CBMS107: Acids and Bases

DEFINITION

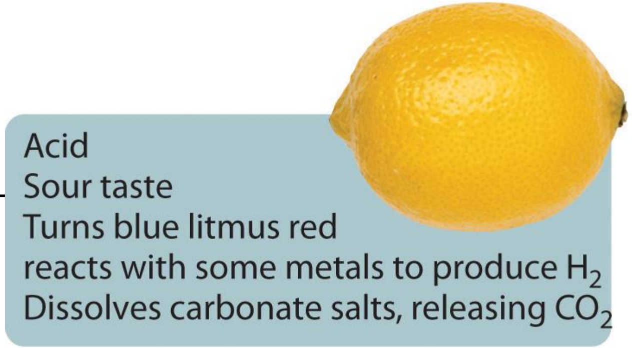
EQUILIBRIUM

BUFFERS

Note1: hydrogen ion, H^+, is also referred to as a **proton**. This is because the H^+ cation is simply a proton with no surrounding valence electron.

Note2: brackets **[ ]** indicate that we are referring to the concentration of species. For example, when we write **[H^+]**, we mean concentration of H^+.

Acids and Bases (AB)



- A further important concept qualitatively related to electronegativity and bond polarity is that of **acidity** and **basicity**.

- For example, the acid-base behaviour of many organic molecules helps to explain why and how they react with other molecules.

- We characterise acids and bases as either “**strong**” or “**weak**”.

	Weak AB	*Strong AB*
Acid	$H_2O(l)$ $HCOOH(aq)$	$HCl(aq)$ $HNO_3(aq)$
Base	$H_2O(l)$ $NH_3(aq)$	$LiOH(aq)$ $NaOH(aq)$

Acids and Bases

ARRHENIUS MODEL

- The simplest definition for AB is the Arrhenius model, which while useful, has limited interpretative value, especially in organic chemistry. In aqueous solution:
  - Acids dissociate to form **hydrogen ions (H^+)**

$$HCl(g) \xrightarrow{\text{water}} \boxed{H^+(aq)} + Cl^-(aq)$$

  - Bases dissociate to form **hydroxide ions (OH^-)**

$$NaOH(s) \xrightarrow{\text{water}} Na^+(aq) + \boxed{OH^-(aq)}$$

- Note: a **solution** is a homogeneous mixture composed of a **solvent** and one or more **solutes**. If the solvent is water, we say that the solution is an aqueous solution and use the symbol **(aq)**.

- For example, sea water is a liquid solution, composed of water and dissolved substances (eg Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, etc).

Acids and Bases

MEASURE OF STRENGTH

Pure water, $H_2O(l)$ does not conduct electricity

Sucrose solution, $C_{12}H_{22}O_{11}(aq)$ non-electrolyte does not conduct electricity

Sodium chloride solution, $NaCl(aq)$ electrolyte conducts electricity

An electrolyte solution contains ions that serve as charge carriers, causing the bulk to light.

- A substance that dissociates into ions when it is in a solution is called an **electrolyte**.

$$AB(aq) \longrightarrow A^{+}(aq) + B^{-}(aq)$$

- **Strong AB** are generally strong electrolytes, as they **dissociate fully** to produce ions. Eg:

$$HCl(g) \xrightarrow{\text{water}} \boxed{H^{+}(aq)} + Cl^{-}(aq)$$

- **Weak AB** are generally weak electrolytes, as they **do not dissociate fully** to produce ions. Eg:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^{-}(aq) + H^{+}(aq)$$

(equilibrium symbol)

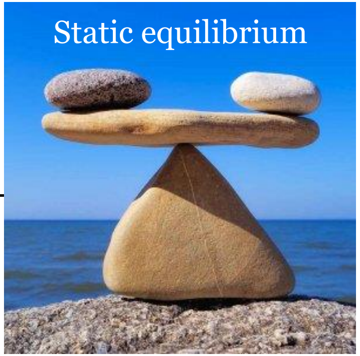
Equilibrium

- **What do we mean when we say that weak AB dissociate fully to produce ions?**

- Some reactions are **reversible** ie they do not reach completion. In a reversible reaction, both the **forward** and **reverse** reactions can occur.

$$\underbrace{CH_3COOH(aq)}_{\text{“left” side}} \underset{\text{“reverse”}}{\overset{\text{“forward”}}{\rightleftharpoons}} \underbrace{CH_3COO^-(aq) + H^+(aq)}_{\text{“right” side}}$$

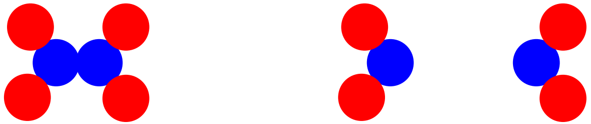
- If a system at equilibrium is disturbed (eg concentration of a species changes), then the system reacts to counteract the disturbance (Le Chatelier’s Principle).



