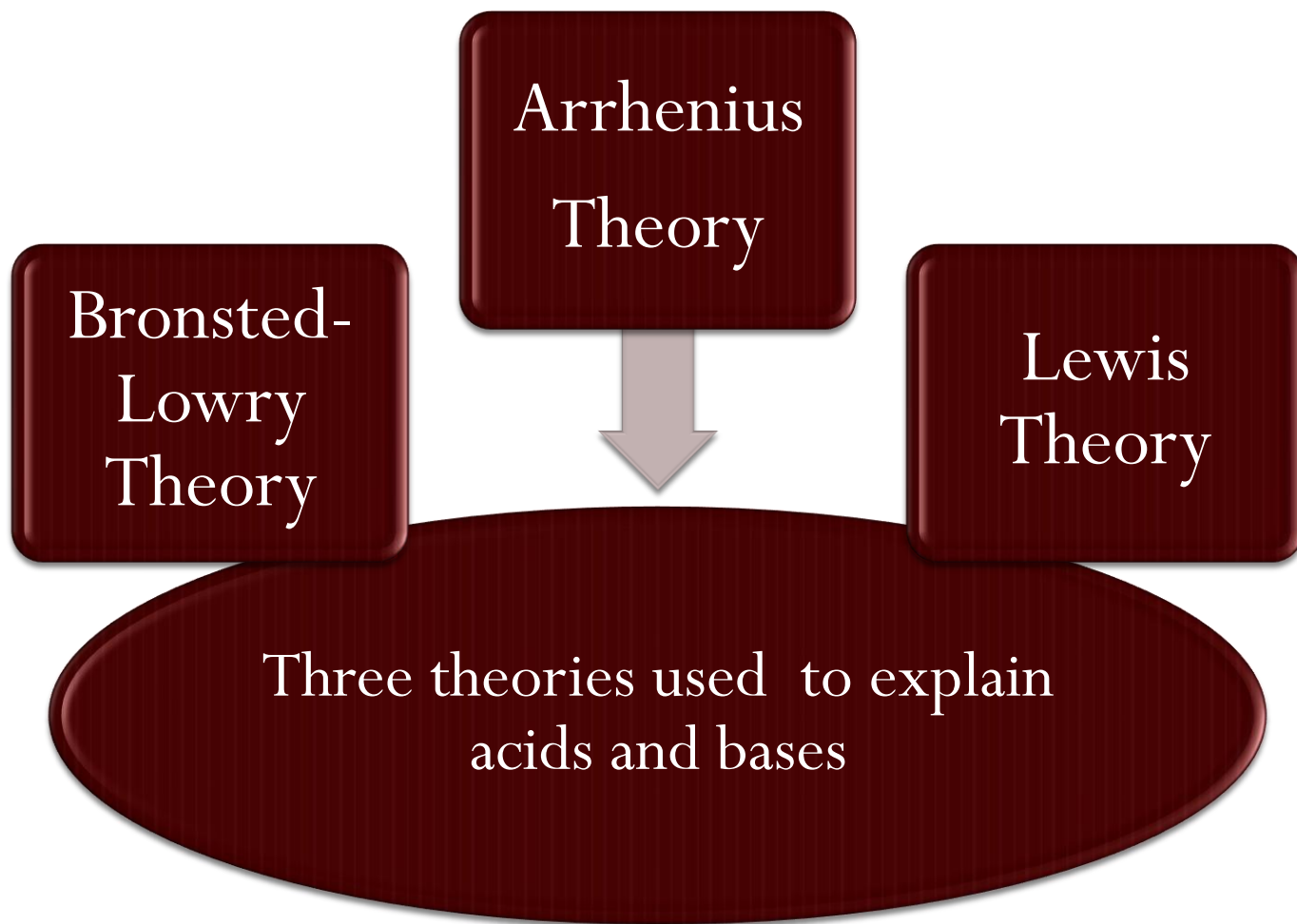


IONIC EQUILIBRIUM

LESSON OUTCOME

- EXPLAIN THE THEORY OF ACID & BASES
- IDENTIFY ACID, BASES CONJUGATE ACID & CONJUGATE BASES
- Calculating pH for acid & bases
- Determination of degree @ % dissociation /ionization.

