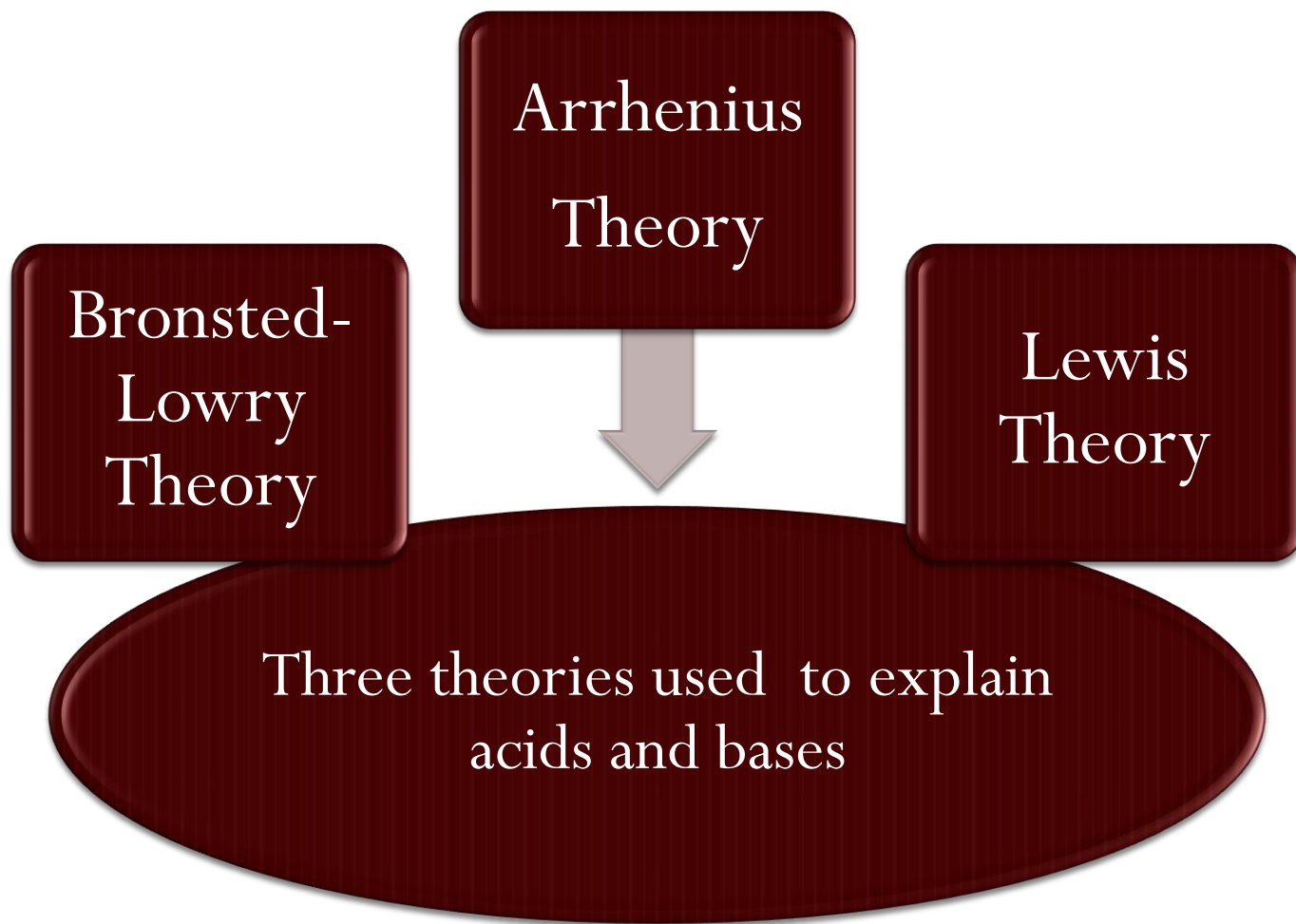# IONIC EQUILIBRIUM

LESSON OUTCOME

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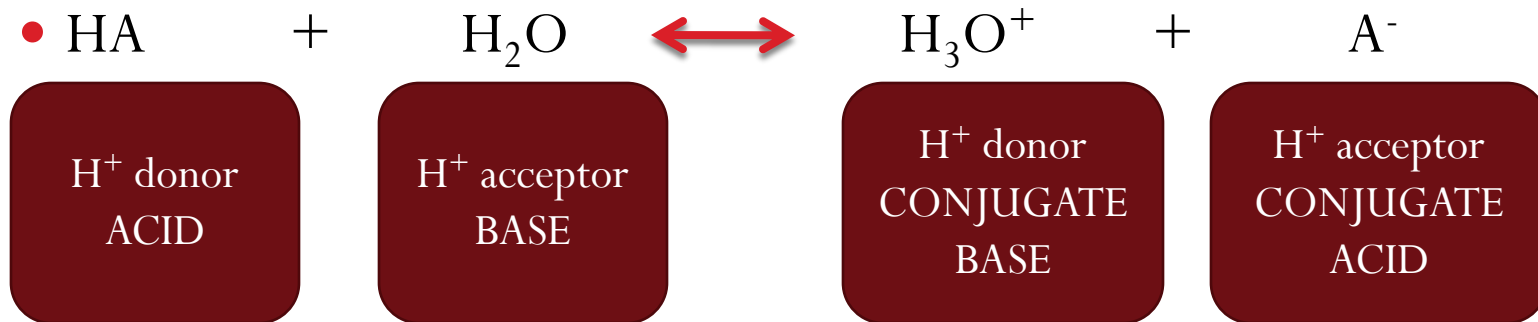- Determination of degree @ % dissociation /ionization.

Theory of Acids and bases

Arrhenius Theory

Bronsted-Lowry Theory

Lewis Theory

Three theories used to explain acids and bases

Arrhenius Theory

- Acid
  - Dissociates in water to produce hydrogen ions (H^+)
- Base
  - Dissociates in water to produce hydroxide ions, (OH^-)
- Examples:
  - $HNO_3 \ (aq) \longrightarrow H^+(aq) \ + \ NO_3^-(aq)$
  - $NaOH \ (aq) \longrightarrow Na^+(aq) + \ OH^-(aq)$
