CHEM 191

Energetics & Equilibria in Biological Systems

Module 1 Lecture 5

Acids and bases

Chapter 17, Brown

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Chemical reactions

- There are only three types of chemical reaction

  1) electron transfer $X + Y \rightarrow X^+ + Y^-$ **Module 2**

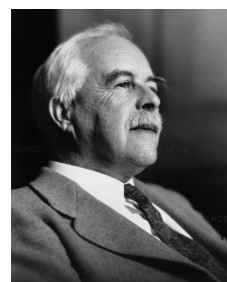 2) precipitation $X^+(aq) + Y^-(aq) \rightarrow XY(s)$ **Lab 1**

  3) acid-base   **acid + base → products**

- Several definitions of acids and bases. The most general is
    due to G.N Lewis (1923)
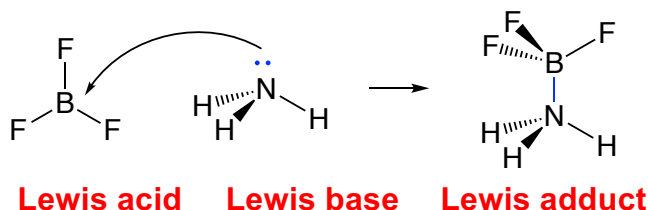
  A Lewis acid is an *electron-pair acceptor*

  A Lewis base is an *electron-pair donor*

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Lewis acids and bases

- The reaction of BF_3 with NH_3 is a Lewis acid-base reaction

Lewis acid   **Lewis base**   **Lewis adduct**

Get formation of a covalent B-N bond, in which both electrons formally derive from the N atom. Such a bond is sometimes called a *coordinate* or *dative* bond.

- Many examples of Lewis acid-base reactions in both **organic** and coordination chemistry.

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Brønsted-Lowry acids and bases

- Proposed by Johannes Brønsted and Martin Lowry in 1923.

An acid is a **proton (H^+) donor**
A base is a **proton (H^+) acceptor**

- Mostly used to describe acid-base behaviour **in aqueous solution**.

- The simplest example is water reacting with itself

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

- One H_2O molecule (acid) donates a proton (H^+) to the other (base) to give H_3O^+ (the **hydronium** ion) and OH^- (the **hydroxide** ion). Water acts as an acid *and* a base. It is *amphiprotic*

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Conjugate acids and bases
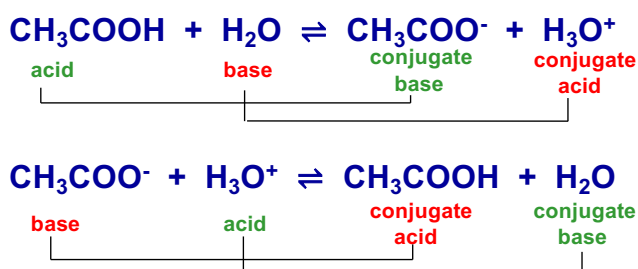
- Note that both the forward and reverse reactions in

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

involve the transfer of a proton and are thus both acid-base reactions.

- Acid-base reactions will always involve two sets of species which differ only by a proton. These species are called ***conjugate acid-base pairs***

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

    acid   base   conjugate   conjugate
                                 base   acid

$$CH_3COO^- + H_3O^+ \rightleftharpoons CH_3COOH + H_2O$$

    base   acid   conjugate   conjugate
                                 acid   base

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Examples

Acid	Conjugate base
HCl	Cl^-
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
CH_3COOH	CH_3COO^-
NH_4^+	NH_3
H_2O	OH^-
H_3O^+	H_2O
H_3PO_4	$H_2PO_4^-$
$H_2PO_4^-$	HPO_4^{2-}
HPO_4^{2-}	PO_4^{3-}

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What makes an acid?

- Methane, CH_4, contains four protons but yet is not measurably acidic.

- Hydrochloric acid, HCl, is an extremely strong acid.
  ### Why??

- In order to act as an acid, a compound must have a proton attached to an **electronegative** element via a polar bond.

- The strongest acids generally have a proton attached to a halogen (Group 17) or oxygen (Group 16).

O 8	F 9
	Cl 17
	Br 35
	I 53
	At 85

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What makes a base?

- Because the base needs to make a new bond to the H^+ when it accepts it, it needs to have **at least one lone pair of electrons**. Therefore, bases usually contain Group 15, 16 or 17 elements.

