

Buffers

A **buffer solution** is a solution that contains comparable amounts of a weak acid and its conjugate base and which is therefore able to maintain an approximately constant pH even when significant amounts of strong acid or strong base are added to it.

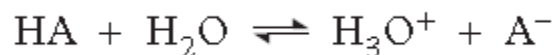
Some common buffer solutions and the pH around which they are effective

Buffer	pH ^a
acetic acid and sodium acetate: CH_3COOH , CH_3COONa	4.6
carbon dioxide (carbonic acid) and hydrogen carbonate: H_2CO_3 , HCO_3^-	6.4 ^b
sodium dihydrogen phosphate and hydrogen phosphate: H_2PO_4^- , HPO_4^{2-}	7.2
ammonium chloride and ammonia: NH_4^+ , NH_3	9.3
sodium carbonate and hydrogen carbonate: CO_3^{2-} , HCO_3^-	10.3

a of equimolar mixtures of the acid and its conjugate base.

Solutions called *buffers* resist changes in pH when small quantities of an acid or base are added to them. By restricting the pH range of body fluids, these buffers ensure that biochemical reactions proceed at their required rate. Buffers keep our bodies in pH balance.

Consider the weak acid HA and its conjugate base, A^- . If HA is added to water, the following equilibrium is established:



Also,



If hydrogen ion is added to this solution, then by Le Chatelier's principle, the equilibrium in the equation above will move to the left.

Base A^- will combine with much of the added H_3O^+ to form HA in order to minimise the change in $[H_3O^+]$ and therefore in pH.

If the environment is acidic, HCO_3^- acts as a base:



If instead hydroxide ion had been added, it would react with the H_3O^+ and cause the pH to rise, but again, by Le Chatelier's principle, the equilibrium in equation 1 will move to the right to try to minimise the change.

HA will ionise to produce more A^- . Because of its ability to maintain an approximately constant pH, such a solution is called a '*buffer solution*.'

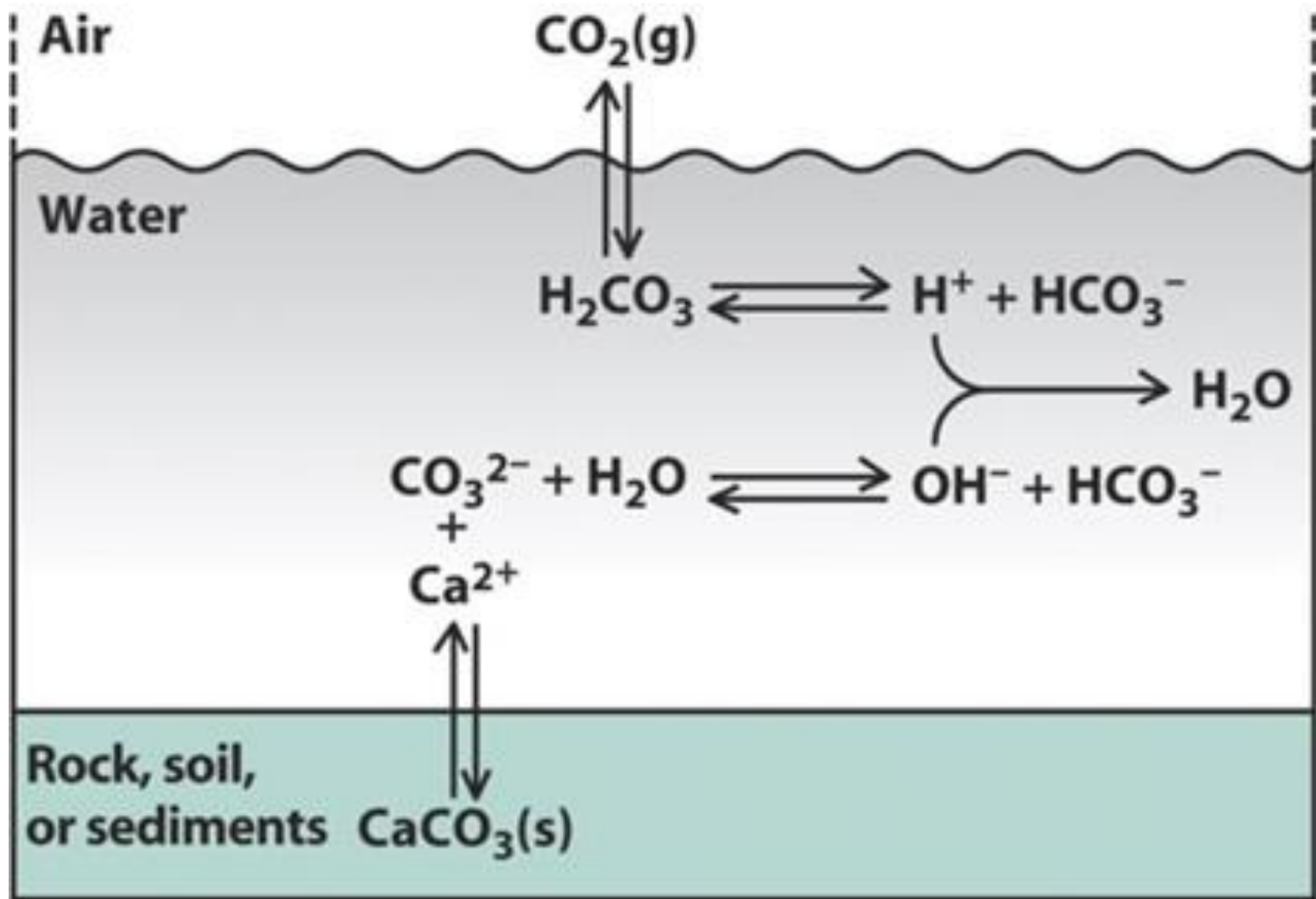
A natural buffer system

Example 1

- CO_2 from the air dissolves in the lake water to form H_2CO_3 .
- H_2CO_3 is a weak acid and undergoes partial ionisation.