- 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 ($\longleftrightarrow$) 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.

- HA + H_2O $\longleftrightarrow$ H_3O^+ + A^-

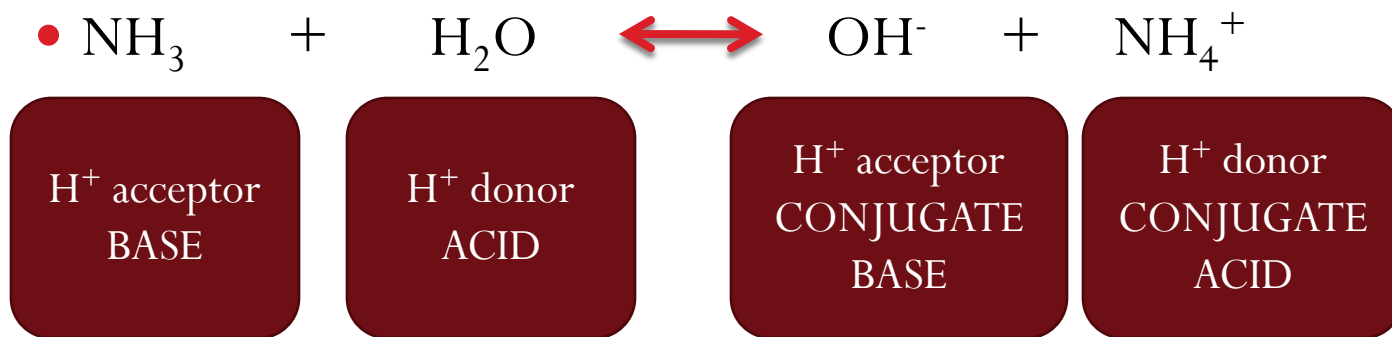| H^+ donor ACID	H^+ acceptor BASE	H^+ donor CONJUGATE BASE	H^+ acceptor CONJUGATE ACID

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

H^+ donor ACID	H^+ acceptor BASE	H^+ donor CONJUGATE BASE	H^+ acceptor CONJUGATE ACID

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

  - NH_3 + H_2O $\longleftrightarrow$ OH^- + NH_4^+

H^+ acceptor BASE	H^+ donor ACID	H^+ acceptor CONJUGATE BASE	H^+ donor CONJUGATE ACID