- The strongest bases are usually formed from deprotonation of molecules containing X-H bonds, where X is a Group 15 or 16 element.

  e.g.   **OH^- hydroxide**, formed by deprotonation of water

  OR^- alkoxide, formed by deprotonation of an alcohol

  (R = any alkyl group; CH_3, C_2H_5 etc)

  NH_2^- amide, formed by deprotonation of ammonia

15	16
N 7	O 8
P 15	S 16
As 33	Se 34
Sb 51	Te 52
Bi 83	Po 84

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Auto-ionisation of water

- The reaction $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ is an equilibrium process and has an associated equilibrium constant, K_w, the *auto-ionisation constant* of water (also known as the *autoprotolysis constant*)

$$K_w = [H_3O^+]_e[OH^-]_e = 1.0 \times 10^{-14} \text{ at } 25.0 \text{ }^oC.$$

- In neutral water, $[H_3O^+] = [OH^-]$ and therefore, at 25.0 ^oC

$K_w = [H_3O^+]^2 = 1.0 \times 10^{-14}$

$[H_3O^+] = 1.0 \times 10^{-7} \text{ mol L}^{-1} = [OH^-]$

- Note we have written $[H_3O^+]$, rather than $[H^+]$. The H^+ ion has no finite lifetime in water. It is so highly polarising that it will immediately bind to a water molecule to form H_3O^+. Note also that water is a weak electrolyte.

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Quantifying Acidity - pH

- Use the pH scale for measuring $[H_3O^+]$ in aqueous solution.

$$pH = -\log [H_3O^+]$$

where p means –$\log_{10}$

- Have seen that $[H_3O^+] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$ in pure water at 25.0 ^oC. Therefore

$pH = -\log(1.0 \times 10^{-7}) = 7$

- To convert from a pH to $[H_3O^+]$, use the relationship

$$[H_3O^+] = 10^{-pH}$$

- A pH of 7 will thus give $[H_3O^+] = 10^{-7} = 1.0 \times 10^{-7} \text{ mol L}^{-1}$

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pOH and pK_w

- Can also define pOH as

$$\boxed{pOH = -\log [OH^-]}$$

- Pure water at 25.0 °C will have pOH = 7.

- Similarly, can define pK_w as

$$\boxed{pK_w = -\log K_w}$$
$$= 14 \text{ at } 25.0 \text{ °C}$$

We know that $[H_3O^+][OH^-] = K_w$

Taking -log of both sides gives

$$-\log [H_3O^+] + (-\log [OH^-]) = -\log (1 \times 10^{-14})$$
$$pH + pOH = pK_w$$

or $\qquad$ pH + pOH $\quad$ = 14.0 (at 25.0 °C)

$[H_3O^+]$ and $[OH^-]$ are related

- Because of the form of the equilibrium expression for the autoprotolysis of water, $[H_3O^+]$ and $[OH^-]$ cannot vary independently. If one increases, the other must decrease.

- e.g. $[H_3O^+] = 3.2 \times 10^{-5}$ mol L^{-1} in a can of beer at 25 °C. Calculate the $[OH^-]$.

$$K_w = [H_3O^+][OH^-] \quad \rightarrow \quad [OH^-] = K_w / [H_3O^+]$$
$$= (1.0 \times 10^{-14}) / (3.2 \times 10^{-5})$$
$$= 3.1 \times 10^{-10} \text{ mol L}^{-1}$$

The pH scale

[H⁺] (M)	pH	pOH	[OH⁻] (M)	
$1 (1 \times 10^0)$	0.0	14.0	1×10^{-14}	
1×10^{-1}	1.0	13.0	1×10^{-13}	Stomach acid
1×10^{-2}	2.0	12.0	1×10^{-12}	Lemon juice
1×10^{-3}	3.0	11.0	1×10^{-11}	Cola, vinegar
1×10^{-4}	4.0	10.0	1×10^{-10}	Wine / Tomatoes
1×10^{-5}	5.0	9.0	1×10^{-9}	Black coffee
1×10^{-6}	6.0	8.0	1×10^{-8}	Rain / Saliva
1×10^{-7}	7.0	7.0	1×10^{-7}	Milk / Human blood
1×10^{-8}	8.0	6.0	1×10^{-6}	Seawater
1×10^{-9}	9.0	5.0	1×10^{-5}	Borax
1×10^{-10}	10.0	4.0	1×10^{-4}	Lime water
1×10^{-11}	11.0	3.0	1×10^{-3}	
1×10^{-12}	12.0	2.0	1×10^{-2}	Household ammonia
1×10^{-13}	13.0	1.0	1×10^{-1}	Household bleach
1×10^{-14}	14.0	0.0	$1 (1 \times 10^0)$	

Increasing acid strength

Increasing base strength

$$pH + pOH = 14$$

$$[H^+][OH^-] = 1 \times 10^{-14}$$

▶ **FIGURE 17.4** Concentrations of H⁺ and pH values of some common substances at 25 °C.

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Temperature effects

- Equilibrium constants change with temperature.

- At 35 °C, $K_w = 4.8 \times 10^{-14}$.

    Therefore, in pure water at 35 °C:

    $[H_3O^+] = [OH^-] \quad = (4.8 \times 10^{-14})^{1/2}$

    $\qquad\qquad\qquad\quad = 2.2 \times 10^{-7}$ mol L⁻¹

    Thus pH = 6.66, pOH = 6.66 at 35 °C.

- Must therefore be careful what we mean by the words 'neutral', 'acidic' and 'basic'. Might usually think of a solution having a pH of 6.66 being slightly acidic, but at 35°C it is in fact neutral (**because [H₃O⁺] still = [OH⁻]**).