Theory of Acids and bases

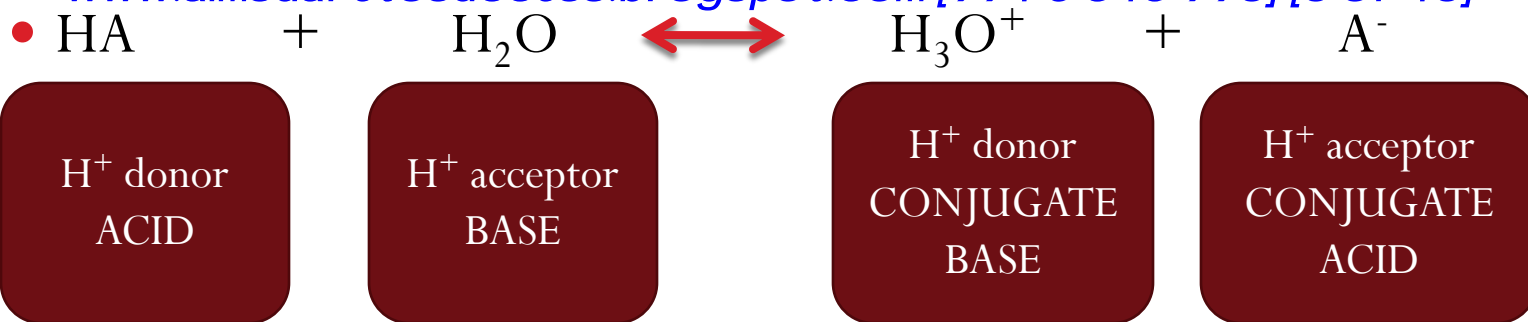


Arrhenius Theory

- Acid
 - Dissociates in water to produce hydrogen ions (H^+)
- Base
 - Dissociates in water to produce hydroxide ions, (OH^-)
- Examples:
 - $\text{HNO}_3 (\text{aq}) \longrightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
 - $\text{NaOH} (\text{aq}) \longrightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$
- The limitations of Arrhenius theory
 - Restricted to aqueous solution
 - Does not account for the basicity of substances, especially ammonia

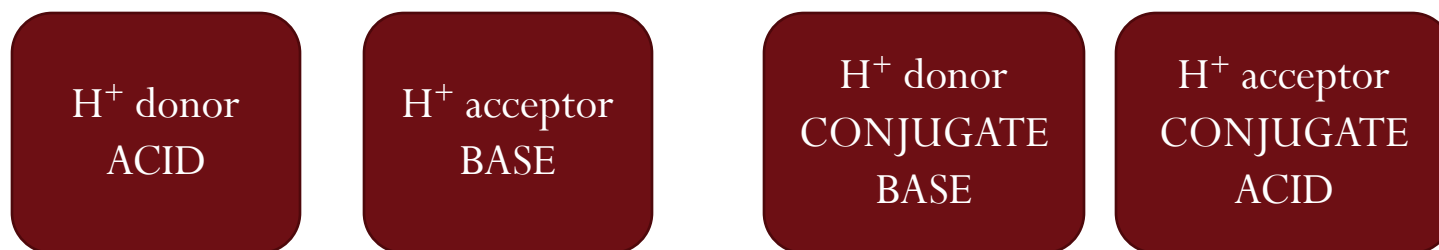
Brønsted – Lowry Theory

- Acid
 - Is a proton donor (a substance that can transfer H^+)
- Base
 - Is a proton acceptor
- So, an acid-base reaction is a proton-transfer reaction
- The theory can explain the acidity and basicity of weak acid and base. This compound partially dissociates in water. Thus, the symbol (\rightleftharpoons) is used to show that the reaction is reversible. When a **Bronsted –Lowry acid** is placed in water, it donates a proton to the solvent. Hence water act as **Bronsted –Lowry base**.

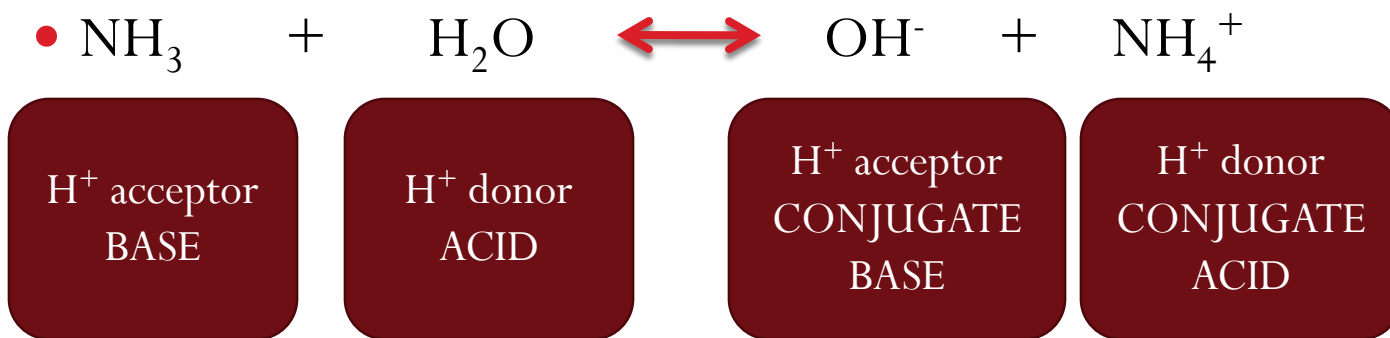


- In the reverse reaction, the **hydroxonium ion** acts as a proton donor(acid), and the A⁻ ion acts as a proton acceptor (base).