  - In the reverse reaction, the **hydroxide ion** acts as a proton acceptor(base), and the $NH4^+$ 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
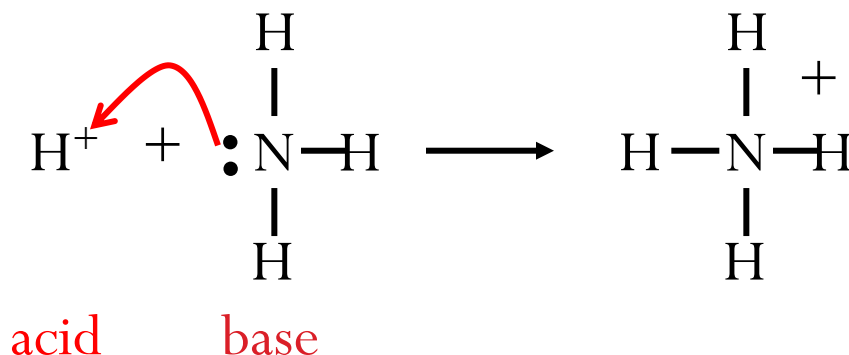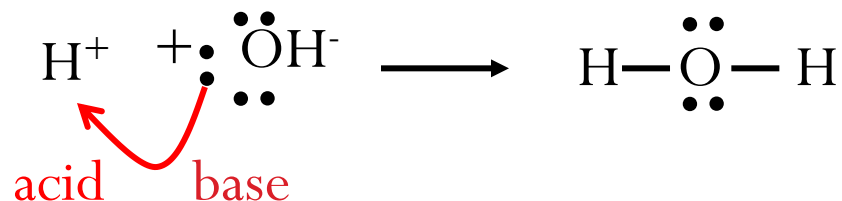
  HSO_4- + H_2O $\longleftrightarrow$ H_3O^+ + SO_4^{2-}

  HSO_4- + H_2O $\longleftrightarrow$ OH^- + H_2SO_4
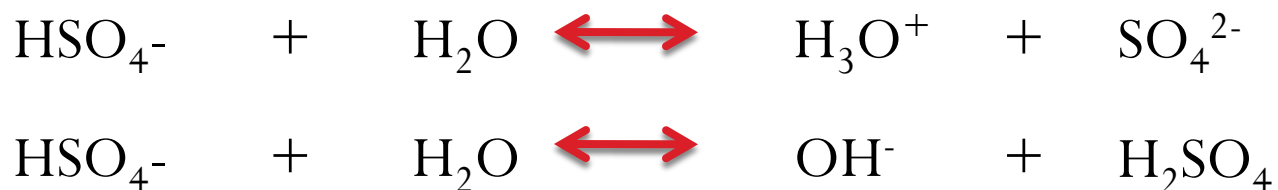
Exercises

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

  - $HCl + H_2PO_4^- \longleftrightarrow H_3PO_4 + Cl^-$
  - $C_6H_5OH + H_2O \longleftrightarrow C_6H_5O^- + H_3O^+$
  - $NH_2OH + H_2O \longleftrightarrow NH_2OH_2 + OH^-$
  - $NH_3 + HSO_4^- \longleftrightarrow NH_4^+ + SO_42^-$

Lewis Theory

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

$$H^+ \quad + \; :\overset{\displaystyle ..}{\underset{\displaystyle ..}{O}}H^- \quad \longrightarrow \quad H-\overset{\displaystyle ..}{\underset{\displaystyle ..}{O}}-H$$

acid   base

$$H^+ \quad + \; :\underset{\displaystyle H}{\overset{\displaystyle H}{N}}-H \quad \longrightarrow \quad H-\underset{\displaystyle H}{\overset{\displaystyle H}{N}}-H \;^+$$

acid   base

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

$$BF_3 + \; :NH_3 \; \longrightarrow \; F_3B:NH_3$$

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:

$$CH_3COOH < HNO_2 < HSO_4^- < HCl$$

  - 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:

$$NO_2^- < CH_3COO^- < NH_3$$

Acid/Base Dissociation Constant (K_a and K_b)

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

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

At equilibrium,

$$\frac{[H_3O^+][A^-]}{[HA]} = K_a$$

- 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:

$$B + H_2O \leftrightarrow HB^+ + OH^-$$

At equilibrium,

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

- 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$_3$COO	NO$_2^-$
K$_b$/mol dm^{-3}	1.8 x 10^{-5}	5.6 x 10^{-10}	2.2 x 10^{-11}

