

UNIT 10: NITROGEN COMPOUNDS AND POLYMERS

Recommended Prior Knowledge: The AS Units 4 and 5 (Organic Chemistry) should have been completed. Parts of A2 Unit 7A (ionic equilibria involving acids and bases) would be useful background to work on the basicities of amines. Sub-unit 10B should be taught after Sub-unit 10A.

Context: These two sub-units can be studied on their own, or in conjunction with each other. They should be studied after the other A2 Organic Chemistry Unit 9, but can come before or after the other A2 Units. Some of their topics are relevant to part of the Applications section (Units 11A and 11C) so should it be studied before those sub-units.

Outline: Sub-unit 10A covers the preparation and properties of amines, the formation of dyes, and the formation and hydrolysis of amides and proteins. Sub-unit 10B covers condensation polymerisation, forming polyesters, polyamides and proteins. It also revises addition polymerisation.

UNIT 10A: NITROGEN COMPOUNDS

AO	Learning Outcomes	Suggested Teaching Activities	Learning Resources
10.1(a)	interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound: (vi) amides and aminoacids	It is important for students to be able to recognise an amide in a non-displayed structural formula. Often the part formula $-\text{CONH}-$ is misinterpreted as $-\text{C}-\text{O}-\text{NH}-$. The chirality of all amino acids except glycine should be mentioned – only α -aminoacids need to be considered.	M 122 C+H 30.2 R+N 21.9
10.7(a)	describe the formation of ethylamine (by nitrile reduction -see also Section 10.4) and of phenylamine (by the reduction of nitrobenzene)	The most common reagent for the transformation $\text{R-CN} \rightarrow \text{R-CH}_2\text{NH}_2$ is LiAlH_4 in dry ether. Catalytic hydrogenation ($\text{H}_2 + \text{Ni}$) is also effective. Cyanohydrins (from carbonyl compounds + HCN) are also reduced, to hydroxyamines. The best reagent for the transformation $\text{ArNO}_2 \rightarrow \text{ArNH}_2$ is $\text{Sn} + \text{conc HCl}$. NaBH_4 only works in the presence of a catalyst, and LiAlH_4 produces many by-products, including azo compounds. If time and apparatus permit, the classical reduction of nitrobenzene, and purifying the phenylamine by steam distillation, is a fine laboratory experience for the student [The phenylamine layer from the steam distillation can be used without further distillation to show its reactions as a base and to make an azo dye].	M 122 C+H 30.4 R+N 21.1 P(A2) 19 site 4 (nitrogen compounds)
10.7(b) 10.7(c)	explain the basicity of amines. explain the relative basicities of ammonia, ethylamine and phenylamine in terms of their structures	This section could start with a revision of the AS topic on Bronsted-Lowry acids and bases. By analogy with ammonia, amines are expected to be weak bases. [Practical work could include dissolving Ph-NH_2 in HCl(aq) and liberating the free oil with NaOH(aq) , and demonstrating that the fishy smell of ethylamine (or butylamine – easier to handle) disappears when it is dissolved in HCl(aq) , but reappears on adding NaOH(aq) . Titrations can also be carried out (using methyl orange as indicator).] Due to the inductive effect, alkyl amines tend to be slightly stronger bases than ammonia, whereas the delocalisation of the nitrogen lone pair over the ring in phenylamine is responsible for it being much less basic than ammonia. This ties in with phenylamine's ready electrophilic substitution, described below.	M 122 C+H 30.3 R+N 21.2 - 21.3