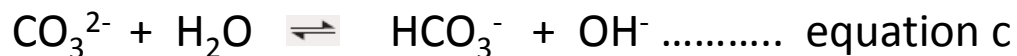
- The pH of rain water is about 5.7 to 6.0 because there is no source of HCO_3^- other than CO_2 from the air .
- Rain water is not a buffer because the only source of HCO_3^- is the ionisation of H_2CO_3 and it is too little to form a buffer.



- In rivers or lakes, some HCO_3^- comes from the surrounding rocks containing salts.



- CO_3^{2-} reacts with the lake water



- HCO_3^- ions added to the lake now form a buffer with H_2CO_3 .
- When acid rain is added to the lake, the concentration of H^+ in equation a rises and pushes the equilibrium to the left, thus lowering the HCO_3^- conc.

- Equation c will now shift to the right to compensate for the change in the previous step.
- This increases the OH^- concentration in equation c.
- The OH^- now can react with the excess H^+ in equation a and the change in pH is minimised.
- The absence of this buffering action in lakes in Scandinavia resulted in the first detection of falling pH from acid rain. The rocks from which the lakes had been carved contained no carbonate to provide HCO_3^- to make the buffer.

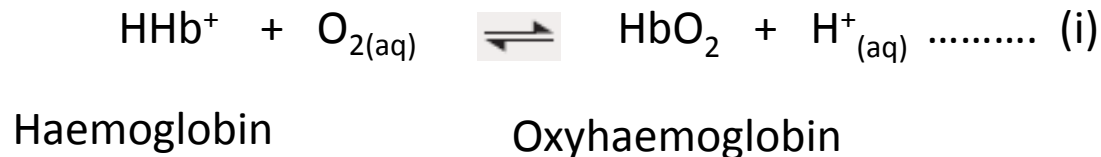
Example 2: Oxygen exchange and blood acidity levels

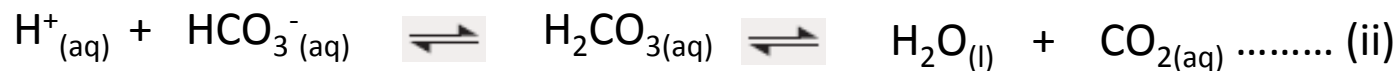
The main chemical buffer in our blood is a solution containing both the bicarbonate ion (HCO_3^-) and its conjugate base, the carbonate ion (CO_3^{2-}).

Our blood is maintained at a pH of 7.4 despite the fact that we keep exchanging CO_2 (acidic), excreting wastes, absorbing foods etc.

Haemoglobin (Hb) is an iron-protein molecule in the blood which is involved in oxygen transport and the maintenance of blood acidity levels.

Several equilibria are involved, including those represented below:





In the lungs, the high oxygen pressure shifts the equilibrium (i) to the right, by Le Chatelier's principle, to form oxyhaemoglobin. This oxyhaemoglobin moves in the blood to an oxygen deficient cell where the same equilibrium (i) shifts to the left and supplies oxygen to the cell.

The equilibrium (i) shift to the right increases the blood acidity. This increase in $[\text{H}^+]$ shifts equilibrium (ii) to the right, by Le Chatelier's principle, to reduce the acidity levels and increases $[\text{CO}_2]$. The CO_2 produced can escape from the lungs.

This maintenance of blood acidity via equilibrium shifts is known as buffering.

8 Which acid / base pair could act as a buffer?



Question 26 (4 marks)

Explain how a buffer works with reference to a specific example in a natural system.

4

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Question 26

Outcomes assessed: H8, H14

MARKING GUIDELINES

Criteria	Marks
<ul style="list-style-type: none">• Correctly defines buffer systems• Shows how a buffer works by giving a relevant example within a natural system• Includes relevant equation with explanation OR equations	3–4
<ul style="list-style-type: none">• Correctly defines buffer systems• Gives a relevant example	2
<ul style="list-style-type: none">• Gives a natural example of a buffer system OR <ul style="list-style-type: none">• Gives partial definition of buffer	1

Sample answer:

Buffers are solutions that resist changes in pH when small quantities of acid or base are added.

A buffer is made by mixing together a weak acid and its conjugate base, or a base with its conjugate acid in approximately equal proportions. A natural example is seen in the HCO_3^- buffering system that maintains blood pH.



When there are changes in acid/base level of the blood, the system is pushed either to the left on addition of an acidic substance or the right on the addition of a basic substance and the pH is maintained.

Answers could include:



ORGANIC ACIDS AND ESTERIFICATION

- *describe the differences between the alkanol and alkanoic acid functional groups in carbon compounds*