  - Arrange the bases in order of increasing strength

Ostwald Dilution Law and Dissociation Constant

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

	HA ⟷	H+ +	A-
Initial	C	0	0
Equilibrium	C(1-α)	Cα	Cα

At equilibrium: $Ka = \dfrac{(Cα)(Cα)}{C(1-α)}$

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

$Ka = c\,α^2$ $\qquad$ Since $H^+ = Cα$

$α = \sqrt{\dfrac{Ka}{C}}$ $\qquad\qquad = C\sqrt{\dfrac{Ka}{C}}$

$\qquad\qquad\qquad\qquad = \sqrt{KaC}$

For weak base

$B + H2O \Longleftrightarrow HB^+ + OH^-$

$[OH] = \sqrt{KbC}$

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

$$H_2O(l) \longleftrightarrow H^+(aq) \ + \ OH^-(aq)$$
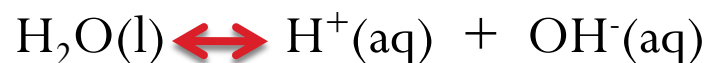
$$K_c = \frac{[H^+]\,[OH^-]}{[H_2O]}$$

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

$$K_c\,[H_2O] = K_w = [H^+]\,[OH^-]$$

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

- The ionic product of water can be expressed in terms of pKw, 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)*

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

solution is

Neutral if, $[H^+] = [OH^-]$; pH = 7

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

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

- The pOH of solution is defined *as negative logarithm of the hydroxide ion concentration (in mol/L)*
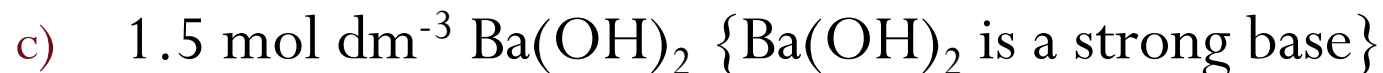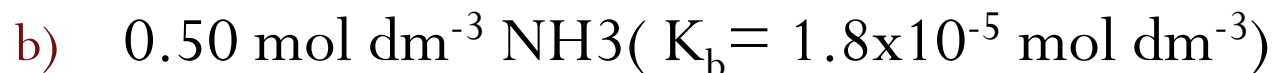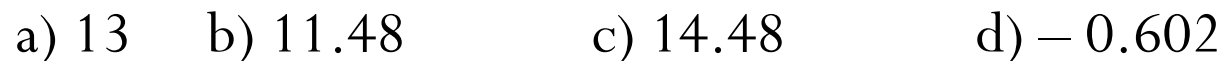
$$pOH = -\log [OH^-]$$

$$pH + pOH = 14.00$$

Exercise

- Calculate the pH of the following solutions at 298 K

a) 0.10 mol dm^{-3} NaOH

b) 0.50 mol dm^{-3} NH3($K_b = 1.8 \times 10^{-5}$ mol dm^{-3})

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

d) 2.0 mol dm^{-3} H$_2$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 speciment containing 7.2×10^{-8} mole/L of hydrogen ion. Is the blood speciment slightly acidic or basic?

d) 0.00035 M $Ba(OH)_2$ where this compound has to be considered to be 100% dissociated.

Relationship between pK_a, pK_b and pK_w

- Consider an aqueous of ethanoic acid:

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

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

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

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

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

- Multiplying K_a and K_b:

$$K_a \times K_b = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \times \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_a \times K_b = [H_3O^+][OH^-]$$

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

- Taking –log throughout:

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

- Hence, for an acid/base conjugate pair:

$$pK_a + pK_b = pK_w$$

example

- Calculate the pH of 0.10 mol dm^{-3} solution of sodium ethanoate. (Ka For CH3COOH= 1.8×10^{-5} moldm^{-3})

Answer

$$CH3COO^- + H_2O \longleftrightarrow CH_3COOH + OH^-$$

[OH-]= KbC

Kb for CH$_3$COO$^-$= $\dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$ = 5.55×10^{-10} mol dm^{-3}

[OH$^-$]= 5.55×10^{-10} x 0.1 = 7.45×10^{-6}

pOH= -log 97.45×10^{-6} = 5.13

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.
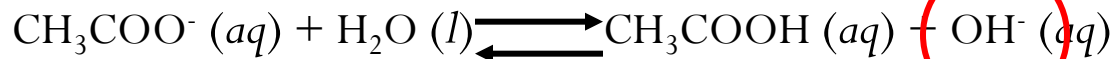
Example: $NaOH + HCl \longrightarrow NaCl + H_2O$

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^-).

$$NaCl \, (s) \xrightarrow{\text{H}_2\text{O}} Na^+ \, (aq) + Cl^- \, (aq)$$

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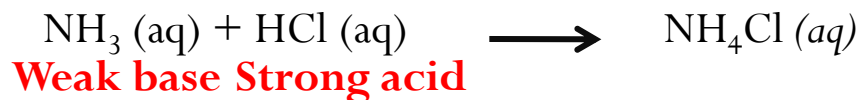
Basic Solutions:

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

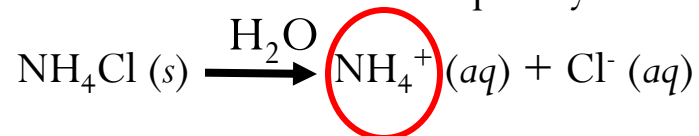$$NaCH_3COOH \, (s) \xrightarrow{\text{H}_2\text{O}} Na^+ \, (aq) + CH_3COO^- \, (aq)$$

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

35

Acid-Base Properties of Salts

Acidic solution.