Dynamic equilibrium
- saturated sodium acetate solution

Equilibrium

- N_2O_4 is a colourless substance that dissociates to form NO_2 (sealed tube):

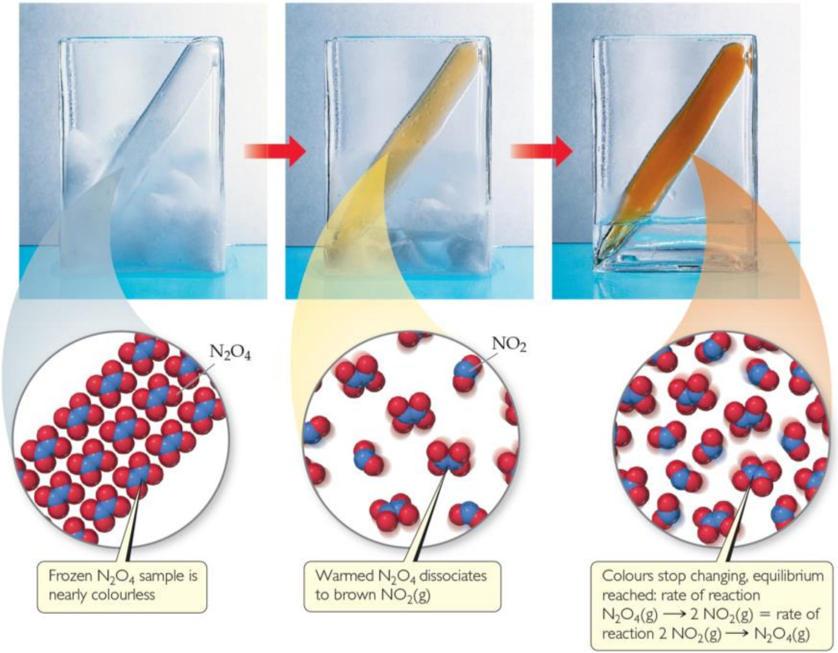


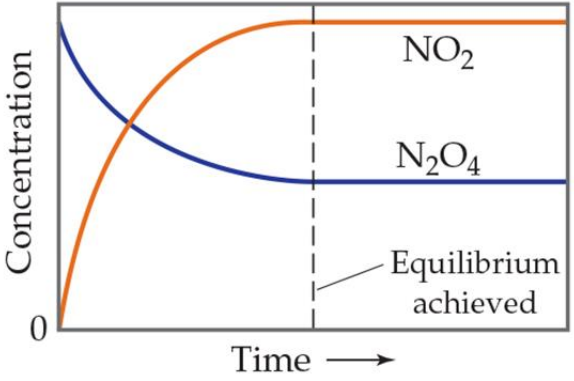
$$N_2O_4(g) \rightleftharpoons NO_2(g) + NO_2(g)$$

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

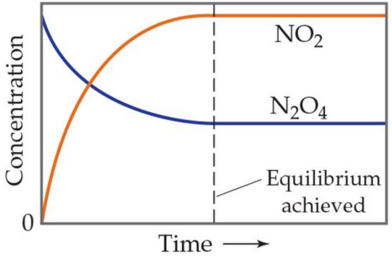
We write equations using coefficients to indicate multiple species.

- At equilibrium, the reactant and product concentrations are not changing (ie constant).