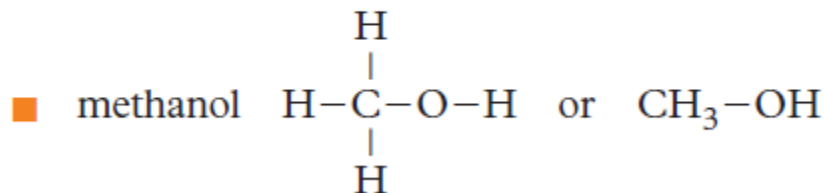
Alkanols and alkanolic acids

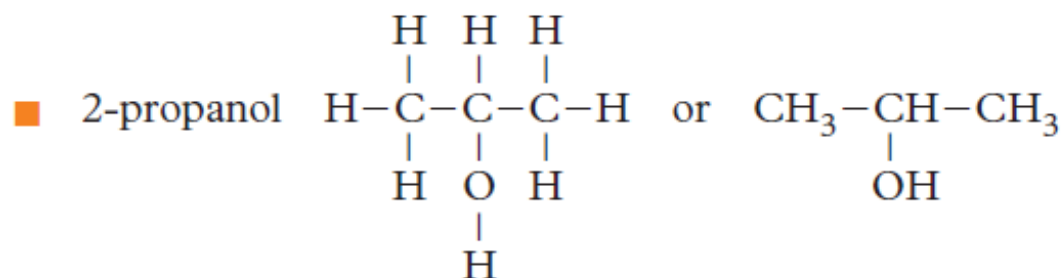
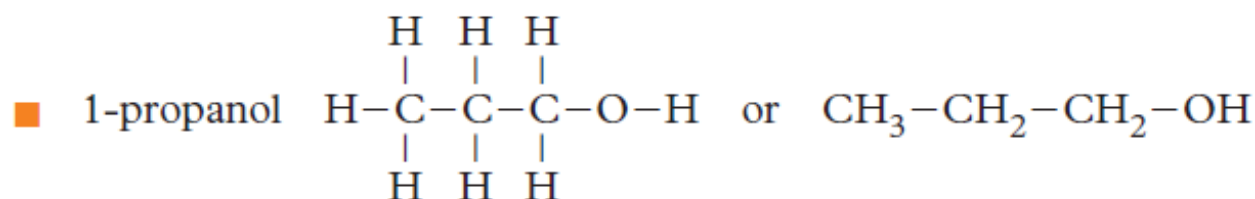
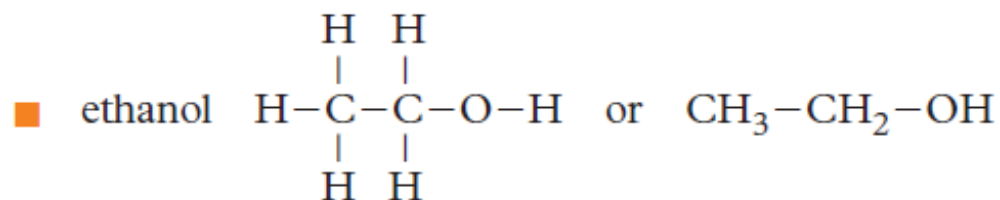
Alkanols and alkanolic acids are important families of organic compounds. Alkanols are compounds that contain the alcohol functional group (—OH). The alkanolic acid family are weak organic acids. They contain the carboxylic acid functional group (—COOH).

Alkanols

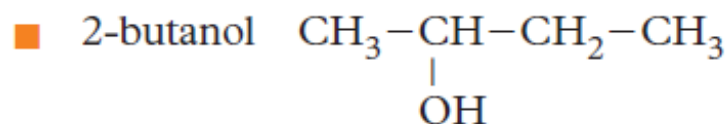
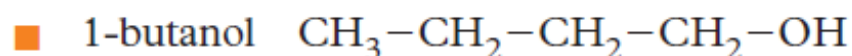
The alkanols form an *homologous series* having the general formula, $\text{C}_n\text{H}_{2n+2}\text{O}$ or $\text{C}_n\text{H}_{2n+1}\text{OH}$.

Some simple alkanols

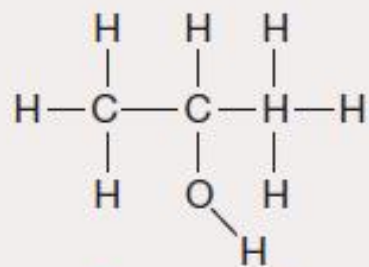
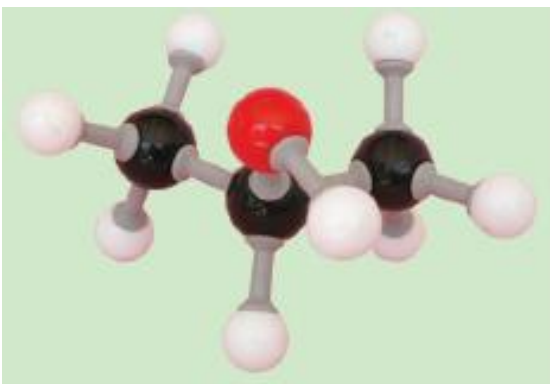




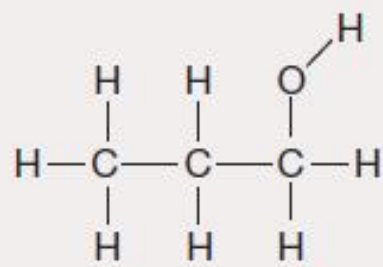
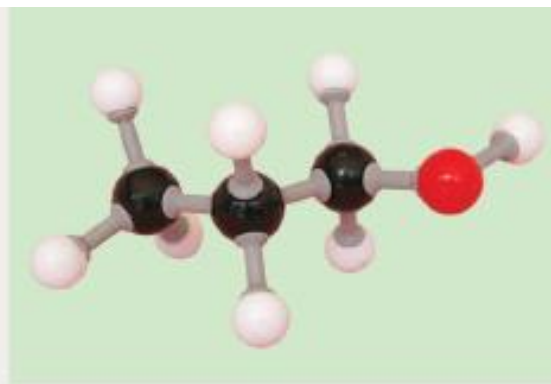
and just in condensed form:



1-propanol and 2-propanol are *isomers*, because they are different compounds having the same molecular formula, $\text{C}_3\text{H}_8\text{O}$. Similarly 1- and 2-butanol are isomers, having the molecular formula, $\text{C}_4\text{H}_{10}\text{O}$.