An example is:

$$NH_3 \text{ (aq)} + HCl \text{ (aq)} \longrightarrow NH_4Cl \text{ (aq)}$$

Weak base Strong acid

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

$$NH_4Cl \text{ (s)} \xrightarrow{H_2O} NH_4^+ \text{(aq)} + Cl^- \text{ (aq)}$$

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

$$NH_4^+ + H_2O \text{(aq)} \rightleftarrows NH_3 \text{ (aq)} + H_3O^+ \text{ (aq)}$$

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

$$Cl^- \text{ (aq)} + H_2O \text{ (l)} \rightleftarrows HCl \text{ (aq)} + OH^- \text{ (this reaction }} \text{\color{red}does not}\text{ take place)}$$
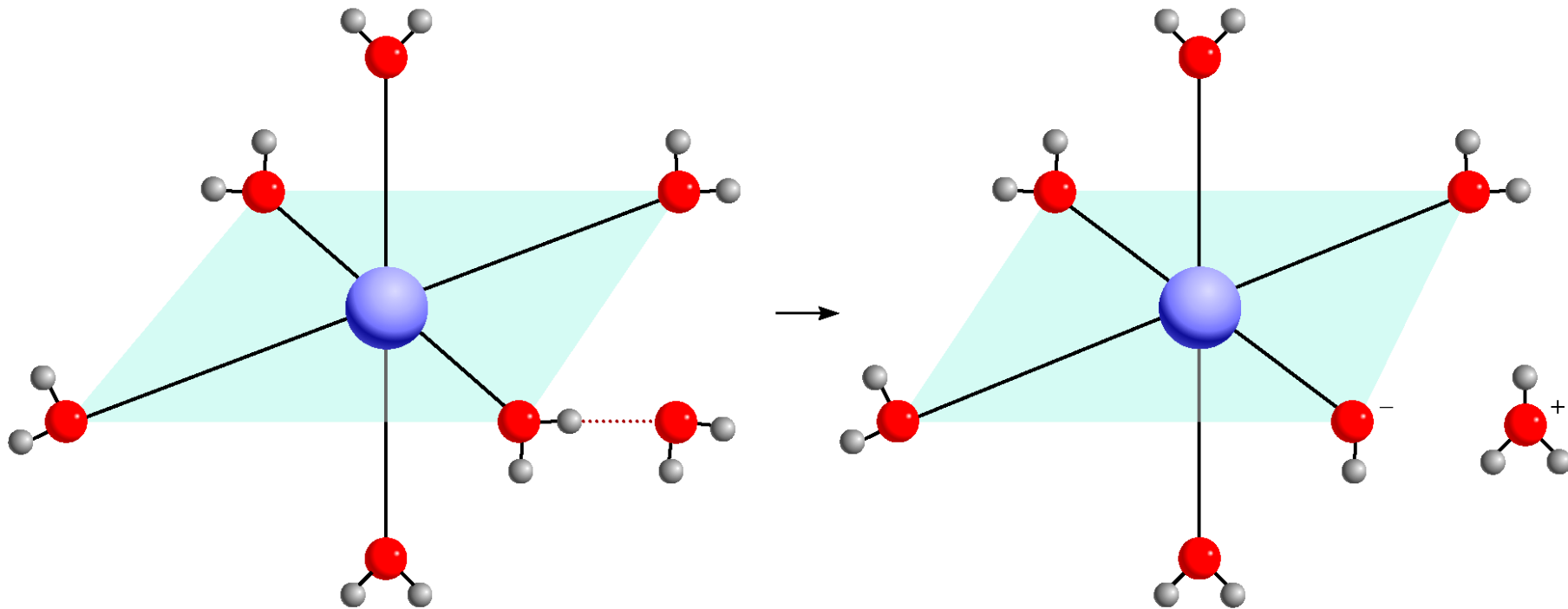
Because HCl (a strong acid) formed must dissociate completely to H^+ and Cl^- ions.

