# Acids and Bases

A common equilibrium situation involves acids and bases.

- Many cell processes rely on the correct pH balance.
- The charge state, and hence solubility, of many biological molecules is pH dependant.

Acids were originally recognized by their sour taste.

Bases often have a bitter taste and slippery feel

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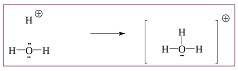
# Acids and Bases

The Danish chemist Johannes Brϕnsted and the English chemist Thomas Lowry put forward a model:

**ACID: proton donor ($H^+$)**
**BASE: proton acceptor**

In this context we are always looking at aqueous solutions in which the 'proton' is extensively hydrated.

It is represented as $H^+(aq)$ or $H_3O^+(aq)$.



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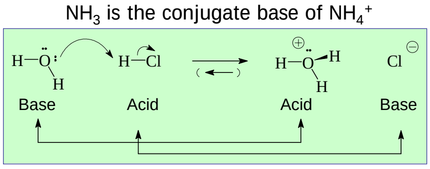
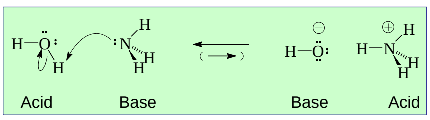
# Conjugate Pair

A conjugate acid - base pair differ by $H^+$

e.g. $NH_4^+$ is the conjugate acid of $NH_3$

$NH_3$ is the conjugate base of $NH_4^+$

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# Question

| Write the formula of the conjugate bases | Write the formula of the conjugate acids |
|---|---|
| $H_3O^+$ | $OH^-$ |
| $H_2SO_4$ | $H_2O$ |
| $HClO_4$ | $Cl^-$ |
| $CH_3COOH$ | $NH_3$ |

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# Strong & weak acids & bases

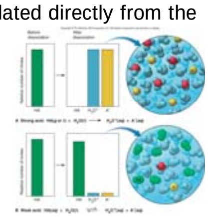
- *Strong* acids and bases completely dissociate in water and the pH of the solution is calculated directly from the *concentration* of the acid.

Common strong acids include:

HCl, HBr, HI, $HNO_3$, $H_2SO_4$

Common strong bases include:

NaOH, KOH, $Ca(OH)_2$



- Weak acids and bases are in an equilibrium

HA (aq) + $H_2O$ $\rightleftharpoons$ $H_3O^+(aq)$ + $A^-(aq)$

in short: HA (aq) $\rightleftharpoons$ $H^+(aq)$ + $A^-(aq)$

$$K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]}$$

# pH Scale

- $[H^+]$ is used as a measure of acidity and for convenience a log scale is employed

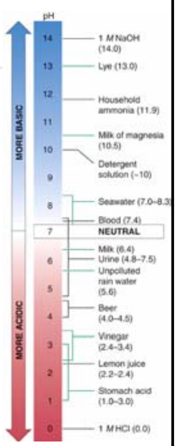
$pH = -\log [H^+(aq)]$

$pOH = -\log [OH^-(aq)]$

In acid solution (pH < 7) $[H^+] > 1 \times 10^{-7}$ M

In basic solution (pH > 7) $[H^+] < 1 \times 10^{-7}$ M

- pH and pOH are interconverted easily and so it is common to refer to just pH even when we have high $[OH^-]$.
  - pH + pOH = 14



## Examples

In strong acids and bases, complete dissociation occurs and pH calculated directly from starting concentrations

- Calculate the pH of:
  - 0.001 M $HNO_3$
    $[H^+]$ = 0.001 M, pH = 3.0
  - 0.001 M NaOH
    $[OH^-]$ = 0.001 M, pOH = 3.0, pH = 11.0
  - 0.001 M $Ca(OH)_2$
    $[OH^-]$ = 0.002 M, pOH = 2.7, pH =11.3



## Neutral solution

$H_2O \rightleftharpoons H^+(aq) + OH^-(aq)$

$K_w = [H^+][OH^-] = 1\times10^{-14}\ M^2$ at 25 °C

In neutral solution $[H^+] = [OH^-] = 1\times10^{-7}$ M
and pH = 7 (25 °C)



## Calculations using $K_a$

Calculate the pH of acetic acid $CH_3COOH$ (0.50 M). $K_a$ = 1.76 x $10^{-5}$ M

| | $CH_3COOH$ ⇌ | $H^+$ + | $CH_3COO^-$ |
|---|---|---|---|
| initial conc / M | 0.50 | - | - |
| change / M | -x | x | x |
| equilibrium conc / M | 0.50 - x | x | x |

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.76 \times 10^{-5}\ M = x^2 / (0.50 - x)$$

assume x << 0.5 then $x^2 = (1.76 \times 10^{-5})(0.50) = 8.76 \times 10^{-6}$
$x = [H^+(aq)] = 2.96 \times 10^{-3}$ M
$pH = -\log[H^+] = -\log[2.96 \times 10^{-3}] = 2.53$



## Question

Benzoic acid is used as a preservative in solutions and in mouth wash. A bottle of Listerine indicates the concentration of benzoic acid used is 1.5 mg $mL^{-1}$, what is the pH? ($C_6H_5COOH$, Molar mass = 122, $K_a = 6.3 \times 10^{-5}$ M)



## Polyprotic acids

Have more than one proton available.