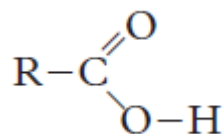


2-propanol

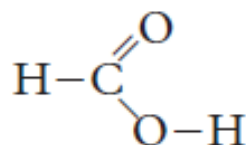


1-propanol

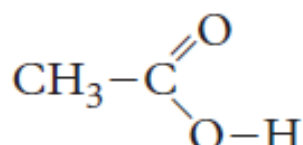
Alkanoic acids



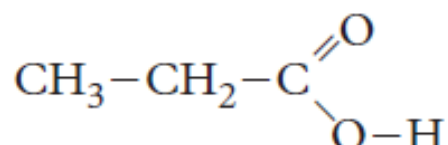
where R is an alkyl group



methanoic acid
(formic acid)

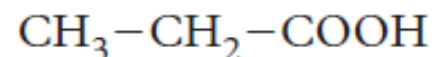
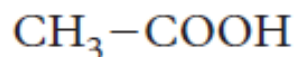


ethanoic acid
(acetic acid)



propanoic acid

For convenience we often write these structures as:



The homologous series called alkanoic acids has the general formula $\text{C}_n\text{H}_{2n}\text{O}_2$ with $n > 0$ or $\text{C}_n\text{H}_{2n+1}\text{COOH}$ with $n \geq 0$.

Identify the number of carbons present in the straight chain. Select the correct stem to name the parent alkane. Remove the 'e' and replace it with the suffix 'oic acid'.

- *explain the difference in melting point and boiling point caused by straight-chained alkanoic acid and straight chained primary alkanol structures*

MELTING AND BOILING POINTS OF ALKANOLS AND ALKANOIC ACIDS

Both the C–O and the O–H bonds are polar.

This means that alkanols are polar molecules.

The C=O bond is also polar,

with these three polar bonds alkanolic acids are even more polar.

O–H bonds are able to form hydrogen bonds.

there are strong intermolecular forces in alkanols and in alkanolic acids.

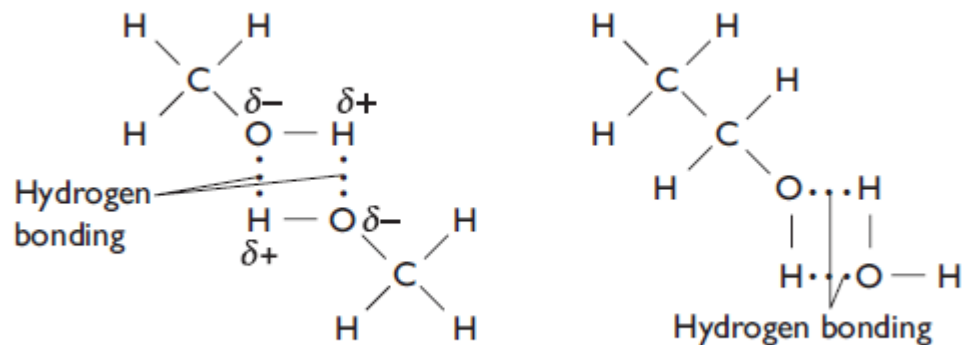
they have much higher melting and boiling points than alkanes of similar molecular weight

They also have quite high solubilities in water.

we generally compare compounds with similar molecular weights

the dispersion forces will be roughly similar in such compounds.

strength of dispersion forces increases as molecular weight increases,

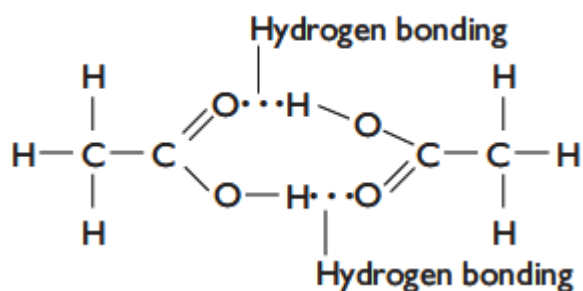


The hydrogen bonding between short-chain alkanol molecules raises their melting points. The hydrogen bonding between short-chain alkanols and water increases their water solubility.

Alkanoic acids are usually slightly more polar than alkanols and thus the dipole–dipole forces are greater.

the alkanoic acid has the higher melting point or boiling point.

This is mainly due to the more extensive hydrogen bonding between alkanoic acid molecules.



The strong hydrogen bonding between acetic acid molecules leads to the formation of dimers.

Boiling points for alkanes, alkanols and alkanolic acids of similar molecular weights

Molecular weights ^a	Alkane	Boiling point (°C)	Alkanol	Boiling point (°C)	Alkanolic acid	Boiling point (°C)
16	methane	-162				
30, 32	ethane	-89	methanol	65		
44, 46	propane	-42	ethanol	78	methanoic	100
58, 60	butane	-0.5	1-propanol	97	ethanoic	118
72, 74	pentane	36	1-butanol	117	propanoic	141
86, 88	hexane	69	1-pentanol	138	butanoic	164
100, 102	heptane	98	1-hexanol	157	pentanoic	186

a The first value is for the alkane; the second is for both the alkanol and the alkanolic acid.

Formulae and properties of common esters

Name ^a	Formula	Molecular weight	Boiling point (°C)	Solubility in water ^b
methyl methanoate (formate)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C} \\ \diagup \\ \text{O}-\text{CH}_3 \end{array}$	60	32	24
methyl ethanoate (acetate)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C} \\ \diagup \\ \text{O}-\text{CH}_3 \end{array}$	74	57	6.7

Esters

The fragrances of flowers and the smell and taste of their fruits are produced by a variety of volatile molecules, including a group of organic compounds called *esters*. Not all esters have pleasant smells, but the low molecular weight esters are usually volatile and aromatic.