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

$$Al(H_2O)_6 \text{ (aq)}^{3+} \rightleftarrows Al(OH)(H_2O)_5^{2+} \text{ (aq)} + H^+ \text{ (aq)}$$

Acid Hydrolysis of Al^{3+}

$$Al(H_2O)_6^{3+} + H_2O \longrightarrow Al(OH)(H_2O)_5^{2+} + H_3O^+$$

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_3COONa, KNO_2	Anion	> 7
Cation from weak base; anion from strong acid	NH_4Cl, NH_4NO_3	Cation	< 7
Cation from weak base; anion from weak acid	NH_4NO_2, CH_3COONH_4, NH_4CN	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**.
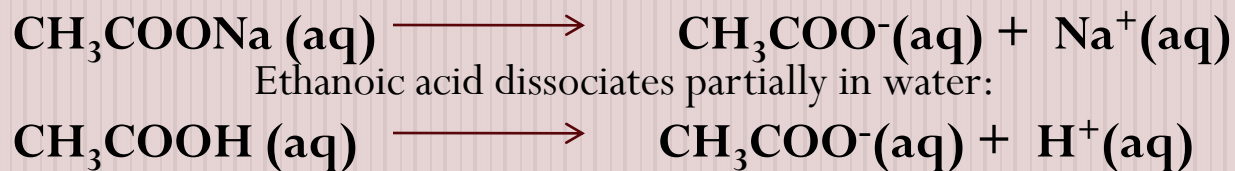
A buffer solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base.

Buffer solution

Acidic Buffer Solution

Basic Buffer Solution
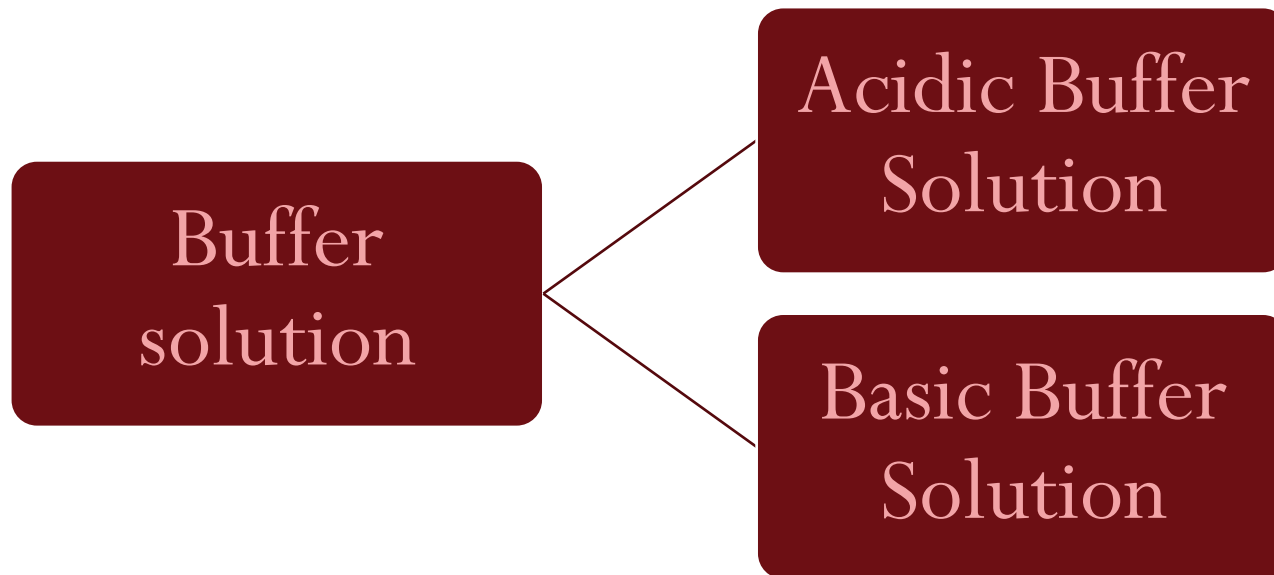
Acidic Buffer Solution