10.7(d)	describe the reaction of phenylamine with: (i) aqueous bromine (ii) nitrous acid to give the diazonium salt and phenol	Point out that just as with phenol, electrophilic substitution is easier with phenylamine than with benzene. Thus bromination merely requires bromine <i>water</i> and no Lewis catalyst. As with phenol, decolourisation occurs, with the formation of a white ppt. Nitrous acid (made <i>in situ</i> from NaNO_2 + excess HCl(aq) at a low temperature (below 5°C) converts phenylamine into (a solution of) benzenediazonium chloride. On warming to about 50°C , this decomposes to phenol and nitrogen gas (usually in not a very good yield, but enough to be able to smell the phenol). Both these reactions can be illustrated by students' own practical work or by demonstration.	M 122 C+H 30.3 R+N 21.4
10.7(e)	describe the coupling of benzenediazonium chloride and phenol and the use of similar reactions in the formation of dyestuff	Pour a cold solution of previous-prepared benzenediazonium chloride into a solution of phenol dissolved in NaOH(aq) to produce an orange-red dye. Other coloured dyestuffs can be made by using different phenols (e.g. 2-naphthol) or different amines (e.g. methyl phenylamines), or whatever happens to be in the store cupboard at the time!	M 122 C+H 30.3 R+N 21.5 – 21.6 P(A2) 24
10.7(f) 10.7(g)	describe the formation of amides from the reaction between RNH_2 and R'COCl / describe amide hydrolysis on treatment with aqueous alkali or acid	The preparations of benzamide (see Unit 9B), and N-phenylethanamide produce readily recrystallisable amides, and are good examples of this nucleophilic substitution (condensation) reaction. The above two amides can be hydrolysed (although with either OH^- or H^+ it takes several hours), and a good sample of benzoic acid can be precipitated by HCl(aq) when benzamide is hydrolysed in alkali.	M 120 C+H 29.4, 29.7 R+N 21.7 – 21.8 P(A2) 23, 25, 26
10.7(h)	describe the acid/base properties of amino acids and the formation of zwitterions	Confine the discussion to α -amino acids only. Point out their amphoteric nature – both with external acids and bases, and also with themselves (forming zwitterions). As evidence for their zwitterionic form mention the typical "ionic" properties they show: solubility in water, high melting point. At this stage it would be worth reminding students of the chiral nature of amino acids. Students should practice writing balanced equations for the reactions between amino acids and mineral acids and bases.	M 123 C+H 30.5 R+N 21.10
10.7(i) 10.7(j) 10.7(k)	describe the formation of peptide bonds between amino acids and, hence, explain protein formation describe the hydrolysis of proteins describe the formation of polyamides	This is an example of <i>condensation polymerisation</i> (see Unit 10B), and is essential knowledge for the later Unit 11A. Explain very briefly to the non-biologists that it is the amino acid sequence in a protein that determines its biological properties (e.g. how it acts as an enzyme). The classic hydrolysis conditions are 50% HCl(aq) for 8 hours. It is possible for students to hydrolyse protein (e.g. hair) and separate the resulting amino acids by paper chromatography. Other (synthetic) polyamides can be produced when an amino acid undergoes self-condensation (e.g. 6-aminohexanoic acid \rightarrow nylon-6).	M 123 C+H 30.6 R+N 21.11 – 21.13 site 17 (biological chemistry)

UNIT 10B: POLYMERS

AO	Learning Outcomes	Suggested Teaching Activities	Learning Resources
10.8(c)	describe the characteristics of condensation polymerisation (i) in polyesters as exemplified by <i>Terylene</i> .	Define <i>condensation polymerisation</i> in terms of monomers joining together with the expulsion of one molecule of water (or other small molecule) for each linkage formed. Use of a diacyl chloride will form HCl as by-product. The monomers that make up <i>Terylene</i> are ethane-1,2-diol and benzene-1,4-dicarboxylic acid, and the sense of direction of the ester bonds alternates (e.g. $-\text{O}-\text{CO}-\text{CO}-\text{O}-$)	M 127 C+H 29.6 R+N 22.4
10.8(c)	describe the characteristics of condensation polymerisation (ii) in polyamides as exemplified by peptides, proteins, nylon 6 and nylon 66.	Once more, point out that a small molecule is released for each amide bond formed. In peptides, proteins and in nylon-6, the amide bonds are all in the same direction (e.g. $-\text{NHCO}-\text{NHCO}-\text{NHCO}-$), whereas in nylon-66 they alternate ($-\text{NHCO}-\text{CONH}-$). Explain that hydrogen bonding can occur between the N-H and C=O of different (or the same) chain, causing some degree of coiling and 'cross-linking' in proteins.	M 127 C+H 30.7 R+N 22.4 site 4 (polymers) site 17 (biological chemistry)
10.8(d)	predict the type of polymerisation reaction for a given monomer or pair of monomers.	Revise the fact that alkenes (including chloroalkenes such as chloroethene and alkene-esters such as methylacrylate) undergo <i>addition polymerisation</i> , whereas compound with functional groups such as alcohols, amines and acids undergo <i>condensation polymerisation</i> . Give students practice in drawing the structural formulae of repeat units of polymers from given pairs of monomers.	M 127 C+H 24.4, 30.7 R+N 22.5
10.8(f)	deduce the type of polymerisation reaction which produces a given section of a polymer molecule.	If the backbone contains just carbon atoms, the polymer must have come from the <i>addition polymerisation</i> of an alkene, whereas if the backbone contains amide or ester functional groups, the polymer is a <i>condensation polymer</i> .	
10.8(e)	deduce the repeat unit of a polymer obtained from a given monomer or pair of monomers.	Repeat units should be drawn using brackets, and showing the structural formula of the unit. For example, that for nylon-6 is $-\text{[NH(CH}_2)_5\text{CO]}-$. If the monomer is an alkene, the repeat unit is merely the alkene moiety with the double bond replaced by repeating single bonds: poly(propene) is $-\text{[CH}_2\text{-CH(CH}_3\text{)]}-$. For an addition copolymer, both monomers should be included in the repeat unit.	M 127 C+H 24.4, 30.7 R+N 22.6
10.8(g)	identify the monomer(s) present in a given section of a polymer molecule.	For an addition polymer, the backbone chain should be broken up into two-carbon units, and a double bond inserted between the two carbon atoms. Students should be aware that copolymers will have two (or more) different monomers. Most condensation polymers are made from two monomers – one a diol or diamine, and the other a diacid. Students find difficulty with both these processes, so much practice ought to be given. Get them to write out the structural formulae of the repeat units from several given pairs of monomers, and also to write out the structural formulae of the monomers responsible for sections of given polymers.	R+N 22.7