Chemists have developed a range of synthetic esters that can be used as food flavourings as well as in perfumes.

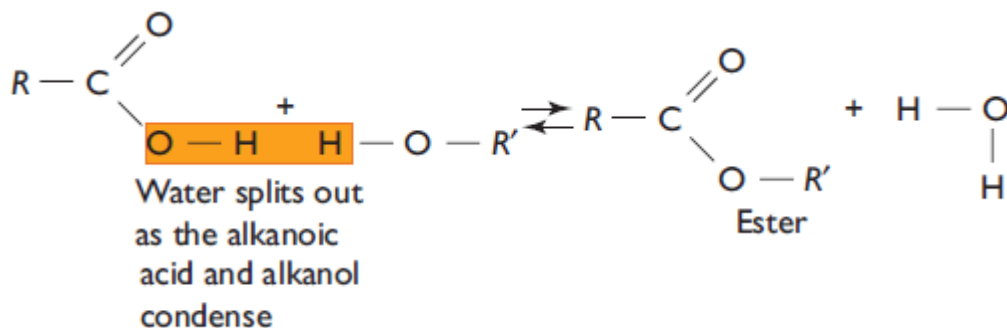
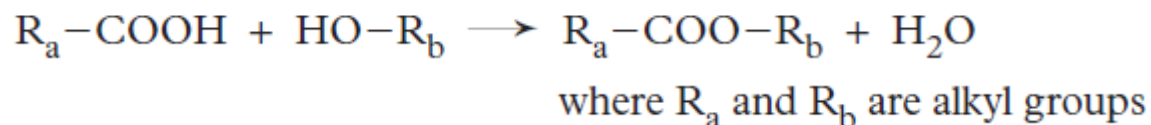
- *identify esterification as the reaction between an acid and an alkanol, and describe, using equations, examples of esterification*

Esters are compounds formed when alkanolic acids react with alkanols, or more generally, when carboxylic acids combine with alcohols.

Synthesis

The reaction between an alkanol and an alkanolic acid is called **esterification**.

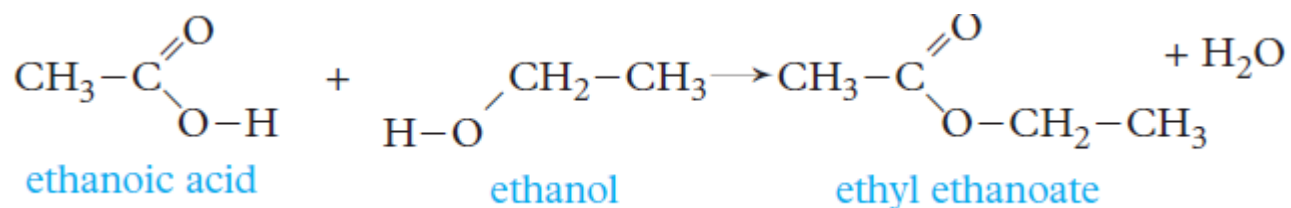
In general terms it can be written as:

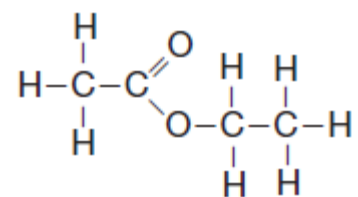
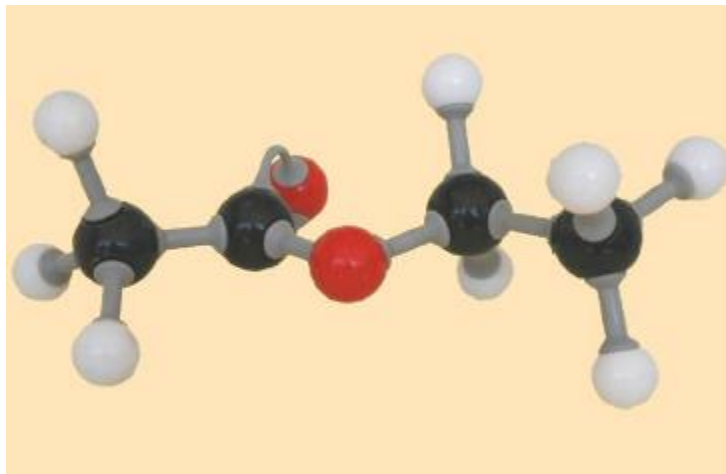


condensation reaction: a reaction in which two molecules combine together with the elimination of a smaller molecule such as water

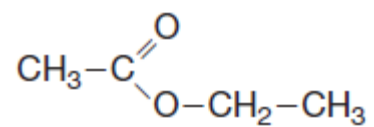
When the alkanol and alkanolic acid condense together, the water that is formed comes from the OH group of the alkanolic acid and the hydrogen from the alcohol functional group of the alkanol.

When ethanoic (acetic) acid and ethanol are heated with a few drops of concentrated sulfuric acid, the ester, ethyl ethanoate (ethyl acetate) is formed:



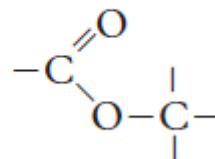


often written as



Ball-and-stick and
space-filling models of
the ester ethyl acetate
(ethyl ethanoate)

Esters contain the structural unit



- *identify the IUPAC nomenclature for describing the esters produced by reactions of straight-chained alkanoic acids from C1 to C8 and straight-chained primary alkanols from C1 to C8*

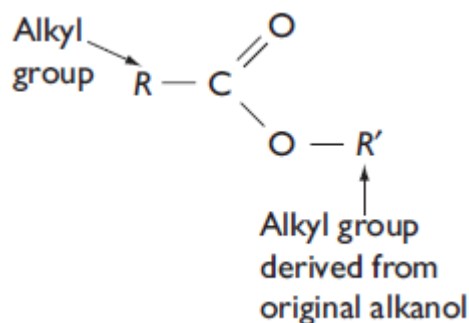
Naming esters

Nomenclature of esters

Alkyl alkanoate esters are named after their parent alkanols and alkanoic acids.