Equilibrium



- At equilibrium, the relationship between reactant and product concentration can be expressed using an **equilibrium constant expression**, $K_{eq.}$

- For an **aqueous** equilibrium, with two reactants and two products dissolved in water, the general expression for $\mathbf{K_{eq}}$ is:

$$aA_{(aq)} + bB_{(aq)} \rightleftharpoons dD_{(aq)} + eE_{(aq)}$$

$$\boxed{K_{eq} = \frac{[D]^d\,[E]^e}{[A]^a\,[B]^b}}$$

- As an example, consider the dissociation of hydrogen cyanide:

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CN^-{}_{(aq)}$$

$$\boxed{K_{eq} = \frac{[H_3O^+][CN^-]}{[HCN]}}$$

Note that we **do not** include solids or pure liquids, like water (ie water$_{(l)}$) in our equilibrium constant expression, K_{eq}.

Equilibrium

- We can calculate a K_{eq} from reactant and product concentrations, by substituting their values into the corresponding equilibrium constant expression.

- For example, consider the hydrolysis of cyanide:

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$$

$$K_{eq} = \frac{[H_3O^+][CN^-]}{[HCN]}$$

Example concentrations:
$[H_3O^+] = 8.6 \times 10^{-6}$ M
$[CN^-] = 8.6 \times 10^{-6}$ M
$[HCN] = 0.15$ M

$$\boxed{\begin{aligned} K_{eq} &= \frac{(8.6 \times 10^{-6})(8.6 \times 10^{-6})}{0.15} \\ &= 4.93 \times 10^{-10} \end{aligned}}$$

- Because K_{eq} is very small, the reaction does not proceed very far forward (toward products) before reaching equilibrium.

Equilibrium

MACQUARIE University

- Most equilibrium reactions do not to have equal reactant and product concentrations, as the equilibrium favours either the forward (products) or reverse (reactants) reactions.

- The magnitude of K_{eq} is very useful for quickly deciding if an equilibrium favours the forward or reverse reaction. For example, when:
  - $K_{eq} = 5.21 \times 10^{17}$, the reaction mixture is dominated by products, as $K_{eq} >>> 1$
  - $K_{eq} = 1.67$, the equilibrium somewhat favours product formation, as $K_{eq} > 1$
  - $K_{eq} = 3.22 \times 10^{17}$, the reaction mixture is dominated by reactants, as $K_{eq} <<< 1$
  - $K_{eq} = 0.49$, the equilibrium somewhat favours the reverse reaction, as $K_{eq} < 1$

Acids and Bases

BRØNSTED-LOWRY MODEL

MACQUARIE University

- Now that we know about equilibrium, we can move from the Arrhenius model to the Brønsted-Lowry model, which is a more general definition of **AB based on the fact that AB reactions involve the transfer of H^+ between substances**.

- Eg, when HCl dissolves in water, we can write this as a proton transfer reaction.

- Arrhenius model $$HCl(g) \xrightarrow{\text{water}} H^+(aq) + Cl^-(aq)$$

- Brønsted-Lowry model $$H_2O(l) + HCl(g) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

The interaction of a proton with a water molecule forms the hydronium ion, $\mathbf{H_3O^+}$(aq). Chemists use H^+(aq) and H_3O^+(aq) interchangeably to represent a hydrated proton.

Acids and Bases

BRØNSTED-LOWRY MODEL

- The Brønsted-Lowry model defines:
  - acid as a substance (molecule or ion) that **donates** H^+ to another substance
  - base as a substance that **accepts** H^+

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{NH_3(aq)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- In the Brønsted-Lowry model, an acid and base always work together to transfer a H^+.

- Note that water acts as either an acid or base. **Amphiprotic** substances act as a:
  - **base** when **combined with** something more **strongly acidic** than itself
  - **acid** when **combined with** something more **strongly basic** than itself

Acids and Bases

BRØNSTED-LOWRY MODEL

MACQUARIE University

- In any acid-base equilibrium, both the forward reaction (to the right) and the reverse reaction (to the left) involve H^+ transfer. Eg:

$$\underset{\text{acid}}{HX(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + X^-(aq)$$