- Example of Bronsted Lowry acids



- A Bronsted –Lowry base such as ammonia accepts a proton from the solvent (water), which acts as a Bronsted –Lowry acid



- In the reverse reaction, the **hydroxide ion** acts as a proton acceptor(base), and the NH_4^+ ion acts as a proton donor (acid).
- Substances such as water, ions such as hydrogen sulphate ion are both Bronsted Lowry acids and bases . They are known as **ampholytes** and show **amphiprotic** behaviour



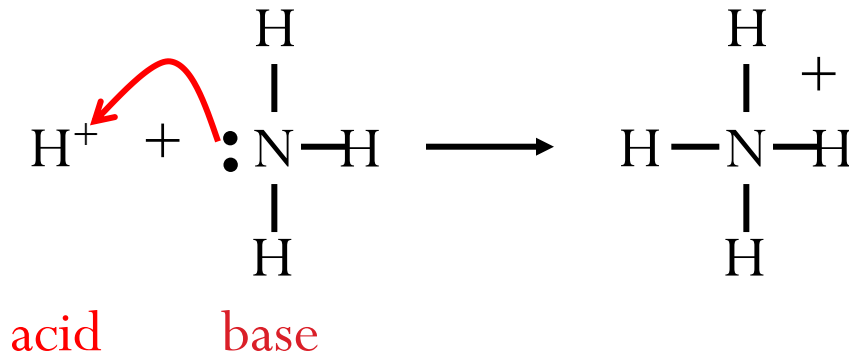
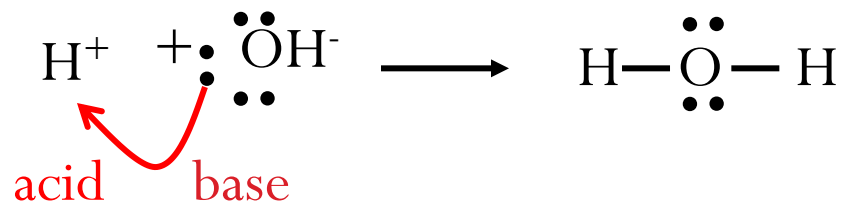
Exercises

- For each of the following identify the acid, base, conjugate acid and conjugate base:



Lewis Theory

- Lewis defined an acid as an electron pair acceptor and a base as an electron pair donor



- Example of reaction between ammonia, NH_3 and boron trifluoride, BF_3



Relative Strength of Bronsted –Lowry Acids and Bases

- **Degree of Dissociation**

- A strong acid will have a higher tendency to dissociate to form the hydroxonium ion as compared to a weaker acid. Hence the higher the degree of dissociation of acids, the stronger the acid.
- The acids in order of increasing strength is:



- The strength of bases depends on their ability to form the OH^- ions in aqueous solution. A strong bases will have a higher 'degree of dissociation' than weak bases
- The bases in order of increasing strength is:



Acid/Base Dissociation Constant (K_a and K_b)

- Consider a weak monoprotic acid, HA, which dissociates partially in water:



At equilibrium,

$$\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K_a$$

- The higher the value of K_a (that is the equilibrium position is more towards the right hand side) the stronger the acid
- Weak base, B, which dissociates partially in water:



At equilibrium,

$$\frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} = K_b$$

- The higher the value of K_b , the stronger the base

pK_a and pK_b

- Is another way of expressing the acid/base dissociation constant

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

- The larger the value of K_a or K_b , the smaller the value of pK_a or pK_b .
- Exercise:
 - Calculate the pK_b for the bases.

Acid	NH_3	CH_3COO	NO_2^-
$K_b/\text{mol dm}^{-3}$	1.8×10^{-5}	5.6×10^{-10}	2.2×10^{-11}

- Arrange the bases in order of increasing strength

Ostwald Dilution Law and Dissociation Constant

- Consider a weak acid, HA, of concentration $C \text{ mol dm}^{-3}$ and degree of dissociation of α

	HA	\longleftrightarrow	H ⁺	+	A ⁻
Initial	C		0		0
Equilibrium	$C(1-\alpha)$		$C\alpha$		$C\alpha$

At equilibrium: $K_a = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)}$

HOWEVER, α is very small, hence $1-\alpha \approx 1$

$$K_a = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

Since $H^+ = C\alpha$

$$= C \sqrt{\frac{K_a}{C}}$$

$$= \sqrt{K_a C}$$

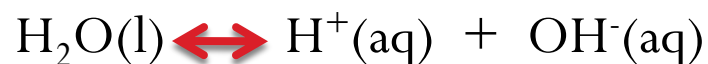
For weak base



$$[OH^-] = \sqrt{K_b C}$$

Ionic Product of Water

- The ion product of water
 - Hydrogen ion (H^+) is key = It indicates the acidity @ basicity of the solution
 - **Equilibrium constant** for the autoionization of water



$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

- Since, the degree of dissociation of water is extremely small, the concentration of water can be considered constant

$$K_c [\text{H}_2\text{O}] = K_w = [\text{H}^+][\text{OH}^-]$$

$$K_w = (1.0 \times 10^{-7} \text{ mol dm}^{-3})(1.0 \times 10^{-7} \text{ mol dm}^{-3}) = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

- The ionic product of water can be expressed in terms of pK_w , where
 - $pK_w = -\log K_w$
 $= -\log(1.0 \times 10^{-14}) = 14$
- From the expression:
 - $K_w = [H^+][OH^-]$
- Another expression can be derived by taking the $(-\log)$ of the K_w expression
 - $pK_w = pOH + pH$
- Thus, if the pOH of the solution is known, its pH value can be calculated from the above relationship