The rules for naming these esters are:

1. Count the number of carbon atoms in the alkyl group that is derived from the original alkanol. Name this alkyl group by deleting the 'anol' suffix from the alkanol and replacing it with the suffix 'yl' (e.g. butanol becomes butyl).
2. Identify the number of carbon atoms in the alkanoate chain that is derived from the alkanoic acid. Name this alkanoate chain by deleting the 'oic acid' suffix and replacing it with the suffix 'oate' (e.g. propanoic acid becomes propanoate).
3. The name of the ester is two separate words. The first name comes from the alkanol and the second from the alkanoic acid.



SAMPLE PROBLEM

Use the nomenclature rules for esters to name the ester whose structural formula is shown in Figure 10.10.

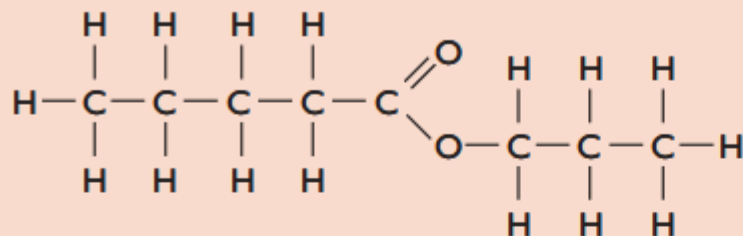


Figure 10.10

Use the nomenclature rules to name this ester.

Step 1. Identify the number of carbon atoms in the alkyl group derived from the original alcohol.

This is the hydrocarbon chain that is attached to the single bonded oxygen atom of the ester linkage.

Number of carbon atoms = 3.

Step 2. Name the alkyl group.

Name = propyl (or, 1-propyl).

Step 3. Identify the number of carbon atoms in the alkanoate chain derived from the original alkanoic acid.

This is the chain that includes the carbon attached to the double bonded oxygen atom (or carbonyl oxygen).

Number of carbon atoms = 5.

Step 4. Name the alkanoate group.

Name = pentanoate.

Step 5. Name the ester.

Name = propyl pentanoate (or 1-propyl pentanoate).

SAMPLE PROBLEM

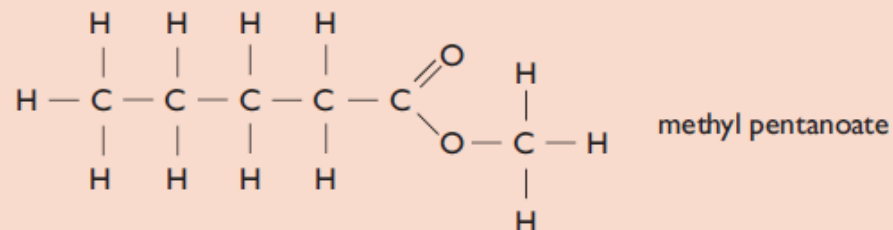
Complete the following table and draw structural formulae for each ester.

Alkanol	Alkanoic acid	Ester
methanol	pentanoic acid	(a)
propan-2-ol (2-propanol)	(b)	2-propyl hexanoate
(c)	propanoic acid	2-pentyl propanoate

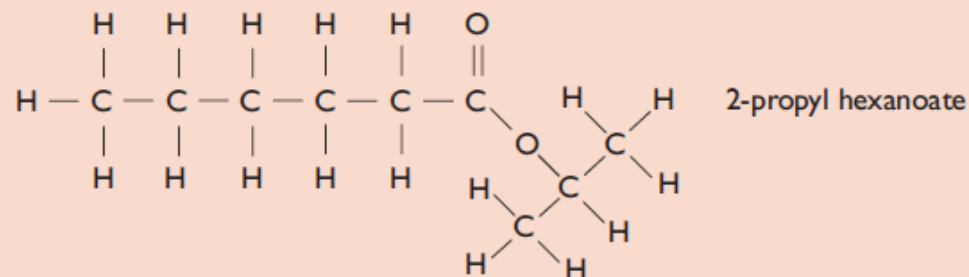
Alkanol	Alkanoic acid	Ester
methanol	pentanoic acid	methyl pentanoate
propan-2-ol (2-propanol)	hexanoic acid	2-propyl hexanoate
pentan-2-ol (2-pentanol)	propanoic acid	2-pentyl propanoate

SOLUTION

- (a) The alkyl group of this ester will be called 'methyl' and the alkanoate group will be 'pentanoate'. The name of the ester is methyl pentanoate.



- (b) The hexanoate group is derived from hexanoic acid.



- (c) The alkyl group is derived from an alkanol with the alcohol functional group on C-2. This alkyl group is called '2-pentyl'.

