** made up from many smaller molecules called **AMINO ACIDS** which are bonded together to form the protein. The really important characteristic of proteins is their ability to take up very complicated 3-dimensional structures. It is such structures that allows them to function as enzymes. The long chains of amino acids of the protein are folded and bent, with hydrogen bonds being one of the means by which the protein is held in its specific structure.

Washing one's hair is another example of breaking hydrogen bonds between the protein chains from which hair is constructed. When this happens, the hair becomes softer and more stretchable. Beating an egg white to use in a pavlova physically breaks hydrogen bonds to denature the egg white protein.

Probably the most important occurrence of hydrogen bonding is in the very basic molecules of life - the DNA that constitutes the genes in cells - and in the cellular processes that allow those cells to function and to divide. DNA contains two very long strands of molecules. The strands, made up of small molecules joined by covalent bonds, contain the genetic code which allows the cell to produce all the proteins required by the cell to function and reproduce. The two strands are held together throughout their length but have to be able to separate in order for the genetic code to be read and to replicate themselves. The bonds between the two strands therefore must be weaker than normal covalent bonds and in fact are hydrogen bonds established between matching molecules that constitute the components of each DNA strand. These hydrogen bonds allow the two DNA strands to open up and be read when required and then join together again, or they can open up and be reproduced to give two copies of the original DNA.
The hydrogen ion.
In Topic 6, acids were referred to as sources of hydrogen ions which were conveniently represented in ionic equations as \( H^+ \) or \( H^+ \) (aq). It was pointed out there that the hydrogen atom has a nucleus containing one proton around which a single electron orbits. Forming an \( H^+ \) ion by the loss of that electron would in fact be releasing a naked proton into the solution. A proton has such a small size and extremely high charge density that it could not exist freely in solution and instead, in water, is bonded to an \( H_2O \) molecule using one of the O atom’s lone pairs of electrons. This process is shown in the representation below.

\[
\begin{array}{c}
\text{H:}\overset{\cdot}{\text{O}}:\text{H} \\
\text{H}
\end{array}
\quad \rightarrow \quad \left[ \begin{array}{c}
\text{H:}\overset{\cdot}{\text{O}}:\text{H} \\
\text{H}
\end{array} \right]^+
\]

Thus the simplest formula for a hydrogen ion in solution is \( H_3O^+ \). The ion carries an overall 1+ charge distributed over the ion as a whole and is not localised on any particular atom. The three O–H bonds are indistinguishable from each other as are the three H atoms. The \( H_3O^+ \) ion is bonded through hydrogen bonds to an indeterminate number other water molecules at any instant. While the representation of the hydrogen ion as \( H^+ \) is inaccurate but convenient, more accurately it should be shown as \( H^+ \)(aq) where this indeterminate number of associated water molecules is implied by the (aq) suffix.

Ionization of water – pH.

Water is dissociated (ionized) very slightly to form \( H^+ \) and \( OH^- \) ions in equal amounts

Electrical conductivity tests show that even the purest water has some ions present, and this is due to a very slight amount of dissociation of water molecules themselves into ions.

The ionization of water is just one example of a chemical equilibrium between species – the reactants and the products. Unlike equilibrium in physical systems which is static, this is a **DYNAMIC EQUILIBRIUM** in which reactants continue to form products at the same rate as products form reactants. The equilibrium then consists of a forward and a backward reaction, each proceeding at the **same rate** so that overall there appears to be no change occurring. In the case of ionization of water, the forward reaction could be represented by the equation

\[ H_2O \rightarrow H^+(aq) + OH^-(aq) \]
while the reverse or backward reaction could be represented as

\[
\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}
\]

The overall equilibrium is represented by the equation

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)
\]

The equilibrium arrows, \(\rightleftharpoons\), mean that \(\text{H}_2\text{O}\) molecules are dissociating at exactly the same rate as \(\text{H}^+\) and \(\text{OH}^-\) ions are combining, and this is the reason it is called a dynamic equilibrium.

In this example, as there are very few ions present, the equilibrium is said to lie to the left or reactants side, favouring the formation of \(\text{H}_2\text{O}\) molecules. The experimentally determined concentration of hydrogen ions, \([\text{H}^+]\), present in water (the square brackets are shorthand for "the concentration of..."), at 25°C is 0.0000001 mole of \(\text{H}^+\) ions per litre of water. This is more conveniently written as \(1 \times 10^{-7}\) M and is necessarily the same as the concentration of hydroxide ions, \([\text{OH}^-]\). Another way of expressing these amounts is that this corresponds to only one \(\text{H}_2\text{O}\) molecule dissociating to \(\text{H}^+\) and \(\text{OH}^-\) ions for every 55 million water molecules.

**Acids and bases.**

In Topic 6, an **ACID** was described as a species which provides \(\text{H}^+\) ions in solution. Any species which accepts the \(\text{H}^+\) ions is called a **BASE**. For example, the hydroxide ion is a base in the reaction \(\text{OH}^-(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}\). In this Topic the concepts of acids and bases are considered in more detail.