- 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.**

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

Ethanoic acid dissociates partially in water:

$$CH_3COOH\ (aq) \longrightarrow CH_3COO^-(aq) +\ H^+(aq)$$

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

$$CH_3COO^-\ +\ H^+ \longrightarrow CH_3COOH$$

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

Added OH^- is mopped up by the acid

$$CH_3COOH +\ OH^- \longrightarrow CH_3COO^-\ +\ H_2O$$

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**

$$NH_4Cl\ (aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

$$NH_3\ (aq) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$$
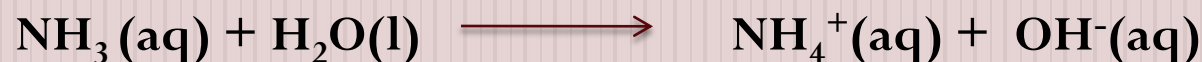
When a little base is added, the above equilibrium will shift to the left to mop up the added of OH^- ion

Added OH^- is mopped up by the conjugate acid

$$NH_4^+(aq) + OH^- \longrightarrow NH_3 + H_2O$$

When a little acid is added, it is removed by the following reaction
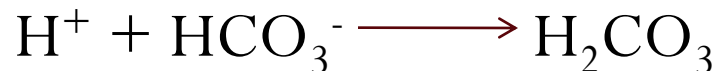
$$NH_3\ (aq) + H^+ \longrightarrow NH_4^+$$

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:

$$H_2CO_3(aq) + H_2O(l) \longleftrightarrow H_3O^+ + HCO_3^-$$

$$NaHCO_3 \longrightarrow Na^+ + HCO_3^-$$
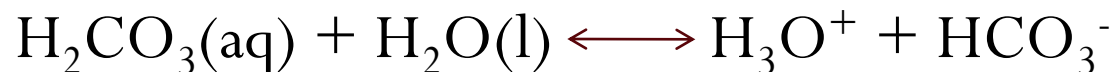
On the addition of a little acid:

$$H^+ + HCO_3^- \longrightarrow H_2CO_3$$

On the addition of a little base:

$$OH^- + H_2CO_3 \longrightarrow HCO_3^- + H_2O$$

pH of Buffer Solutions

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

$$MA \xrightarrow{\quad 100\% \quad} M^+ + A^-$$

$$HA \longleftrightarrow H^+ + A^-$$

- Applying the equilibrium law to the above system

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

The [A⁻] at equilibrium can be assumed to be the concentration of MA which dissociates 100%

The [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

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

- Taking –log throughout:

$$pH = pK_a - \log \frac{[Acid]}{[salt]}$$

- Similarly for a basic buffer solution:

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

- Taking –log throughout:

$$pOH = pK_b - \log \frac{[base]}{[salt]}$$

Examples

- Calculate the pH of buffer solution consisting of 0.10 M CH_3COOH and 0.25 M CH_3COONa. (K_a for CH_3COOH= 1.8 x 10^{-5} M)

- Answer

Using: $pH = pK_a - \log \dfrac{[Acid]}{[salt]}$

$$= 4.74 - \log \dfrac{0.1}{0.25} = \mathbf{5.14}$$

- 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 x 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 $\qquad [H^+(aq)] \ = \ \dfrac{[HA(aq)] \times K_a}{[A^-(aq)]}$

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

$[HA] = 0.1$ mol dm^{-3}

If the K$_a$ of the weak acid HA is 2 x 10^{-4} mol dm^{-3}.

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

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

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

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

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

The solutions have been mixed; the volume is now 1 dm^3

therefore $\qquad$ [HX] $\qquad$ = 0.05 mol dm^{-3} and

$\qquad\qquad\qquad$ [X$^-$] $\qquad$ = 0.10 mol dm^{-3}

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

pH = - log$_{10}$ [H$^+$(aq)] $\quad$ = $\quad$ 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 pH $= 5.2$

Answer

Ethanoic acid with $pK_a = 4.74$ is chosen

Using: $pH = pK_a - \log \dfrac{[Acid]}{[salt]}$

$$5.2 = 4.74 - \log \dfrac{[Acid]}{[salt]} \quad :- \quad \dfrac{[Acid]}{[salt]} = 0.35$$

- Dissolve a mixture containing ethanoic acid and sodium ethanoate in the mole ratio $0.35 : 1$ in $1 dm^3$ of water.

