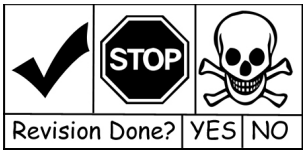
Unit 15 Aromatic etc. (Paper 2 & 3)

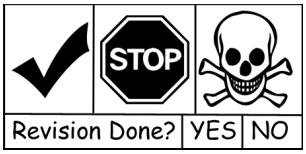
15.1 Aromatic chemistry

Bonding
The nature of the bonding in a benzene ring, limited to planar structure and bond length intermediate between single and double.
Delocalisation of p electrons makes benzene more stable than the theoretical molecule cyclohexa-1,3,5-triene.
You should be able to:
• use thermochemical evidence from enthalpies of hydrogenation to account for this extra stability
• explain why substitution reactions occur in preference to addition reactions.



15.2 Electrophilic substitution

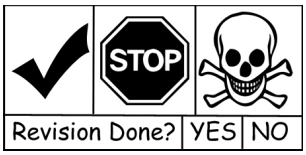
Electrophilic attack on benzene rings results in substitution, limited to monosubstitutions.
Nitration is an important step in synthesis, including the manufacture of explosives and formation of amines.
Friedel–Crafts acylation reactions are also important steps in synthesis.
You should be able to outline the electrophilic substitution mechanisms of:
• nitration, including the generation of the nitronium ion
• acylation using AlCl 3 as a catalyst.



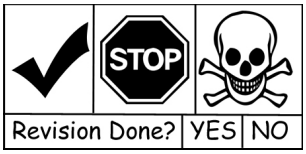
15.3 Amines

Preparation
Primary aliphatic amines can be prepared by the reaction of ammonia with halogenoalkanes and by the reduction of nitriles.
Aromatic amines, prepared by the reduction of nitro compounds, are used in the manufacture of dyes.

Base properties
Amines are weak bases.
The difference in base strength between ammonia, primary aliphatic and primary aromatic amines.
You should be able to explain the difference in base strength in terms of the availability of the lone pair of electrons on the N atom.



Nucleophilic properties
Amines are nucleophiles.
The nucleophilic substitution reactions of ammonia and amines with halogenoalkanes to form primary, secondary, tertiary amines and quaternary ammonium salts.
The use of quaternary ammonium salts as cationic surfactants.
The nucleophilic addition–elimination reactions of ammonia and primary amines with acyl chlorides and acid anhydrides.
You should be able to outline the mechanisms of:
• these nucleophilic substitution reactions
• the nucleophilic addition–elimination reactions of ammonia and primary amines with acyl chlorides.



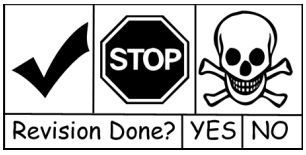
15.4 Polymers

Condensation polymers

Condensation polymers are formed by reactions between:
- dicarboxylic acids and diols
- dicarboxylic acids and diamines
- amino acids.

The repeating units in polyesters (eg Terylene) and polyamides (eg nylon 6,6 and Kevlar) and the linkages between these repeating units.
Typical uses of these polymers.

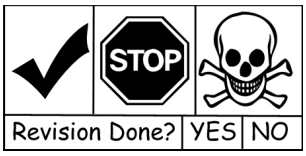
You should be able to:
- draw the repeating unit from monomer structure(s)
- draw the repeating unit from a section of the polymer chain
- draw the structure(s) of the monomer(s) from a section of the polymer
- explain the nature of the intermolecular forces between molecules of condensation polymers.



Biodegradability and disposal of polymers

Polyalkenes are chemically inert and non-biodegradable.
Polyesters and polyamides can be broken down by hydrolysis and are biodegradable.
The advantages and disadvantages of different methods of disposal of polymers, including recycling.

You should be able to explain why polyesters and polyamides can be hydrolysed but polyalkenes cannot.

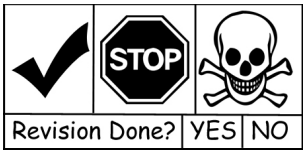


15.5 Amino acids, proteins and DNA

Amino acids

Amino acids have both acidic and basic properties, including the formation of zwitterions.

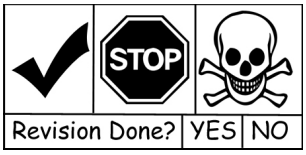
You should be able to draw the structures of amino acids as zwitterions and the ions formed from amino acids:
- in acid solution
- in alkaline solution.



Proteins

Proteins are sequences of amino acids joined by peptide links.
The importance of hydrogen bonding and sulfur–sulfur bonds in proteins.
The primary, secondary (α-helix and β–pleated sheets) and tertiary structure of proteins.
Hydrolysis of the peptide link produces the constituent amino acids.
Amino acids can be separated and identified by thin-layer chromatography.
Amino acids can be located on a chromatogram using developing agents such as ninhydrin or ultraviolet light and identified by their R_f values.

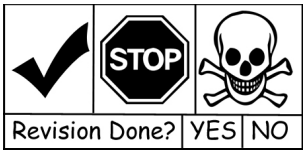
You should be able to:
- draw the structure of a peptide formed from up to three amino acids
- draw the structure of the amino acids formed by hydrolysis of a peptide
- identify primary, secondary and tertiary structures in diagrams
- explain how these structures are maintained by hydrogen bonding and S–S bonds
- calculate R_f values from a chromatogram.



Enzymes

Enzymes are proteins.
The action of enzymes as catalysts, including the concept of a stereospecific active site that binds to a substrate molecule.
The principle of a drug acting as an enzyme inhibitor by blocking the active site.
Computers can be used to help design such drugs.

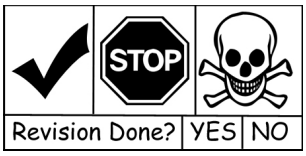
You should be able to explain why a stereospecific active site can only bond to one enantiomeric form of a substrate or drug.



DNA

The structures of the phosphate ion, 2-deoxyribose (a pentose sugar) and the four bases adenine, cytosine, guanine and thymine **are given in the Chemistry Data Booklet.**
A nucleotide is made up from a phosphate ion bonded to 2-deoxyribose which is in turn bonded to one of the four bases adenine, cytosine, guanine and thymine.

A single strand of DNA (deoxyribonucleic acid) is a polymer of nucleotides linked by covalent bonds between the phosphate group of one nucleotide and the 2-deoxyribose of another nucleotide. This results in a sugar-phosphate- sugar-phosphate polymer chain with bases attached to the sugars in the chain.
DNA exists as two complementary strands arranged in the form of a double helix.
You should be able to explain how hydrogen bonding between base pairs leads to the two complementary strands of DNA.



Action of anticancer drugs
The Pt(II) complex cisplatin is used as an anticancer drug.
Cisplatin prevents DNA replication in cancer cells by a ligand replacement reaction with DNA in which a bond is formed between platinum and a nitrogen atom on guanine.
Appreciate that society needs to assess the balance between the benefits and the adverse effects of drugs, such as the anticancer drug cisplatin.
You should be able to:
• explain why cisplatin prevents DNA replication
• explain why such drugs can have adverse effects.