![Acid and Base Diagram](image)

**The role of the solvent.**

Consider the species \(\text{HNO}_3\) which was observed earlier to behave as an acid. When \(\text{HNO}_3\) molecules are dissolved in water, they completely dissociate into ions to form aquated hydrogen ions which have previously been written as \(\text{H}^+(aq)\), and nitrate ions, \(\text{NO}_3^-(aq)\). For convenience, the \(\text{H}^+(aq)\) ion is usually written as \(\text{H}_3\text{O}^+\) in discussions of acids and bases, this being the simplest formula for the combination of an \(\text{H}^+\) ion with a water molecule. This convention will be used for the remainder of the discussion here. Then the equation for the dissociation of nitric acid in water, (deleting the (aq) suffixes) is

\[
\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^- \quad \text{.............(1)}
\]
From the equation it is seen that the solvent, water, has accepted the H\(^+\) ion from the donor species, HNO\(_3\). This reaction is complete in that virtually all HNO\(_3\) molecules react with H\(_2\)O molecules to form the ions on the right hand side, and there are no HNO\(_3\) molecules remaining in solution. When an acid is completely dissociated in a given solvent (water in this instance) it is called a **STRONG ACID**, and there is none of the non-ionised (molecular) form remaining.

*Hence it is a nonsense to write HNO\(_3\)(aq) as found in many texts, because in water solution, there would be almost no undisassociated molecules of HNO\(_3\) present.*

Because the solvent molecules, H\(_2\)O, accept the H\(^+\) ions, they are acting as bases and the dissociation of HNO\(_3\) is an acid/base reaction between the HNO\(_3\) molecules acting as an acid and the H\(_2\)O molecules acting as the base. Due to the way water dissociates into ions, it is called a **SELF-IIONIZING SOLVENT**.

**Conjugate acid-base pairs.**

Returning to equation (1) above, the species left after an acid has dissociated (NO\(_3^-\) in this example) is called the **CONJUGATE BASE** of the acid. A conjugate acid/base pair are any two species that differ in formula by a single H\(^+\). Similarly, as the difference between the formulas H\(_3\)O and H\(_3\)O\(^+\) is a single H\(^+\), then this is also a conjugate acid/base pair - the H\(_3\)O\(^+\) ion must be the acid as it has the extra H\(^+\) in its formula, and the H\(_2\)O molecule is its conjugate base.

Thus for any acid dissociating in water, the process can be represented as

\[
\text{ACID} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CONJUGATE BASE OF THE ACID}
\]

\[
\uparrow \quad \uparrow
\]

(acting as a base) (conjugate acid of H\(_2\)O)

The following Table lists some commonly encountered conjugate acid/base pairs.

<table>
<thead>
<tr>
<th>ACID</th>
<th>BASE</th>
<th>ACID</th>
<th>BASE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)SO(_4)</td>
<td>HSO(_4^-)</td>
<td>HSO(_4^-)</td>
<td>SO(_4^{2-})</td>
</tr>
<tr>
<td>H(_3)PO(_4)</td>
<td>H(_2)PO(_4^-)</td>
<td>HI</td>
<td>I(^-)</td>
</tr>
<tr>
<td>H(_2)PO(_4^-)</td>
<td>HPO(_4^{2-})</td>
<td>HBr</td>
<td>Br(^-)</td>
</tr>
<tr>
<td>HPO(_4^{2-})</td>
<td>PO(_4^{3-})</td>
<td>HCl</td>
<td>Cl(^-)</td>
</tr>
</tbody>
</table>

Note that in two of these examples the acid species was capable of donating more than a single H\(^+\). The sulfuric acid molecule, H\(_2\)SO\(_4\), has two dissociations possible and is called a **DIPROTIC ACID**, while the phosphoric acid molecule is capable of donating...
up to three $H^+$ ions and is called a **TRIPROTIC ACID**. Note also however, that each
dissociation involves a particular acid/conjugate base pair such as $H_2SO_4/HSO_4^-$, and
that there is no conjugate relationship between the species $H_2SO_4$ and $SO_4^{2-}$ which
differ in formula by **two** hydrogen ions.

**Weak acids.**
In the previous example (1), because the dissociation is complete, the nitric acid,
HNO$_3$, is a strong acid. However, there are many species which provide $H^+$ ions in
water solution without being completely dissociated. For example, the molecule
CH$_3$COOH (acetic acid, the main constituent of vinegar) is typical of a very large group
of compounds, many of which contain the COOH group as part of their molecule and
which only slightly dissociate in water. Such acids are called **WEAK ACIDS** and
represent another example of a chemical equilibrium. Again, this equilibrium process
is one in which reactants on the left hand side of the equation form products on the
right hand side at exactly the same rate as the reverse reaction occurs. At any given
instant some species are actually reacting yet at the same time the overall amounts of
all species present is constant, so this also is a dynamic equilibrium. As used above in
the equation for the dissociation of water molecules, reversible or equilibrium arrows
replace the "one way" arrows. Thus the equation for a weak acid such as CH$_3$COOH
dissociating in water would be

\[
CH_3COOH(aq) + H_2O \rightleftharpoons CH_3COO^-(aq) + H_3O^+
\]

This means that CH$_3$COOH molecules are reacting with H$_2$O molecules to form their
conjugates at exactly the same rate as those conjugates, CH$_3$COO$^-$ ions and H$_3$O$^+$ ions,
are recombining to form CH$_3$COOH and H$_2$O molecules.