Measurement of acidity and basicity

- The pH of solution is defined as *negative logarithm of the hydrogen ion concentration (in mol/L)*

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

solution is

Neutral if, $[\text{H}^+] = [\text{OH}^-]$; $\text{pH} = 7$

Acidic if, $[\text{H}^+] > [\text{OH}^-]$; $\text{pH} < 7$

Basic if, $[\text{H}^+] < [\text{OH}^-]$; $\text{pH} > 7$

- The pOH of solution is defined as *negative logarithm of the hydroxide ion concentration (in mol/L)*

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

$$\text{pH} + \text{pOH} = 14.00$$

Exercise

- Calculate the pH of the following solutions at 298 K

a) $0.10 \text{ mol dm}^{-3} \text{ NaOH}$

b) $0.50 \text{ mol dm}^{-3} \text{ NH}_3$ ($K_b = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$)

c) $1.5 \text{ mol dm}^{-3} \text{ Ba(OH)}_2$ { Ba(OH)_2 is a strong base}

d) $2.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$

- Answers

a) 13 b) 11.48 c) 14.48 d) -0.602

Calculate the value of both pH and pOH of the following solution.

- a) 0.020 M HCl
- b) 0.0050 M NaOH
- c) A blood specimen containing 7.2×10^{-8} mole/L of hydrogen ion. Is the blood specimen slightly acidic or basic?
- d) 0.00035 M $\text{Ba}(\text{OH})_2$ where this compound has to be considered to be 100% dissociated.

Relationship between pK_a , pK_b and pK_w

- Consider an aqueous solution of ethanoic acid:



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

- Consider an aqueous solution containing the ethanoate ion (which is the conjugate base of CH_3COOH):



$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

- Multiplying K_a and K_b :

$$K_a \times K_b = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$K_a \times K_b = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

- Taking $-\log$ throughout:

$$-\log K_a + -\log K_b = -\log K_w$$

- Hence, for an acid/base conjugate pair:

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

example

- Calculate the pH of 0.10 mol dm^{-3} solution of sodium ethanoate. (K_a For $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$)

Answer



$$[\text{OH}^-] = K_b C$$

$$K_b \text{ for } \text{CH}_3\text{COO}^- = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10} \text{ mol dm}^{-3}$$

$$[\text{OH}^-] = 5.55 \times 10^{-10} \times 0.1 = 5.55 \times 10^{-11}$$

$$\text{pOH} = -\log 5.55 \times 10^{-11} = 10.25$$

$$\text{pH} = 14 - 5.13$$

$$= 8.87$$

Acid-Base Titration

- Purpose- **to determine** the volume of two solutions(acid and base) which will exactly neutralize each other
- Most acids, bases and salts are colorless in water. Therefore, an indicator is necessary to pin-point the end point of the titration

Acid-Base Indicators

- Substances which change color according to the pH of the solution to which they are added
- examples

indicator	Color in acid	Color in base
phenolphthalein	colorless	purple
Methyl orange	red	yellow
Methyl red	yellow	red

Equivalent point and End point of Acid-Base Titration

- **The equivalent point** is when the amount of acid and base present exactly neutralises one another. At this point, neither acid nor alkali are present in excess. The solution consists of **salt** and **water** only
- The end point of titration is when the **indicator** changes **color**.
- The indicator must change color at the equivalent point, not before or after

Suitable Indicator

Titration	Suitable Indicator
Strong acid + Weak base	Methyl Orange
Weak acid + Strong base	Phenolphthalien
Strong acid + Strong base	Methyl Orange or Phenolphthalien
Weak acid + Weak base	No suitable indicator

LESSON OUTCOME

- IDENTIFY TYPE OF SALTS
- CALCULATE pH of salts
- Define and example of buffer
- Identify types of buffer
- Calculate pH of buffer
- Solve the problem for buffer system

Acid-Base Properties of Salts

Neutral Solutions:

Salt formed from a strong acid and a strong base is dissolved in water.



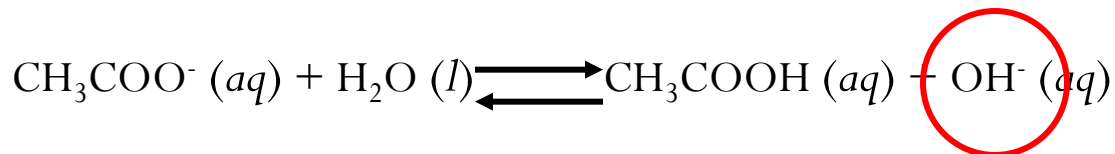
Salts containing an alkali metal or alkaline earth metal ion (except Be^{2+}) **and** the conjugate base of a **strong** acid (*e.g.* Cl^- , Br^- , and NO_3^-).



Na^+ and Cl^- are not hydrolysed by water. There is no production of extra H^+ or OH^- ions. Hence, the solution is **neutral**.