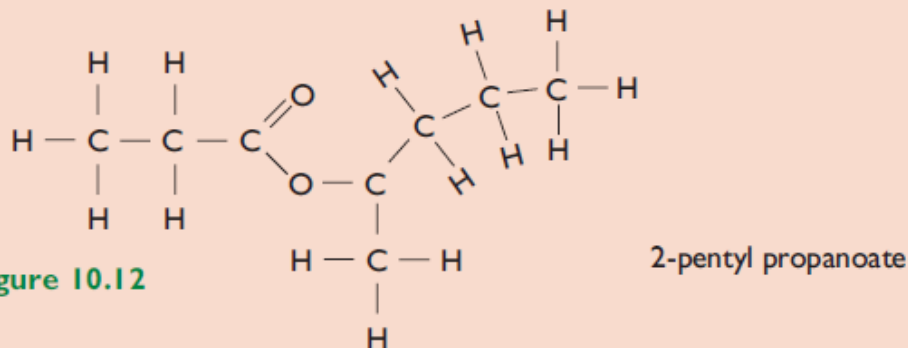


Figure 10.12

Properties

The $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bonds make esters *polar substances*.

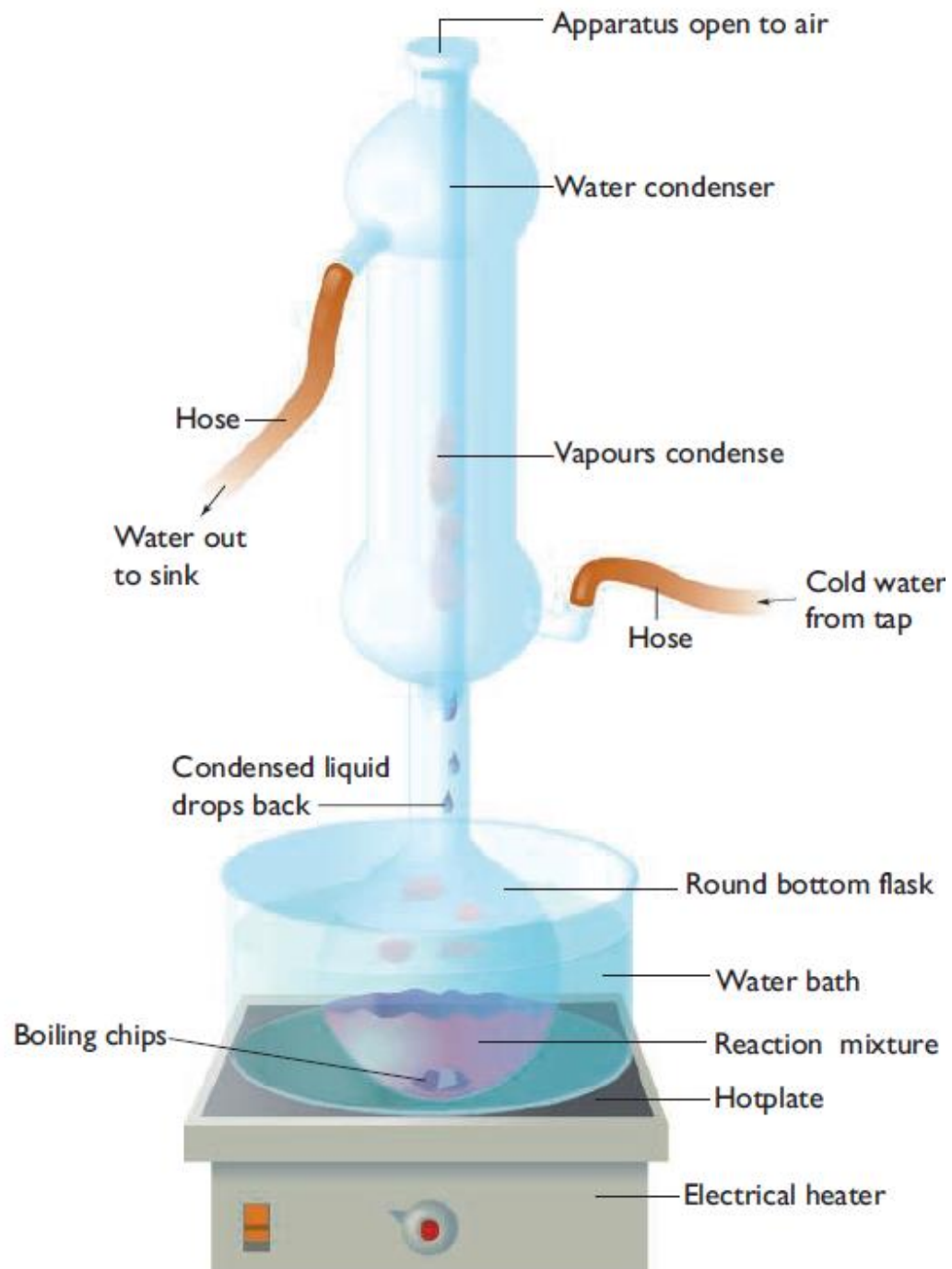
However the lack of hydrogen bonding means that esters have much lower boiling points than acids or alkanols of the same molecular weight. They are also much less soluble in water.

- *describe the purpose of using acid in esterification for Catalysis*
- *explain the need for refluxing during esterification*

Esterification

Refluxing is the process of heating a reaction mixture in a vessel with a cooling condenser attached in order to prevent loss of any volatile reactant or product.

Esterification reactions do not go into completion and are usually quite slow	<ul style="list-style-type: none">• Increase the rate of reaction by• Adding a suitable catalyst (conc. Sulphuric acid)• Heating the reaction mixture to increase the kinetic energy of the molecules
To increase the yield, the equilibrium must shift to the right	<ul style="list-style-type: none">• The conc. Sulphuric acid acts as a dehydrating agent and removes the water• An excess of one of the reactants is used
The reactants and products are volatile and vaporise readily on heating	<ul style="list-style-type: none">• A water condenser is mounted above the reaction flask. The vapours condense back to the liquid state and drip back into the flask so that the reaction can continue without a loss of reactants or products. This is refluxing.
There is a production of vapours	<ul style="list-style-type: none">• The system is open
The organic liquids and vapours are flammable and care must be taken to avoid fires and explosions	<ul style="list-style-type: none">• Use an electric heating mantle or a water bath supported on a hot plate.• Naked flames must be avoided to reduce the risk of fire.
Risks of sudden superheating and explosive ejection of vapours	<ul style="list-style-type: none">• Boiling chips prevent a process called 'bumping' as they provide a large surface area on which vaporisation can occur.