*Note that for water solutions of weak acids as distinct from strong acids, it is
appropriate to write formulas such as CH$_3$COOH(aq) for acetic acid showing the
molecular form associated with water molecules as this compound is present mostly as
undissociated aquated CH$_3$COOH molecules. However, the (aq) suffixes are often
deleted for convenience.*

There are relatively few strong acids but many acids are weak. The following list gives
some examples from both groups.
**STRONG ACIDS:** HCl, HBr, HI, H$_2$SO$_4$, HNO$_3$, HClO$_4$, (but not HF).
**WEAK ACIDS:** HF, HSO$_4^-$, H$_3$PO$_4$, H$_2$PO$_4^-$, H$_2$CO$_3$, HNO$_2$, H$_2$SO$_3$, CH$_3$COOH.

**Strong and weak are not the same as concentrated and dilute.**
In common parlance concentrated solutions are often referred to as being “strong”
while dilute solutions might be called “weak”. It is important to note that in chemistry
the terms “strong” and “weak” as applied to solutions have the special meanings
defined on the previous pages. Strong and weak refer to the degree of dissociation of
the particular species under consideration while concentrated and dilute refer to the concentration of the solute present. It is possible to have a dilute solution of a strong acid - e.g. 0.1 M nitric acid would be considered dilute while a 10 M solution of nitric acid would be deemed to be concentrated. Likewise, one can have a concentrated solution of a weak acid - e.g. 10 M acetic acid would be a concentrated solution while 0.1 M acetic acid is a dilute solution. The following diagrams illustrate the difference between a strong and a weak acid in solution. The representation on the left is of a strong acid such as HNO₃ while that on the right is of a weak acid such as CH₃COOH.

![HNO₃ in solution. The small discs represent H⁺ ions, the large discs represent NO₃⁻ ions. Dissociation into H⁺ and NO₃⁻ ions is complete with no undissociated HNO₃ remaining.](image)

![CH₃COOH in solution. The small discs represent H⁺ ions, the large discs represent CH₃COO⁻ ions and the ovals represent undissociated CH₃COOH molecules.](image)

The following diagram shows another comparison between the extent of dissociation of the strong acid HCl and the weak acid CH₃COOH.

![Before dissociation After dissociation](image)

Strong acid e.g. HNO₃

Weak acid e.g. CH₃COOH
The pH scale.

From the previous examples, it can be seen that expressing the amount of $\text{H}_3\text{O}^+$ present in pure water or dilute solutions of acids in water involves inconveniently small numbers if moles per litre is used as the concentration unit. To overcome this inconvenience, when the amount of $\text{H}_3\text{O}^+$ present in a given solution is small (say less than 1 M), it is usually expressed in terms of a quantity called the pH. The symbol "p" is simply shorthand for "–log$_{10}$" and "pH" means "–log$_{10}$ [H$_3$O$^+$]". The square brackets are commonly used to mean "the concentration in moles/litre of" whatever is enclosed within them. Thus, for pure water, the amount of $\text{H}_3\text{O}^+$ present can be conveniently given by the pH which at $25^\circ\text{C}$ would be

$$\text{pH} = \text{–log}_{10}[\text{H}_3\text{O}^+] = \text{–log}_{10}(0.0000001) = \text{–log}(1 \times 10^{-7}) = -(–7.0) = 7.0$$

Note the pH is purely a number and has no units. Also note that, because pH is a logarithm, only the digits to the right of the decimal point are significant figures while the digits to the left of it give the scale factor. See Appendix 2 for more information on exponentials and logarithms.

Similarly, the hydrogen ion concentration of dilute solutions of acids is usually expressed via the pH rather than directly in moles/litre. Acidic solutions must have a greater concentration of hydrogen ions than that present in pure water so it follows that at $25^\circ\text{C}$ the pH of acidic solutions must be less than 7, the pH of pure water. Provided the acid is strong, the pH can be calculated as in the following examples.

**Example 1.** Calculate the pH of 0.10 M HNO$_3$.

As the acid is completely dissociated, then the [H$_3$O$^+$] in the solution is the same as that of the HNO$_3$ dissolved = 0.10 M.

$$\therefore \text{pH} = \text{–log}(0.10) = -(–1.00) = 1.00$$

**Example 2.** Calculate the pH of 0.010 M HNO$_3$.

$$\text{pH} = \text{–log}(0.010) = -(–2.00) = 2.00$$

Notice that because of the log scale employed, a change of 1 pH unit represents a ten fold change in the concentration of hydrogen ions.

**Example 3.** Calculate the pH of $4.3 \times 10^{-4}$ M hydrochloric acid solution.

Again the acid is strong, so the [H$_3$O$^+$] is also $4.3 \times 10^{-4}$ M, and

$$\therefore \text{pH} = \text{–log}(4.3 \times 10^{-4}) = -(–3.37) = 3.37$$

Notice the pH of acidic solutions approaches 7 from below as the acid is diluted.

**Example 4.** Given the pH of a solution of HNO$_3$ is 3.37, calculate the concentration of H$^+$ in that solution.

If $\text{pH} = 3.37$, then $\text{–log}[\text{H}_3\text{O}^+] = 3.37$ and thus $[\text{H}_3\text{O}^+] = 10^{-3.37}$ M = $4.3 \times 10^{-4}$ M.
It is normal to express concentrations with integer powers of 10, so this would be better given as $4.3 \times 10^{-4}$ M. [Use the $10^x$ button on your calculator to make this conversion.]

Note in this example the calculation is from pH to hydrogen ion concentration. In general terms, this can be expressed as

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} \text{ M}$$

---

**Check your understanding of this section.**

When large icebergs melt, do they lead to a rise in sea level?

Give a definition of an acid and of a base.