Basic Solutions:

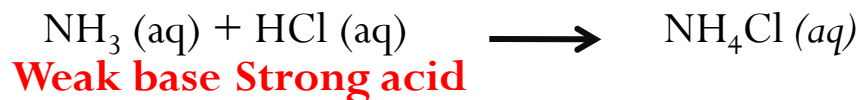
Salts derived from **a strong base and a weak acid**.



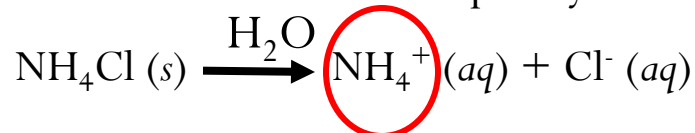
Acid-Base Properties of Salts

Acidic solution.

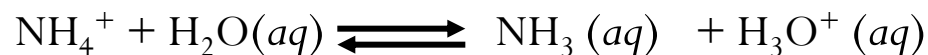
An example is:



In water, ammonium chloride dissociates completely into ammonium ions and chloride ions:



The ammonium ion, NH_4^+ , acts as a Bronsted-Lowry acid and donates a proton to water



On the other hand, **the Cl^- ions do not react with water:**

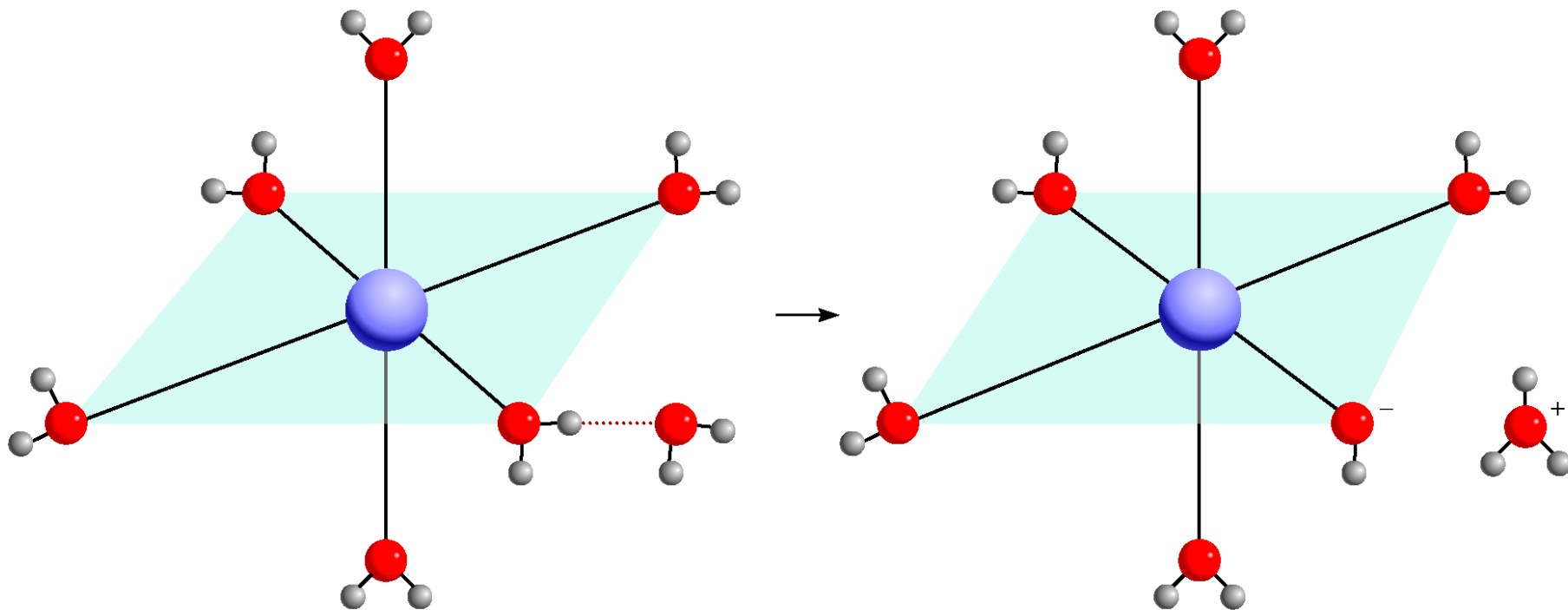


Because HCl (a strong acid) formed must dissociate completely to H^+ and Cl^- ions.

Salts with small, highly charged metal cations (*e.g.* Al^{3+} , Cr^{3+} , and Be^{2+}) and the conjugate base of a strong acid.