- Example**:** $H_2CO_3$ (carbonic acid) has 2 protons that can be donated stepwise, one at a time - *diprotic acid.*
  - **$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$** $K_{a1} = 4.3 \times 10^{-7}$ M
  - **$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$** $K_{a2} = 5.6 \times 10^{-11}$ M
- Phosphoric acid is a *triprotic acid.*
  - **$H_3PO_4 \rightleftharpoons H^+ + H_3PO_4^-$** $K_{a1} = 7.5 \times 10^{-3}$ M
  - **$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$** $K_{a2} = 6.2 \times 10^{-8}$ M
  - **$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$** $K_{a3} = 4.8 \times 10^{-13}$ M
- For a typical weak polyprotic acid $K_{a1} > K_{a2} > K_{a3}$ indicating that the loss of the first proton is always much easier than subsequent ones.



## p$K_a$ and p$K_b$

$pH = -\log[H^+]$
$pOH = -\log[OH^-]$ and pH + pOH = 14

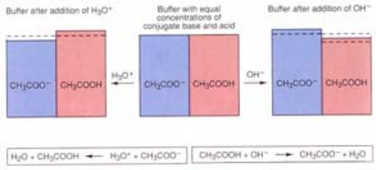
Similarly $pK_a = -\log K_a$
and $pK_b = -\log K_b$ and $pK_a + pK_b = 14$

The smaller p$K_a$, the stronger the acid.
The smaller p$K_b$, the stronger the base.

Usually p$K_a$ is reported for acids and bases – for bases it refers to the conjugate pair.

## Buffer solutions

- A buffer solution withstands changes in pH when a limited amount of acid or base is added.
- It is composed of a weak acid and a salt of a weak acid with a strong base (e.g. $CH_3COOH$ + $CH_3COONa$) or a weak base and a salt of a weak base with a strong acid (e.g. $NH_3$ + $NH_4Cl$).

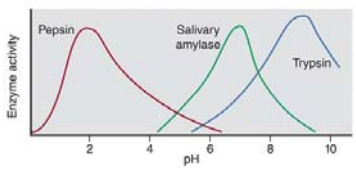





## Charge and pH

Many biological molecules are sensitive to pH

- Proton transfer is involved in many reactions.
- The charge on a molecule containing acid & base groups depends on the pH.




- Salivary amylase starts the digestion of starches in the mouth and has an optimum activity at pH = 6.8
- Pepsin starts the digestion of proteins in the stomach which is very acidic. It has an optimum activity at pH = 2.0
- Protein digestion continues in the small intestine where the pancreas releases trypsin which has an optimum activity at pH = 9.5

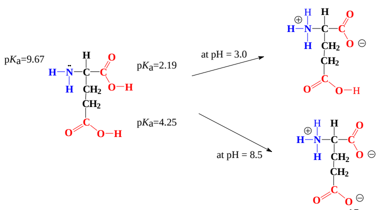


## Charge and pH

This is how to work out the charge on a molecule at a given pH

- When pH = p$K_a$, then [acid] = [base].
- When pH < p$K_a$, then protonated form dominates.
- When pH > p$K_a$, then de-protonated form dominates.

Example: Glutamic acid has the following structure; what is the charge on the molecule at pH 3.0 and pH 8.5?






## Solutions

- In a solution a *solute* dissolves homogenously in a *solvent*
- Usually there is much more solvent than solute
- The *solubility* of a substance is the maximum that can dissolve in a fixed amount of a particular solvent at a certain temperature

Solubility of NaCl in 100 mL water at 100 °C is 39.12 g

Solubility of AgCl in 100 mL water at 100 °C is 0.0021 g

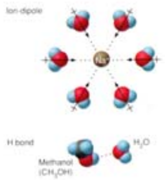


## Factors Affecting Solubility

In order for one substance to dissolve in another:

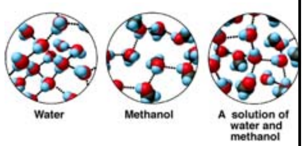
- Solute molecules must separate from each other
- Solvent molecules must make room for the ions/molecules of the solute
- Solute and solvent molecules must mix

- Whether a substance dissolves or not will depend on relative strengths of solute-solute, solute-solvent and solvent-solvent intermolecular forces

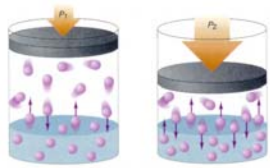



## Structure and Pressure Effects

- Structure Effects: Solubility is favoured if the solute and the solvent have similar polarities. Thus the structure of the molecules plays a definite part in the solubility of compounds.