What is (i) a strong acid  (ii) a weak acid?

What does the term “conjugate acid base pair” mean?

Write the formula for the conjugate acid of chloride ion.

Write the formula for the conjugate base of $\text{H}_2\text{O}$.

Are the species $\text{H}_3\text{O}^+$ and $\text{OH}^-$ a conjugate pair? Justify your answer.

The term “dynamic equilibrium” might appear to be self-contradictory. Explain what this term means in the context of acid/base theory.

Distinguish between the terms (i) strong vs concentrated and (ii) weak vs dilute.

What is the role of water molecules in the reaction of hydrogen chloride with water?

---

**Basic solutions.**

Up to this point we have only considered water itself or acidic solutions. At 25°C, pure water has $[\text{H}^+] = 1 \times 10^{-7}$ M while acidic solutions have $[\text{H}^+]$ greater than this. In pure water, the concentrations of $\text{H}^+$ and $\text{OH}^-$ ions are equal, as one of each ion results from the dissociation of a single water molecule.

At 25°C,  
$[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}$ M in pure water (at 25°C).

In acidic solutions, the concentration of $\text{H}^+$ ions exceeds that of $\text{OH}^-$ ions - i.e. $[\text{H}^+]$ is greater than $1 \times 10^{-7}$ M.

$[\text{H}^+] > 1 \times 10^{-7}$ M in acidic solutions

One characteristic of the equilibrium between $\text{H}_2\text{O}$, $\text{H}^+$ and $\text{OH}^-$ is that $[\text{H}^+]\times[\text{OH}^-]$ is a constant, which at 25°C $= 1 \times 10^{-14}$ M$^2$, determined by experiment. This can be written as an equilibrium expression

$$[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$ M$^2$ in all dilute water solutions.$$

Thus in acidic solutions, as the $[\text{H}^+]$ is increased, then the $[\text{OH}^-]$ decreases. Basic solutions are those where $[\text{OH}^-] > [\text{H}^+]$. Consequently, for such solutions, $[\text{H}^+]$
must be less than the value in pure water, $1 \times 10^{-7}$ M. Like a see-saw, if one end goes up, the other goes down. Increased $[H^+]$ means decreased $[OH^-]$ and vice versa.

$$[OH^-] > 1 \times 10^{-7} \text{ M in basic solutions}$$
$$[H^+] < 1 \times 10^{-7} \text{ M in basic solutions}$$

The pH of a basic solution can be calculated by first using the equilibrium relation $[H^+] \times [OH^-] = 1 \times 10^{-14}$ to calculate the $[H^+]$ and then using the expression for $pH = -\log[H^+]$ as before. Note that the pH of basic solutions will always be greater than 7.

At $25^\circ C$, acidic solutions have $[H^+] > 1 \times 10^{-7}$ M and pH < 7
pure water has $[H^+] = [OH^-] = 1 \times 10^{-7}$ M and pH = 7
basic solutions have $[H^+] < 1 \times 10^{-7}$ M and pH > 7

Example 5. Calculate the pH of 0.10 M sodium hydroxide solution.
The formula of sodium hydroxide is NaOH and this compound is completely soluble. Therefore $[OH^-]$ ion in solution = 0.10 M.
As $[H^+] \times [OH^-] = 1.0 \times 10^{-14}$, then $[H^+] = 1.0 \times 10^{-14} / [OH^-]$
i.e. $[H^+] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}$ M
and $pH = -\log[H^+] = -\log(1.0 \times 10^{-13}) = -(-13.00) = 13.00$

Example 6. Calculate the pH of 0.010 M sodium hydroxide solution.
As in the previous example, because NaOH is completely soluble in water, $[OH^-]$ ion in solution = 0.010 M.
As $[H^+] \times [OH^-] = 1.0 \times 10^{-14}$, then $[H^+] = 1.0 \times 10^{-14} / [OH^-]$
i.e. $[H^+] = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12}$ M
and $pH = -\log[H^+] = -\log(1.0 \times 10^{-12}) = -(-12.00) = 12.00$

Notice how the pH of basic solutions approaches 7 from above as the base is diluted.

**Calculation of pH of weak acid solutions.**
In the previous examples, as the acid used in each case was strong, then there was equality between the concentration of acid used and the concentration of hydrogen ions resulting. For weak acids, because they are dissociated to only a small extent, an additional step is required to connect these two quantities and will not be dealt with here. However, once the hydrogen ion concentration has been calculated using that step, the pH is calculated in the same way as for strong acids.
Biological systems and pH.
Most biological systems require the pH of their environment to be within a small and stable range. Environments ranging from as tiny as the cytoplasm of cells to the enormous volumes of earth’s oceans all have an ideal pH which, if significantly altered, can cause serious damage to living organisms. For example, post world war 2 industrial development involved the burning of much sulfur-containing oil and coal which lead to high concentrations of sulfuric acid in the atmosphere. When precipitated as rain, acids cause vast tracts of land to be denuded of all vegetation and the acidic run off to waterways and lakes cause further considerable damage to aquatic life. This problem was addressed eventually in most countries by restrictions on the amount of the oxides of sulfur and nitrogen permitted to be released into the atmosphere and considerable progress has been made in reducing acid rain.