Acid Hydrolysis of Al^{3+}



Acid-Base Properties of Salts

Solutions in which both the cation and the anion hydrolyze:

- K_b for the anion $> K_a$ for the cation, solution will be basic
- K_b for the anion $< K_a$ for the cation, solution will be acidic
- K_b for the anion $\approx K_a$ for the cation, solution will be neutral

Acid-Base Properties of Salts

TABLE 15.7 Acid-Base Properties of Salts

Type of Salt	Examples	Ions That Undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KI, KNO ₃ , RbBr, BaCl ₂	None	≈ 7
Cation from strong base; anion from weak acid	CH ₃ COONa, KNO ₂	Anion	> 7
Cation from weak base; anion from strong acid	NH ₄ Cl, NH ₄ NO ₃	Cation	< 7
Cation from weak base; anion from weak acid	NH ₄ NO ₂ , CH ₃ COONH ₄ , NH ₄ CN	Anion and cation	< 7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ > 7 if $K_b > K_a$
Small, highly charged cation; anion from strong acid	AlCl ₃ , Fe(NO ₃) ₃	Hydrated cation	< 7

Hydrolysis

- Remembering the following equations must hold simultaneously

$$K_w = [H^+] \times [OH^-]$$

$$K_a = \frac{[H^+] \times [Ac^-]}{[HAc]} \text{ and } K_b = \frac{[NH_4^+] \times [OH^-]}{NH_4OH}$$

- Also, it can be shown that

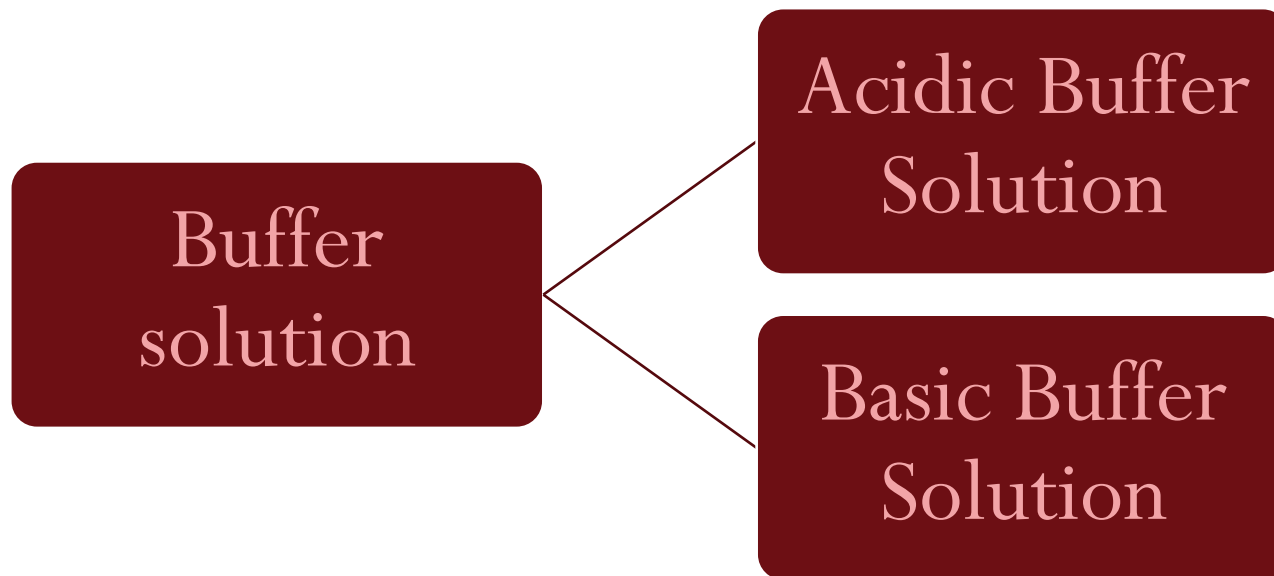
$$K_h = K_w / K_a \times K_b$$

$$pK_h = pK_w - pK_a + pK_b$$

Buffer System

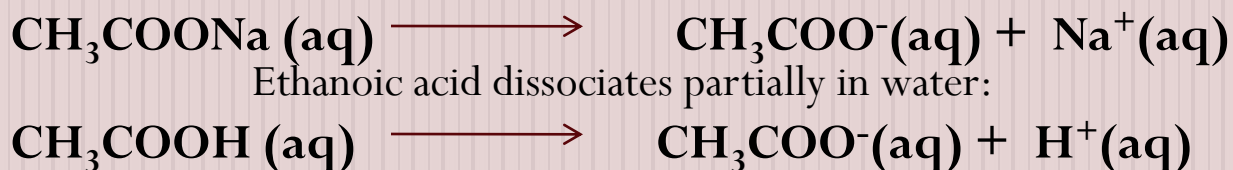
Is a solution of a weak acid and its salt to form **acidic buffer solution** or weak base and its salt to form **basic buffer solution**.

A buffer solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base.



Acidic Buffer Solution

- With pH between 4 and 7
- Can be prepared from a weak acid and its conjugate base.
- Example; an aqueous mixture of **ethanoic acid** and **sodium ethanoate**.