- Pressure Effects: Gases - Carbonated beverages are always bottled at high pressures of $CO_2$ to ensure a high concentration of $CO_2$ in the drink



## Henry's Law $p = kC$

- The relationship between the gas pressure and the concentration of dissolved gas is given by Henry's Law
  - **$p$ is the partial pressure of the gas above the solution**
  - **$C$ represents the concentration of the dissolved gas**
  - **$k$ is a constant characteristic of a particular gas-solution**
- The smaller the value of $k$ the more *SOLUBLE* the gas

| EXAMPLE: | Gas | $k$ | |
|---|---|---|---|
| | **Helium** | **2700** | **atm $M^{-1}$** |
| | **Nitrogen** | **1600** | **atm $M^{-1}$** |
| | **Carbon dioxide** | **29** | **atm $M^{-1}$** |



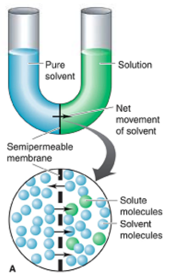
## Deep Sea Diving

- Helium used instead of nitrogen mixed with $O_2$ in deep sea diving
  - At significant depths (eg 30 m) the air in the lungs is around 4 atm, which causes a large amount of $N_2$ and $O_2$ to dissolve in the blood. $O_2$ can be metabolised but as the diver ascends, if done too quickly, the $N_2$ cannot be released quickly enough into the lungs and so the diver suffers 'the bends'.
  - He is ~half as soluble as nitrogen and so less must be released avoiding this problem.
  - He also has a higher rate of diffusion in the blood which makes He more acceptable.



## Osmotic Pressure

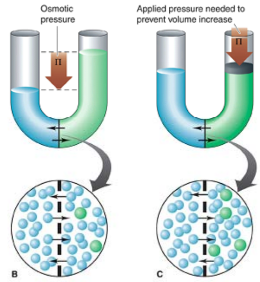
- The flow of solvent molecules into a solution through a semi-permeable membrane is called OSMOSIS.
- It is the number of particles in the solution which is important, not their chemical nature.
- More solvent molecules enter the solution than leave it. As a result the solution volume increases and its concentration decreases.






## Osmotic Pressure

- The solution exerts a backward pressure - the osmotic pressure ($\pi$) that eventually equalises the flow of solvent molecules in both directions
- The osmotic pressure is also defined as the applied pressure required to *prevent* this volume change






## Osmotic Pressure

- $\pi$ = ***cRT***
  - $\pi$ is the osmotic pressure in atm,
  - $c$ is the molarity of the solute (mol $L^{-1}$)
  - $R$ is the gas law constant and
  - $T$ is the temperature in $K$



## Example

Contact lens rinses consist of 0.015 M NaCl solution to prevent any changes in volume of corneal cells. What is the osmotic pressure of this saline solution at 38 °C?

$\pi$ = ***cRT***

$\pi$ = (2 x 0.015 mol $L^{-1}$)(0.082 L atm $K^{-1}$ $mol^{-1}$)(273 + 38 K)
= 0.77 atm

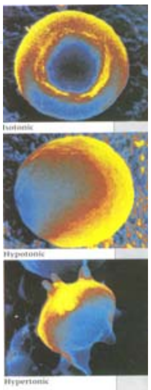
# Isotonic Solutions

ISOTONIC SOLUTION - identical osmotic pressure to cell fluid

HYPOTONIC SOLUTIONS – lower osmotic pressure than cell fluid - cell swells & ruptures - transfer of fluid INTO CELL – LYSIS

HYPERTONIC SOLUTIONS - higher osmotic pressure than cell fluid - cell shrivels - transfer of fluid OUT OF CELL – CRENATION

The word “tonocity” refers to the tone, or firmness of a biological cell.





# Question

Solutions for an intravenous injection must have the same osmotic pressure as blood. According to the label on the bottle each 100 mL of normal saline solution used for intravenous injection contains 900 mg of NaCl.

- What is the molarity of NaCl in normal saline solution?

- What is the osmotic pressure of normal saline solution at the average body temperature of 37 °C?

- What concentration of glucose ($C_6H_{12}O_6$) has the same osmotic pressure as normal saline solution.