Unfortunately no progress has been made in another area where increasing acidity threatens dire consequences, namely the decreasing pH of the oceans. The pH of sea water has decreased from about 8.18 in the mid-1700s to about 8.10 by 1994. Currently the pH of sea water has reduced by 0.11 compared with the pre-industrial era. The source of the increased hydrogen ion concentration lies mostly in the reaction between carbon dioxide and water to produce the weak acid $\text{H}_2\text{CO}_3$ which dissociates slightly to form $\text{H}^+(\text{aq})$ ions and the conjugate base, hydrogencarbonate ion ($\text{HCO}_3^-$). Although a decrease in pH of 0.11 might not seem a lot, remember that pH is a logarithmic scale which means that a decrease of just 1 unit corresponds to a tenfold increase in hydrogen ion concentration. Thus this decrease in pH of the oceans amounts to an increase in hydrogen ion concentration of 30 % which has serious implications for marine organisms that have calcium carbonate based exoskeletons and shells. The consequences affect not only the organisms themselves but other creatures which feed on them further up the food chain. There is also a possibility that a loss of some of these minute organisms may have secondary effects on climate, decreasing the Earth's albedo via their effects on oceanic cloud cover.

Indicators.
Some substances when dissolved in solution have the ability to change their colour, depending on the solution pH. These are called ACID-BASE INDICATORS. Indicators are themselves weak acids which are either colourless or which have a very intense colour that is a characteristic of each particular indicator. The conjugate base of the weak acid must have a different colour.

When the pH of the solution is increased to a suitable value (i.e. the solution is made less acidic or more basic), the weak acid is converted into its conjugate base by loss of an $\text{H}^+$ ion and the colour of the solution is seen to change from that of the acidic form of the indicator to the colour of its conjugate base. There are many compounds that serve as indicators, some of them being common natural products found in plants.
Each indicator has a characteristic pH at which it changes from the acid form to the base form. For example, the best known indicator, litmus, changes at pH = 7. Other common indicators include methyl orange which changes colour from red to yellow at pH = 4 and phenolphthalein which changes from colourless to red at pH = 10. Universal indicator contains a number of indicators in the same solution and shows the pH of solutions within the range from pH = 4 to pH = 11.

### Check your understanding of this section.

What does the term self-ionising solvent mean?

What does the operator designated by the symbol p represent?

Why is pH a convenient way of expressing the concentration of dilute acid solutions?

If the pH of a solution is 1 unit greater than another solution, what would be the relative H\(^+\) concentrations of the two solutions?

Would the pH of pure water be 7 at a temperature of 50°C?

If a solution has a pH = 5, what does this mean (i) qualitatively and (ii) quantitatively regarding its acid/base properties?

What generalisation can be made regarding the pH of basic solutions?

Give the relationship which connects the concentrations of H\(^+\) and OH\(^-\) ions in water at room temperature.

What would be the pH of a 0.10M water solution of sodium hydroxide at 25°C?

Why can’t the pH of a weak acid be calculated directly from the concentration of the acid solution?

What are the characteristics required of a useful acid/base indicator?

### Objectives of this Topic.

When you have completed this Topic, including the tutorial questions, you should have achieved the following goals:

1. Know that an acid is a species which donates H\(^+\) and a base accepts H\(^+\).

2. Know the meaning of the terms: hydrogen bonding; strong acid; weak acid; conjugate base; conjugate acid; concentrated solution; dilute solution; dissociation.

3. Be able to write the formula for the conjugate base of any given acid or the conjugate acid of any base.

4. Know the meaning of the terms diprotic and triprotic acids.
5. Understand the concept of dynamic equilibrium as applied to weak acids, and be able to write an equilibrium equation for the partial dissociation of weak acids.

6. Know that water is slightly ionised and is capable of being both an acid and a base, and be familiar with the various representations used for the hydrogen ion.

7. Know the meaning of the symbol "pH" and understand why it is used.

8. Be able to calculate the pH of a strong acid solution and be able to convert pH to concentration of $\text{H}^+$.

9. Know that at 25°C, water contains $\text{H}^+$ ions and $\text{OH}^-$ ions both at an equal concentration of $1 \times 10^{-7}$ M and thus has a pH of 7.

10. Know that in acidic solutions, the concentration of $\text{H}^+$ ions is greater than the concentration of $\text{OH}^-$ ions and the pH < 7.

11. Know that in basic solutions the concentration of $\text{OH}^-$ ions is greater than the concentration of $\text{H}^+$ ions and the pH > 7.

12. Know the relationship between the concentrations of $\text{H}^+$ and $\text{OH}^-$ ions in water solutions at 25°C by experiment is $[\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14}$ M² and be able to calculate the pH of a strong base in solution.

13. Know why the pH of a weak acid cannot be calculated directly from the acid concentration.

14. Understand the principles underlying the operation of acid/base indicators.

If you are unsure about the interconversion of numbers to their logarithmic form and vice versa, please consult Appendix 2 at the end of these notes or the on-line maths revision notes available from the downloads page of the School of Chemistry and on the memory stick which also show how to use a calculator for this purpose at https://scilearn.sydney.edu.au/fychemistry/bridging_course/.

**Recommended follow up chemical modules:**
Section: Acids and Bases
Module: Acids and Bases
Topics covered: *Strong acids and bases; conjugate pairs; pH and pOH.*

Module: Weak acids and Bases
Topics covered: *Weak acids and bases; $K_a$ and $K_b$*
SUMMARY

Water has many unusual properties which arise from the highly polar O-H bonds between the O and H atoms of the water molecule. One such property is the ability to form weak intermolecular bonds to other water molecules in a form of bonding known as hydrogen bonding. For example, hydrogen bonding accounts for the anomalously high melting and boiling points of water. In other systems, hydrogen bonding is essential for the stability of proteins and the DNA double helix.