When a little acid is added, the above equilibrium will shift to the left to mop up the added of H^+ ion

Added H^+ is mopped up by the conjugate base



When a little base is added, it is removed by the following reaction

Added OH^- is mopped up by the acid



Basic Buffer Solution

- With pH between 7 and 10
- Can be prepared from a weak base and its conjugate acid.
- Example; an aqueous mixture of **ammonia** and **ammonium chloride**



When a little base is added, the above equilibrium will shift to the left to mop up the added of OH^- ion

Added OH^- is mopped up by the conjugate acid



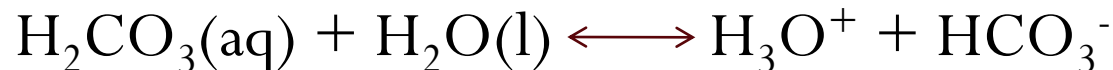
When a little acid is added, it is removed by the following reaction



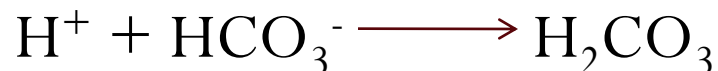
Added H^+ is mopped up by the base

Exercise

- An aqueous mixture of carbonic acid and sodium hydrogen carbonate can function as a buffer solution. Write a balanced equation to show how the system works.
- Answer:



On the addition of a little acid:



On the addition of a little base:



pH of Buffer Solutions

- Consider an aqueous mixture of a weak acid , HA and its salt MA.



- Applying the equilibrium law to the above system

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The $[\text{A}^-]$ at equilibrium can be assumed to be the concentration of MA which dissociates 100%

The $[\text{HA}]$ at equilibrium can be assumed to be equal to the original concentration of HA (since the degree of dissociation is very small)

- Rearranging the equation

$$[\text{H}^+] = K_a \frac{[\text{Acid}]}{[\text{salt}]}$$

- Taking $-\log$ throughout:

$$\text{pH} = \text{p}K_a - \log \frac{[\text{Acid}]}{[\text{salt}]}$$

- Similarly for a basic buffer solution:

$$[\text{OH}^-] = K_b \frac{[\text{base}]}{[\text{salt}]}$$

- Taking $-\log$ throughout:

$$\text{pOH} = \text{p}K_b - \log \frac{[\text{base}]}{[\text{salt}]}$$

Examples

- Calculate the pH of buffer solution consisting of 0.10 M CH_3COOH and 0.25 M CH_3COONa . (K_a for $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ M)
- Answer

$$\begin{aligned}\text{Using: } \text{pH} &= \text{p}K_a - \log \frac{[\text{Acid}]}{[\text{salt}]} \\ &= 4.74 - \log \frac{0.1}{0.25} = \mathbf{5.14}\end{aligned}$$

- 4.28g of ammonium chloride was added to 250 cm^3 of 0.50 mol dm^{-3} ammonia solution. Calculate the pH of the resulting solution. (K_b for ammonia = 1.8×10^{-5} mol dm^{-3})
- Answer = 9.45

Calculating the pH of an acidic buffer solution

Calculate the pH of a buffer whose [HA] is 0.1 mol dm^{-3} and $[A^-]$ of 0.1 mol dm^{-3} .

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

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

from information given $[A^-] = 0.1 \text{ mol dm}^{-3}$
 $[HA] = 0.1 \text{ mol dm}^{-3}$

If the K_a of the weak acid HA is $2 \times 10^{-4} \text{ mol dm}^{-3}$.

$$[H^+(aq)] = \frac{0.1 \times 2 \times 10^{-4}}{0.1} = 2 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10} [H^+(aq)] = 3.699$$

Calculate the pH of the solution formed when 500cm³ of 0.1 mol dm⁻³ of weak acid HX is mixed with 500cm³ of a 0.2 mol dm⁻³ solution of its salt NaX. $K_a = 4 \times 10^{-5}$ mol dm⁻³.

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

re-arrange $[H^+(aq)] = \frac{[HX(aq)] K_a}{[X^-(aq)]}$

The solutions have been mixed; the volume is now 1 dm³

therefore	$[HX]$	=	0.05 mol dm ⁻³ and
	$[X^-]$	=	0.10 mol dm ⁻³

Substituting $[H^+(aq)] = \frac{0.05 \times 4 \times 10^{-5}}{0.1} = 2 \times 10^{-5}$ mol dm⁻³

$$pH = -\log_{10} [H^+(aq)] = 4.699$$

Preparation of Buffer Solution

1. Choose a suitable weak acid (or weak base) whose pK_a (or pK_b) is almost equal to the required pH of the buffer solution
2. Calculate the ratio of the concentration of the acid (or base) to that concentration of the salt
3. Add the required amount of salt to the acid (or base) as determined by step 2 above.

Example

1. Explain how you would prepare a buffer solution of $\text{pH} = 5.2$

Answer

Ethanoic acid with $\text{pK}_a = 4.74$ is chosen

Using: $\text{pH} = \text{pK}_a - \log \frac{[\text{Acid}]}{[\text{salt}]}$

$$5.2 = 4.74 - \log \frac{[\text{Acid}]}{[\text{salt}]} \quad \therefore \frac{[\text{Acid}]}{[\text{salt}]} = 0.35$$

- Dissolve a mixture containing ethanoic acid and sodium ethanoate in the mole ratio 0.35: 1 in 1dm^3 of water.
- Alternatively, prepare a 1.0 mol dm^{-3} solution of ethanoic acid and sodium ethanoate and mix the two solutions together in a volume ratio of 0.35: 1

1. Explain how you would prepare a buffer solution of $\text{pH} = 9.5$

Answer:

$$\frac{[\text{base}]}{[\text{salt}]} = 1.27$$

[salt]

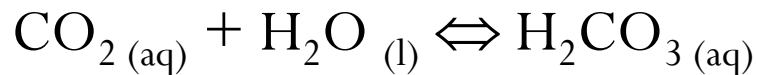
Theory and application of buffer system

Maintaining the pH of blood

- Are important in the proper functioning of cells and blood.
- Help maintain the pH of blood close to 7.4.