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Acid strengths

- Some acids donate their protons essentially completely to water. We say they undergo **complete dissociation** (i.e. strong electrolytes)

    e.g. **HCl + H$_2$O → H$_3$O$^+$ + Cl$^-$**

    The solution consists of only H$_3$O$^+$ and Cl$^-$.

- Acids which donate their protons on reactions which got to completion are called **strong acids**.

    Examples include HCl (hydrochloric, present in gastric acid), H$_2$SO$_4$ (sulfuric), HNO$_3$ (nitric), HBr (hydrobromic), HI (hydroiodic), HClO$_4$ (perchloric)

- Can calculate [H$_3$O$^+$] in strong acid solutions from the stoichiometry of the dissociation reaction.
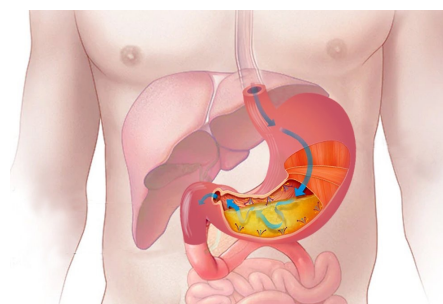
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Example

- The strong acid HCl, which is a key component of the gastric acid in your stomach, typically has an *in vivo* concentration of 0.16 mol L^{-1}. Calculate [H$_3$O$^+$] and the pH of the HCl.

    HCl + H$_2$O → H$_3$O$^+$ + Cl$^-$

- As the reaction proceeds to completion

    [H$_3$O$^+$] = [HCl]$_i$ = 0.16 mol L^{-1}

    pH = -log [H$_3$O$^+$]

      = -log (0.16)

      = 0.80

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Base strengths

- Some bases react with water to give essentially complete formation of hydroxide ion, OH⁻.

$$e.g. \; NH_2^- + H_2O \rightarrow NH_3 \; + \; OH^-$$

The resulting solution consists of only NH_3 and OH^-

Alternatively, an ionic compound, such as NaOH, can dissolve completely in water to give OH⁻

$$NaOH(s) \rightarrow Na^+ + OH^-$$

- Bases which generate OH⁻ in reactions which go to completion are called *strong bases*.

- Can calculate [OH⁻] in solutions of strong bases from the reaction stoichiometry.

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Example

- Calculate the pH of a 0.0675 mol L⁻¹ solution of the strong base NaOH

- NaOH is a strong electrolyte and undergoes complete dissociation. The reaction is therefore

$$NaOH(aq) \; \rightarrow \; Na^+(aq) \; + \; OH^-(aq)$$

and we assume complete formation of $Na^+(aq)$ and $OH^-(aq)$.

Thus $[OH^-] = [NaOH]_i = 0.0675$ mol L⁻¹

- pOH = -log(0.0675) = 1.17
- pH   = 14 − pOH
          = 14 − 1.17
          = 12.83

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Note - [H₃O⁺] from water

- The auto-ionisation reaction adds $[H_3O^+]$ (and OH^-) to any aqueous solution, even one containing another acid.

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

- Usually negligible, **but** must sometimes take it into account.

e.g. calculate the pH of a 1×10^{-10} mol L^{-1} solution of HCl.
    Would normally just say
$$pH = -\log [H_3O^+] = -\log(1 \times 10^{-10}) = 10$$
    This is obviously wrong! (*pH = 10 is a <u>basic</u> solution*)

- Have neglected contribution to $[H_3O^+]$ from water

[H₃O⁺] from water

Here there are two sources of H_3O^+;
        H_3O^+ from HCl (1×10^{-10} mol L^{-1})
        H_3O^+ from H_2O (1×10^{-7} mol L^{-1})

Therefore
        $[H_3O^+]_{total} = (1 \times 10^{-10} + 1 \times 10^{-7}) \approx 1 \times 10^{-7}$ mol L^{-1}
        $pH = -\log [H_3O^+] = -\log(1 \times 10^{-7}) = 7$

So, if $[H_3O^+]$ from the acid (strong or weak) is comparable to 1×10^{-7} mol L^{-1}, must take the contribution from water into account. The ***maximum*** contribution from water is 1×10^{-7} mol L^{-1}

Antacids

- the stomach secretes acids (including HCl) to help digest foods
- a mucosal lining protects the stomach and digestive tract from the corrosive effects of such acids

- if there is excessive acid production or a weakness in the lining, ulcers can develop
- can treat ulcers by : (1) removing excess acid, or (2) decreasing production of acid

   Antacids are simple bases that neutralise excess digestive acid

e.g. Gaviscon® $CaCO_3$, $NaHCO_3$

   Mylanta® $Mg(OH)_2$ + $Al(OH)_3$

   Quick-Eze® $CaCO_3$ + $MgCO_3$ + $Mg_2Si_3O_8$

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✳ Homework ✳

Brown (15th)

Problems 16.63, 16.64, 16.73, 16.77, 16.79

Answers on Blackboard

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