Water is slightly dissociated into hydrogen ions and hydroxide ions in a dynamic equilibrium and is referred to as a self-ionizing solvent. The extent of this dissociation depends on the temperature. The H$^+$ ion, being a naked proton, is incapable of free existence in water and instead is bonded to an H$_2$O molecule using one of the O atom’s lone pairs of electrons to form a positively charged ion represented most simply as H$_3$O$^+$. As in all water solutions, there are a number of other water molecules joined to it by hydrogen bonding. The O atoms in the H$_3$O$^+$ ion are all equivalent as are the H atoms and the positive charge is distributed over the ion as a whole rather than being localised on any given atom.

Acids are species which can donate hydrogen ions, H$^+$, while bases are species which can accept them. A strong acid in any given solvent (usually water) is one which is completely dissociated to H$^+$(aq) ions and its conjugate base. A conjugate acid/base pair is any pair of species whose formulas differ by a single H$^+$ ion. Some acid species can donate more than a single H$^+$ ion, for example H$_2$SO$_4$ and H$_3$PO$_4$ are diprotic and triprotic acids respectively.

Weak acids are those that are only partially dissociated to H$^+$ ions and conjugate base and remain for the most part in the non-dissociated form. Such acids exist in a dynamic equilibrium wherein acid species are dissociating at exactly the same rate as their conjugate base and H$^+$ ions are recombining. There are relatively few strong acids but many weak acids including organic acids containing the COOH group.

For acids that are dissociating in water as solvent, the water molecules behave as the base and accept the H$^+$ from the acid in an acid/base reaction. Water is an example of a self-ionising solvent as it can react with itself slightly to form H$_3$O$^+$ and OH$^-$ ions. Experimentally the concentration of each of these ions at 25°C is found to be 1 × 10$^{-7}$ M and they exist in a dynamic equilibrium with undissociated H$_2$O molecules. As a consequence of this equilibrium, if more H$^+$ is added to water by adding an acid, the concentration of H$^+$ in solution increases and the concentration of OH$^-$ decreases. Alternatively, adding a base to water removes H$^+$ ions and so their concentration decreases while the concentration of OH$^-$ increases.

In dilute water solutions of acids, the concentration of H$^+$ is still only small even for
strong acids, so it is more convenient to express it via the negative log of the concentration, the pH. Thus instead of referring to the H⁺ concentration of a solution as say 0.001 M, it is customary to quote this as its pH which is –log₁₀[H⁺]. In this example the pH would be –log(0.001) = –log(10⁻³) = 3.0. For strong acid solutions more concentrated than about 1 M, pH is not useful. Given that pure water has equal concentrations of H⁺ and OH⁻ and that at 25°C this is 1 × 10⁻⁷ M, then pure water has a pH = 7.0. Acidic solutions have a pH < 7 and basic solutions have a pH > 7. The pH of a strong acid solution can be calculated directly from the acid concentration because this is the same as the resultant concentration of H⁺. The pH of a basic solution can be calculated by first calculating the H⁺ concentration from the equilibrium expression [H⁺]× [OH⁻] = 1 × 10⁻¹⁴ at room temperature. The pH of weak acids cannot be calculated directly from the concentration of the acid as it is only partially dissociated.

An acid-base indicator is a weak acid which is either colourless or has an intense colour and whose conjugate base has a different colour. As the pH of a solution containing a small amount of indicator is increased, e.g. by adding OH⁻ solution, the relative amounts of the acid and base form of the indicator change. Ultimately as the weak acid form of the indicator is converted to its conjugate base, the colour of the solution changes to that of the conjugate base. The actual pH at which an indicator changes colour is a characteristic of each indicator and is not necessarily at pH = 7 although for the most commonly known indicator, litmus, the colour change does occur at pH = 7.

TUTORIAL QUESTIONS - TOPIC 13.

1. Explain the meaning of each of the following terms:
   - conjugate acid/base pair;
   - diprotic acid;
   - triprotic acid;
   - dynamic equilibrium;
   - strong acid;
   - weak acid;
   - self-ionising solvent;
   - pH.

2. Give the formula for the conjugate base of each of the following acids:
   - HNO₃ → HNO₂
   - HClO₄ → H₂SO₄
   - CH₃COOH → CH₃CH₂COOH
   - H₃PO₄ → HCOOH

   - HCN → HF
   - H₂SO₄ → HPO⁴²⁻
   - CH₃CH₂COOH → HSO₄⁻
   - H₂S
   - NH₄⁺ → HS⁻
3. Give the formula for the conjugate acid of each of the following bases:

- Cl<sup>−</sup>
- CN<sup>−</sup>
- SO<sub>4</sub><sup>2−</sup>
- CO<sub>3</sub><sup>2−</sup>
- HCOO<sup>−</sup>
- I<sup>−</sup>
- NH<sub>3</sub>
- O<sup>2−</sup>
- IO<sub>4</sub><sup>−</sup>
- HSO<sub>3</sub><sup>−</sup>
- NO<sub>2</sub><sup>−</sup>
- C<sub>2</sub>H<sub>5</sub>O<sup>−</sup>
- HS<sup>−</sup>
- H<sub>2</sub>O
- OH<sup>−</sup>
- C<sub>6</sub>H<sub>5</sub>COO<sup>−</sup>

4. The following are strong acids in water solution. Write an equation for the ionisation of each in water.

   (i) HI
   (ii) HBrO<sub>4</sub>
   (iii) HNO<sub>3</sub>
   (iv) HCl

5. The following are weak acids in water solution. Write an equation for the equilibrium which is established in each case.