- Alternatively, prepare a $1.0 \ moldm^{-3}$ solution of ethanoic acid and sodium ethanoate and mix the two solutions together in a volume ration of $0.35 : 1$

1. Explain how you would prepare a buffer solution of pH $=9.5$

Answer:

$\dfrac{[\underline{base}]}{[salt]} = 1.27$

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:
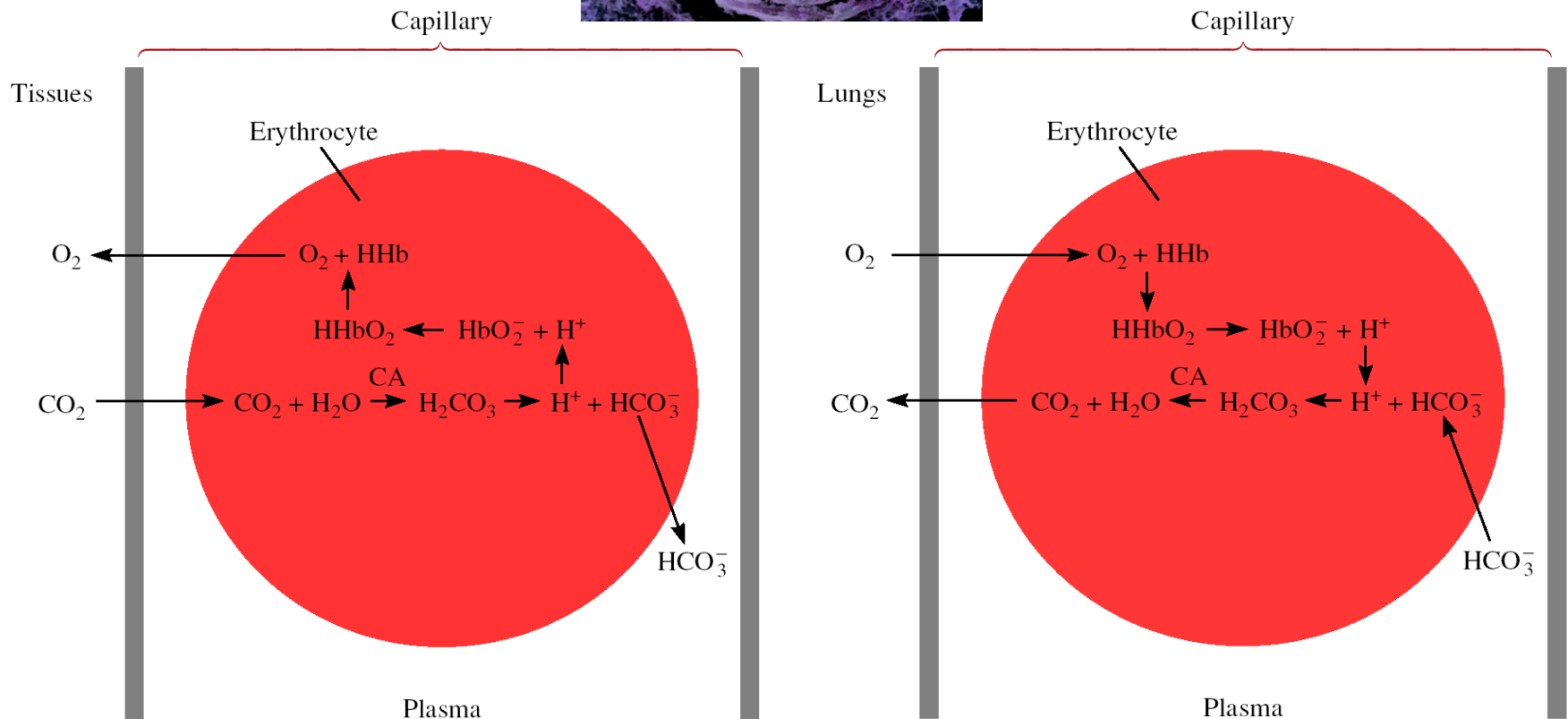
$$CO_{2\,(aq)} + H_2O_{\,(l)} \Longleftrightarrow H_2CO_{3\,(aq)}$$
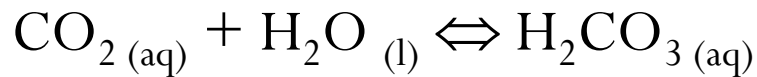
Theory and application of buffer system

Chemistry In Action: Maintaining the pH of Blood
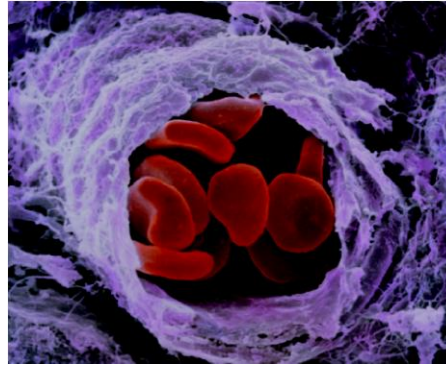
Red blood cells in a capillary

THE END