- As a result we can define so called **conjugate acid-base pairs**, where:
  - an acid has a conjugate base, formed by removing H^+ from the acid
  - a base has a conjugate acid, formed by adding H^+ to the base

remove H^+

$$\underset{\text{acid}}{HX(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{X^-(aq)}$$

add H^+

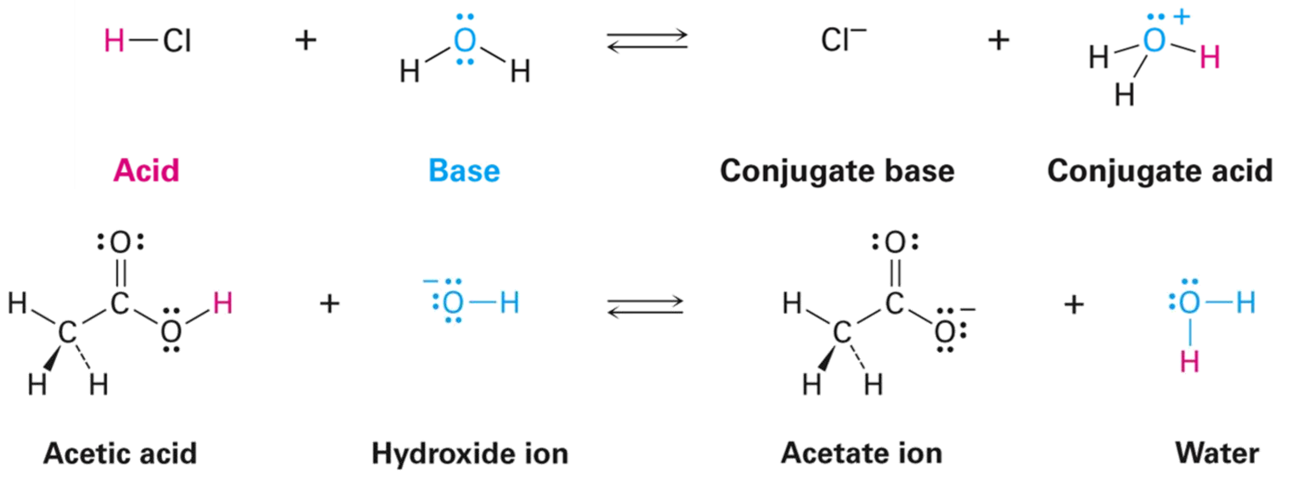
Acids and Bases

BRØNSTED-LOWRY MODEL

- Visualizing proton exchange reactions using Lewis structures can be helpful when you are starting out.

$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{NH_4^{+}(aq)} + \underset{\text{conjugate base}}{OH^{-}(aq)}$$

$$\underset{\text{acid}}{HNO_3(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^{+}(aq)} + \underset{\text{conjugate base}}{NO_3^{-}(aq)}$$



Acids and Bases

RELATIVE AB STRENGTH

- Some acids are better H^+ donors than others; likewise, some bases are better H^+ acceptors than others.

- The **stronger an acid**, the **weaker its conjugate base**; the **stronger a base**, the **weaker its conjugate acid**.

- There is an inverse relationship between the strength of an acid (base), and the strength of its conjugate base (acid).

	Acids	Bases	
Strong acids	HCl	Cl^-	Negligible basicity
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	$H_3O^+(aq)$	H_2O	
Weak acids	HSO_4^-	SO_4^-	Weak basicity
	H_3PO_4	$H_2PO_4^-$	
	CH_3COOH	CH_3COO^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HPO_4^{2-}	PO_4^{3-}	
	H_2O	OH^-	
Negligible acidity	H_2	H^-	Strong base
	CH_4	CH_3^-	