   (i) HF
   (ii) HCN
   (iii) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH
   (iv) H<sub>2</sub>S

6. Calculate the pH of the following solutions of strong acids.

   (i) 0.010 M HNO<sub>3</sub>
   (ii) 0.15 M HI
   (iii) 0.05 M HClO<sub>4</sub>
   (iv) 1.5 × 10<sup>−3</sup> M HCl
   (v) 5.8 × 10<sup>−4</sup> M HBr
   (vi) 0.020 M HNO<sub>3</sub>
7. Calculate the concentration of $H^+$ present in solutions having the following pH values.

(i) 3.10  
(ii) 5.21  
(iii) 2.66  
(iv) 7.00  
(v) 1.55  
(vi) 4.10

8. (i) Express the following $H_3O^+$ concentrations as a pH and describe each as either “acidic” or “basic”:

(a) $1.0 \times 10^{-3}$ M  
(b) $5.4 \times 10^{-9}$ M

(ii) Calculate the pH of a $6.3 \times 10^{-6}$ M hydrochloric acid solution.

(iii) Calculate the concentration of $H^+$ in a solution which has pH = 8.37.

9. (a) Calculate the pH of the following sodium hydroxide solutions which contain the strong base, $OH^-$:

(i) NaOH (0.010 M)  
(ii) NaOH ($1.0 \times 10^{-3}$ M)  
(iii) NaOH ($1.0 \times 10^{-4}$ M)  
(iv) NaOH ($1.0 \times 10^{-5}$ M)
(b) What do you notice about the pH of basic solutions as the concentration of hydroxide ion decreases? How does this compare with the pH of an acid as it is progressively diluted with water?

10. Self Help Problems module “Acids and Bases” Q 1, 3.

ANSWERS TO TUTORIAL TOPIC 13

1. Conjugate acid/base pair: Any two species whose formulas differ by a single H⁺ ion - e.g. HCl and Cl⁻ where HCl is the conjugate acid of Cl⁻ and Cl⁻ is the conjugate base of HCl.

Diprotic acid: An acid that can donate two H⁺ ions - e.g. H₂SO₄.

Triprotic acid: An acid that can donate three H⁺ ions - e.g. H₃PO₄.

Dynamic equilibrium: The state achieved in a chemical reaction whereby the rate at which the reaction is proceeding from left to right is equal to the rate at which the reverse reaction is proceeding - the nett effect is that there is no overall change in the amounts of any of the components involved in the reaction even though they are reacting.

Strong acid: If all of the molecules or ions of a species in solution donate H⁺ ions to the solvent, that substance is called a strong acid. The solvent is usually (but not necessarily) water. This is shown by the use of a single arrow. e.g. hydrogen chloride

\[ \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \]

Weak acid: A substance whose molecules or ions do not all react to donate H⁺ ions to the solvent. Instead a dynamic equilibrium is established between the acid and its conjugate base. This is shown by use of the equilibrium arrows. e.g. acetic acid

\[ \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^- \]

Self ionising solvent: Any species that can both accept and donate an H⁺ ion to form the conjugate acid and the conjugate base of that solvent - e.g. water forms H₃O⁺ and OH⁻ when undergoing self ionization.

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]

pH: Defined as \(-\log_{10}[\text{H}^+]\) and used to conveniently represent the very small concentrations of H⁺ ions present in dilute water solutions of acids and bases. A change of one unit on the pH scale corresponds to a tenfold change in the concentration of H⁺ ions.
2. \( \text{NO}_3^- \) \( \text{NO}_2^- \) \( \text{CN}^- \) \( \text{F}^- \) 
\( \text{ClO}_4^- \) \( \text{HSO}_4^- \) \( \text{PO}_4^{3-} \) \( \text{I}^- \) 
\( \text{CH}_3\text{COO}^- \) \( \text{CH}_3\text{CH}_2\text{COO}^- \) \( \text{SO}_4^{2-} \) \( \text{HS}^- \) 
\( \text{H}_2\text{PO}_4^- \) \( \text{HCO}_2^- \) \( \text{NH}_3 \) \( \text{S}^{2-} \) 

3. \( \text{HCl} \) \( \text{HCN} \) \( \text{HSO}_4^- \) \( \text{HCO}_3^- \) 
\( \text{HCOOH} \) \( \text{HI} \) \( \text{NH}_4^+ \) \( \text{OH}^- \) 
\( \text{HIO}_4 \) \( \text{H}_2\text{SO}_3 \) \( \text{HNO}_2 \) \( \text{C}_2\text{H}_5\text{OH} \) 
\( \text{H}_2\text{S} \) \( \text{H}_3\text{O}^+ \) \( \text{H}_2\text{O} \) \( \text{C}_6\text{H}_5\text{COOH} \) 

4. (i) \( \text{HI} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{I}^- \) 
(ii) \( \text{HBrO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{BrO}_4^- \) 
(iii) \( \text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^- \) 
(iv) \( \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \) 