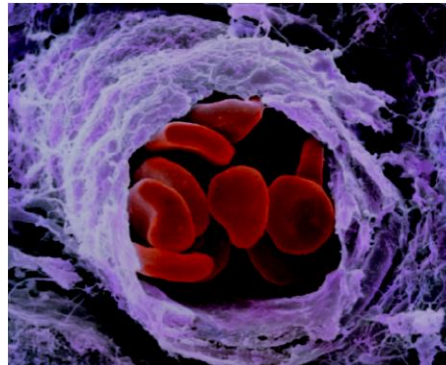
A change in the pH of the blood affects the uptake of oxygen and cellular processes.

→ Human blood must be maintained at a pH of 7.40 ± 0.05 for the rest of the body biochemistry to function. This is achieved with a buffer made from CO_2 :

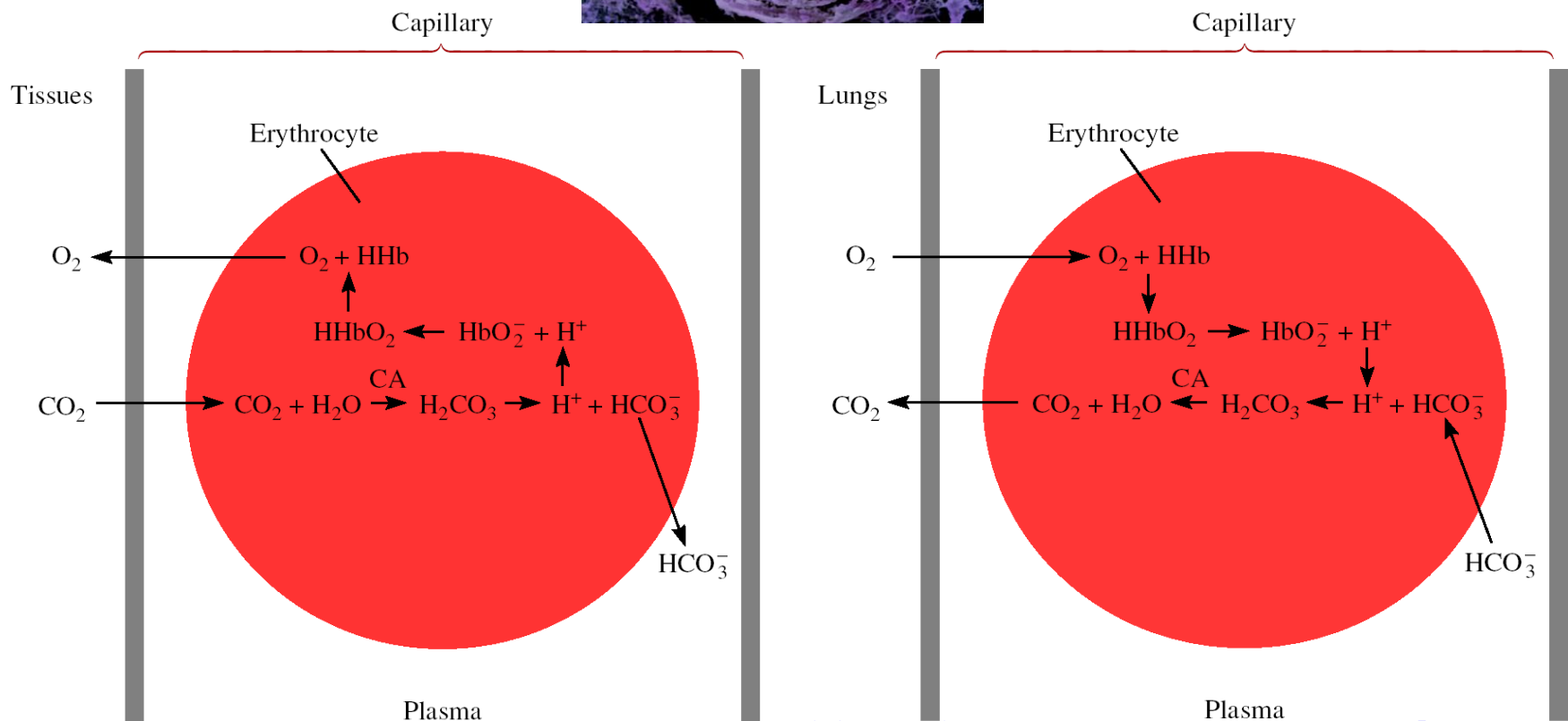


Theory and application of buffer system

Chemistry In Action: Maintaining the pH of Blood



Red blood cells in a capillary



THE END