Acid strength increasing

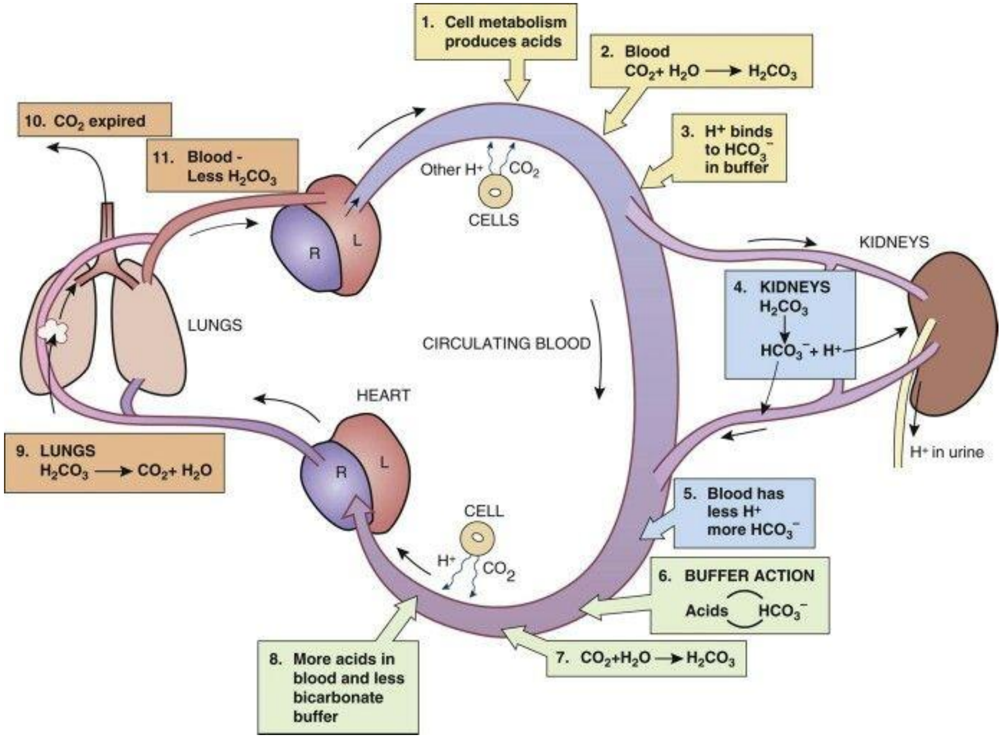
Base strength increasing

Acids and Bases

BUFFERS

MACQUARIE University

- Most acids and bases are weak.
- In nature eg biological systems, weak acids and bases are able to form a special kind of solution called a **buffer**.
- Buffers are special, as they are able to **resist changes** in H^+ and OH^- concentration.



Acids and Bases

BUFFERS - COMMON-ION EFFECT

- We have seen that the Brønsted-Lowry equilibrium for weak acids and bases lies to the **left** (ie not dissociated):

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

- Imagine a solution that contains not only a **weak acid** (CH_3COOH), but also a **soluble salt of its conjugate base** (CH_3COONa).

$$\boxed{CH_3COOH(aq)} \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$$\boxed{CH_3COONa(aq)} \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

Acids and Bases

BUFFERS - COMMON-ION EFFECT

- A solution containing both CH_3COOH and CH_3COONa has what is known as a **common ion** (CH_3COO^-).

$$CH_3COOH(aq) \rightleftharpoons \boxed{CH_3COO^-(aq)} + H^+(aq)$$

$$CH_3COONa(aq) \longrightarrow \boxed{CH_3COO^-(aq)} + Na^+(aq)$$

- By combining the CH_3COOH and CH_3COONa in the same solution, the **equilibrium shifts to the left** (Le Chatelier's principle)

- The common ion reduces the quantity of $H^+(aq)$ present in the solution

Acids and Bases

BUFFERS - COMMON-ION EFFECT

- In other words, the presence of the added acetate ion causes the acetic acid to ionise less than it normally would. This is called the *common-ion effect*.

- *Whenever a weak electrolyte and a strong electrolyte containing a common ion are together in solution, the* ***weak electrolyte ionises less than it would if it were alone in solution****.*

weak electrolyte $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

strong electrolyte $CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$

Acids and Bases

BUFFERS

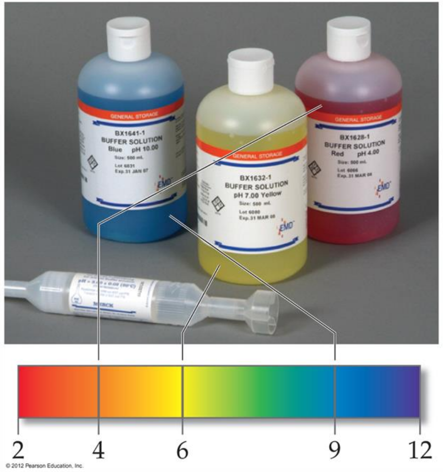
- Buffer solutions are usually prepared from a weak acid and a salt of that acid, or from a weak base and a salt of that base.

- A buffered solution is able to resist large changes in acidity (basicity) following the addition of a strong acid (strong base), as it contains:

  - an acidic species to neutralise OH^- anions

  - a basic species to neutralise H^+ cations.

- **Buffers have specific acidity (basicity) ranges over which they "work" (resist change) most effectively.**



Stop