5. (i) \( \text{HF} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{F}^- \) 
(ii) \( \text{HCN} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CN}^- \) 
(iii) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^- \) 
(iv) \( \text{H}_2\text{S} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{HS}^- \) 

6. (i) \( \text{pH} = \text{log}_{10}[\text{H}^+] = \text{log}_{10}(0.010) = -(2.00) = 2.00 \) 
(2 significant figures - see Appendix 2 page 6) 
(ii) \( \text{pH} = \text{log}_{10}[\text{H}^+] = \text{log}_{10}(0.15) = -(0.82) = 0.82 \) 
(iii) \( \text{pH} = \text{log}_{10}[\text{H}^+] = \text{log}_{10}(0.05) = -(1.3) = 1.3 \) 
(iv) \( \text{pH} = \text{log}_{10}[\text{H}^+] = \text{log}_{10}(1.5 \times 10^{-3}) = -(2.28) = 2.82 \) 
(v) \( \text{pH} = \text{log}_{10}[\text{H}^+] = \text{log}_{10}(5.8 \times 10^{-4}) = -(3.24) = 3.24 \) 
(vi) \( \text{pH} = \text{log}_{10}[\text{H}^+] = \text{log}_{10}(0.020) = -(1.70) = 1.70 \) 

7. (i) \( \text{pH} = \text{log}_{10}[\text{H}^+] \) \( \therefore [\text{H}^+] = 10^{-\text{pH}} = 10^{-5.10} = 0.00 \times 10^{-6} \text{ M} \) 
(ii) \( \text{pH} = \text{log}_{10}[\text{H}^+] \) \( \therefore [\text{H}^+] = 10^{-\text{pH}} = 10^{-5.21} = 0.00 \times 10^{-5} \text{ M} \)
(iii) \( \text{pH} = -\log_{10}[H^+] \) \\
\( \therefore [H^+] = 10^{-\text{pH}} = 10^{-2.66} = 2.2 \times 10^{-3} \text{ M} \)

(iv) \( \text{pH} = -\log_{10}[H^+] \) \\
\( \therefore [H^+] = 10^{-\text{pH}} = 10^{-7.00} = 1.0 \times 10^{-7} \text{ M} \)

(v) \( \text{pH} = -\log_{10}[H^+] \) \\
\( \therefore [H^+] = 10^{-\text{pH}} = 10^{-1.55} = 2.8 \times 10^{-2} \text{ M} \)

(vi) \( \text{pH} = -\log_{10}[H^+] \) \\
\( \therefore [H^+] = 10^{-\text{pH}} = 10^{-4.10} = 7.9 \times 10^{-5} \text{ M} \)

8. (i) (a) \( \text{pH} = -\log_{10}[H^+] = -\log_{10}(1.0 \times 10^{-3}) = -(3.00) = 3.00 \) \\
As the pH is less than 7, the solution is acidic.

(b) \( \text{pH} = -\log_{10}[H^+] = -\log_{10}(5.4 \times 10^{-9}) = -(8.27) = 8.27 \) \\
As the pH is greater than 7, the solution is basic.

(ii) (a) \( \text{pH} = -\log_{10}[H^+] = -\log_{10}(6.3 \times 10^{-6}) = -(5.20) = 5.20 \)

(iii) \( \text{pH} = -\log_{10}[H^+] \) \\
\( \therefore [H^+] = 10^{-\text{pH}} = 10^{-8.37} = 4.3 \times 10^{-9} \text{ M} \)

9.(a) (i) As the solutions are those containing the strong base \( \text{OH}^- \) and it is the concentration of \( \text{OH}^- \) that is given, the first step is to calculate the concentration of \( H^+ \) using the relation \( [H^+] \times [\text{OH}^-] = 10^{-14} \) at 25°C.
\( [H^+] \times [\text{OH}^-] = 10^{-14} \) \\
\( \therefore [H^+] \times (0.010) = 10^{-14} \) \\
\( [H^+] = 10^{-14} / (0.010) = 10^{-12.00} \) \\
\( \text{pH} = -\log_{10}(10^{-12.00}) = -(-12.00) = 12.00 \)

(ii) \( [H^+] \times [\text{OH}^-] = 10^{-14} \) \\
\( \therefore [H^+] \times (1.0 \times 10^{-3}) = 10^{-14} \) \\
\( [H^+] = 10^{-14} / (1.0 \times 10^{-3}) = 10^{-11.00} \) \\
\( \text{pH} = -\log_{10}(10^{-11.00}) = -(-11.00) = 11.00 \)

(iii) \( [H^+] \times [\text{OH}^-] = 10^{-14} \) \\
\( \therefore [H^+] \times (1.0 \times 10^{-4}) = 10^{-14} \) \\
\( [H^+] = 10^{-14} / (1.0 \times 10^{-4}) = 10^{-10.00} \) \\
\( \text{pH} = -\log_{10}(10^{-10.00}) = -(-10.00) = 10.00 \)

(iv) \( [H^+] \times [\text{OH}^-] = 10^{-14} \) \\
\( \therefore [H^+] \times (1.0 \times 10^{-5}) = 10^{-14} \) \\
\( [H^+] = 10^{-14} / (1.0 \times 10^{-5}) = 10^{-9.00} \) \\
\( \text{pH} = -\log_{10}(10^{-9.00}) = -(-9.00) = 9.00 \)

(b) When a basic solution is diluted, its pH approaches 7 from above while the pH of an acidic solution approaches 7 from below when diluted.