Extraction of the ester from the reaction mixture

Example 1:

Methyl acetate — Following reflux, the reaction mixture is distilled and the crude ester vaporises at 57°C and forms the distillate. The excess acetic acid (b.p. = 118°C) and most of the methanol (b.p. = 65°C) stays in the distillation flask. The crude ester is washed in a separating funnel with a little saturated salty water containing sodium hydrogen carbonate to neutralise any acetic acid. The ester layer is removed, dried and then re-distilled to obtain the pure ester.

Example 2:

Ethyl acetate — The reaction mixture cannot be distilled as the boiling points of the ethanol (78°C) and the ester (77°C) are too close. Therefore, following reflux, the reaction mixture is added to an equal volume of water and saturated with salt to reduce the solubility of the ethyl acetate and produce an ester layer. The ester layer is treated with sodium hydrogen carbonate to neutralise any acetic acid and then saturated with salt again. The ester layer is removed and dried before distillation to obtain the pure ester. Much ester is lost due to its solubility in water. Fractional distillation can be used to improve the yield.

- *outline some examples of the occurrence, production and uses of esters*

- *process information from secondary sources to identify and describe the uses of esters as flavours and perfumes in processed foods and cosmetics.*

Occurrence, production and uses of esters

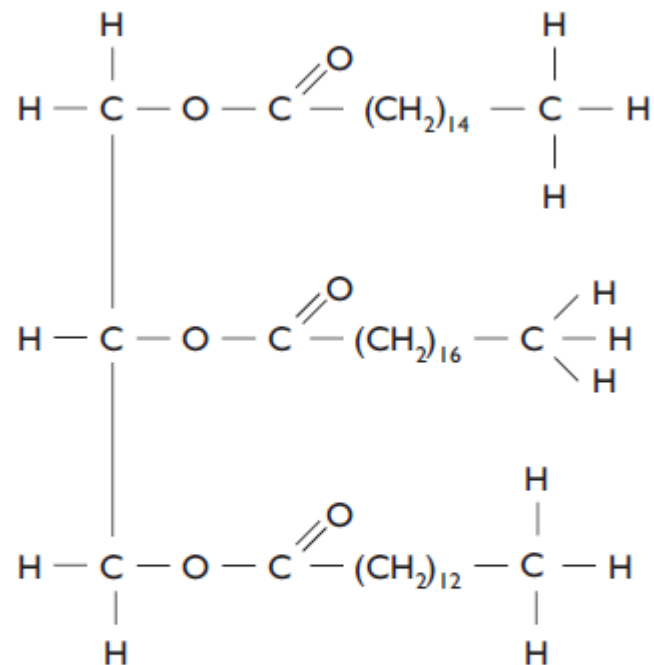
Esters occur widely in nature. They are also produced by various industries.

Esters in nature

Esters occur in all natural systems. Esters can be formed not only from alkanolic acids, but also from other organic and inorganic acids. Phosphate esters are esters formed from phosphoric acid

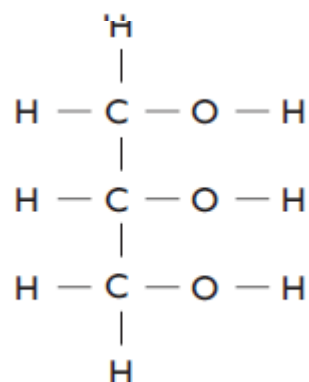
Fats and oils are triesters

of glycerol and various long-chain carboxylic acids. They are commonly known as *triglycerides*. Natural waxes consist of mixed esters of long-chain alkanols and long-chain alkanolic acids (fatty acids).



Derived from
glycerol

Derived from long-chain
fatty acids of variable
chain length



Glycerol is a alkantriol. Its has three alcohol functional groups. Each of these can bond with a long-chain carboxylic acid (or fatty acid) to form a triester or fat.

Esters as lubricants in refrigeration systems.

Esters as solvents and coatings

Many natural and synthetic esters are used in wood lacquers, thinners and some solvents used in surface finishes.

Esters of propanoic acid improve solvent diffusion from coating films. They are used in automotive refinishing and in cosmetics.

Esters as plasticisers

Phthalate esters are oily liquids that are added to hard plastics (such as PVC) in order to soften them and increase their flexibility.

Examples

(including tubing, gloves and medical containers), shower curtains, toys

Esters as alternative fuels

Esters of natural fatty acids are used as biofuels.

Esters as flavours, fragrances and emulsifiers

Flavour	Main ester(s) present
apple	methyl butanoate and iso-pentyl pentanoate
banana	iso-pentyl ethanoate ^b
grape	ethyl methanoate and ethyl heptanoate
orange	octyl thanoate
pear	pentyl ethanoate
raspberry	butyl ethanoate
rum	ethyl methanoate
jasmine	benzyl ethanoate

Methyl salicylate or *oil of wintergreen* is used in lotions and creams to soothe sore muscles. Esters that have a high molecular weight are also used in cosmetics and the food industry as emulsifying agents.

Myristyl myristate is a solid **emollient** ester that liquefies on contact with the body, enhances spreadability of the cream and delivers a velvety feel to the skin.