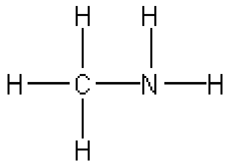
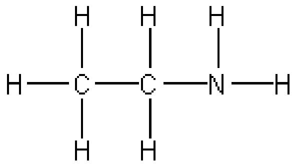
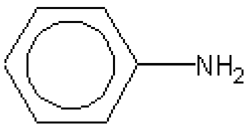
Topic 7 – Nitrogen compounds
Revision Notes

1) Amines

- In primary amines, a nitrogen atom is attached to one alkyl group and two hydrogen atoms. The general formula for a primary amine is RNH_2
- The simplest amine is methylamine, CH_3NH_2. Other amines of interest are ethylamine, $CH_3CH_2NH_2$, and phenylamine, $C_6H_5NH_2$







- $(CH_3)_2NH$ is dimethylamine, a secondary amine
- $(CH_3CH_2)_3N$ is triethylamine, a tertiary amine
- $(CH_3)_4N^+Cl^-$ is a quaternary ammonium salt

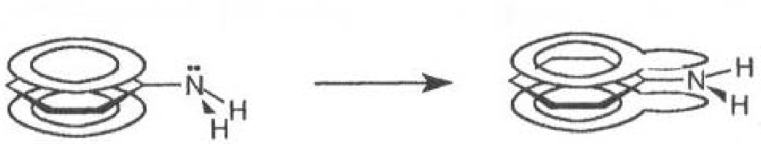
2) Amines as bases

- Bases are proton (H^+) acceptors.
- Amines can accept protons because of the lone pair on the N
- This lone pair forms a co-ordinate bond with an H^+ e.g.

with an acid $\mathbf{CH_3NH_2 + HCl \rightleftharpoons CH_3NH_3^+ + Cl^-}$
Methylamine — methylammonium chloride

with water $\mathbf{CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-}$
Ethylamine — ethylammonium hydroxide

- Base strength (ability to accept H^+) depends on the availability of the N's lone pair
- **In ethylamine, the ethyl group releases electrons towards the N making its lone pair more available (the alkyl group has an inductive effect)**
- **In phenylamine, the lone pair on the N is delocalised into the ring making the lone pair less available**



- Base strength is reduced because H^+ is less easily accepted due to the reduced electron availability
- Phenylamine is, therefore, a weaker base than ethylamine
- In general, aliphatic amines are stronger bases than aromatic amines

3) Nucleophilic substitution reactions

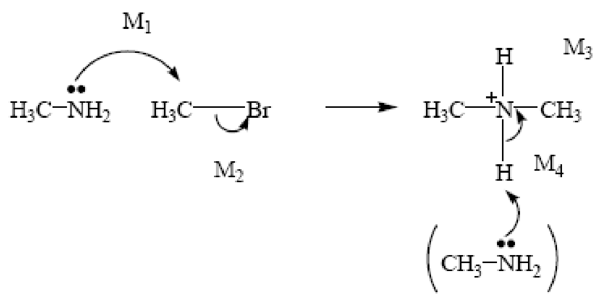
- Ammonia reacts with haloalkanes to form a primary amine e.g.

$$CH_3Br + NH_3 \rightarrow CH_3NH_2 + HBr$$

- To make a primary amine in this reaction, excess ammonia is needed. Otherwise, with excess chloroethane, the reaction can continue and will produce a mixture of products

$$CH_3Br + CH_3NH_2 \rightarrow (CH_3)_2NH + HBr$$
$$CH_3Br + (CH_3)_2NH \rightarrow (CH_3)_3N + HBr$$
$$CH_3Br + (CH_3)_3N \rightarrow (CH_3)_4N^+ + Br^-$$

- The quaternary ammonium salt produced in the fourth step are used as cationic surfactants (detergents)
- The mechanism for this reaction is called nucleophilic substitution. Ammonia and amines are lone pair donors in these reactions



4) Preparation of amines

a) Preparation of aromatic amines by reduction of nitro compounds

- Here, reduction means gain of hydrogen

$C_6H_5NO_2 + 6[H] \rightarrow$	$C_6H_5NH_2 + 2H_2O$
Nitrobenzene	phenylamine

Reagents Tin (Sn) and concentrated hydrochloric acid
Conditions Reflux

b) Reduction of nitriles to make primary amines

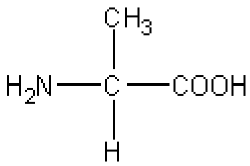
- Again, reduction means gain of hydrogen

$CH_3CH_2CN + 4[H] \rightarrow$	$CH_3CH_2CH_2NH_2$
Propanenitrile	propylamine

Reagents $LiAlH_4$ in dry ether

5) <u>Optical isomers</u>

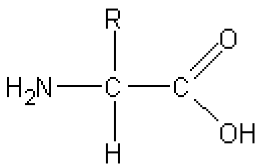
- An optical isomer is one that cannot be superimposed on its mirror image.
- This occurs when a carbon is attached to four different groups. Such a carbon is known as a chiral centre or an asymmetric carbon
- Optical refers to the ability of these molecules to rotate plane-polarised light. D isomers rotate light to the right and L isomers rotate light to the left. This difference in rotation can be used to distinguish between two optical isomers
- Enantiomer is another term for optical isomer. A racemic mixture is a 50:50 mixture of enantiomers which is optically inactive (as the rotational effects cancel)
- Most amino acids display optical isomerism e.g. alanine



- The central carbon is a chiral centre because it is attached to four different groups, namely: $-NH_2$, -H, -COOH and $–CH_3$

6) <u>Amino acids</u>

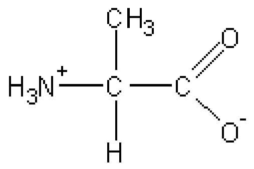
- Amino acids found in living things have the general formula $RCH(NH_2)COOH$ where R is an alkyl group



- Amino acids contain an acidic functional group (-COOH) and a basic functional group ($-NH_2$). This means they can act as both acids and bases
- Technically, these are ¯-amino acids because the $–NH_2$ is on the C next to the –COOH. ¯-amino acids have the $-NH_2$ on the next but one C to the –COOH
- If R is H, the amino acid is glycine, NH_2CH_2COOH. The proper chemical name for glycine is 2-aminoethanoic acid
- If R is CH_3, the amino acid is alanine, $CH_3CH(NH_2)COOH$. The proper chemical name for alanine is 2-aminopropanoic acid
- All amino acids, apart from glycine, show optical isomerism as the central C has four different groups attached to it
- There are 20 different amino acids in the human body

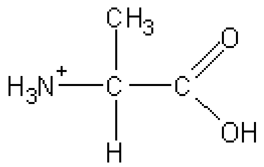
7) <u>Forms of amino acid</u>

- In solid form and in neutral solutions, amino acids exist as **zwitter ions** (zwitter is a German word whose English equivalent is hybrid)**.** These ions contain a full positive charge and a full negative charge
- The –COOH has lost H^+ and the $–NH_2$ has gained H^+

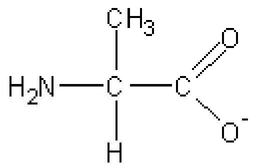


Solid amino acids have high melting points because there are strong ion-ion forces between molecules

- At low pH/in acidic solution (one that contains H^+) the amino acid has the following form

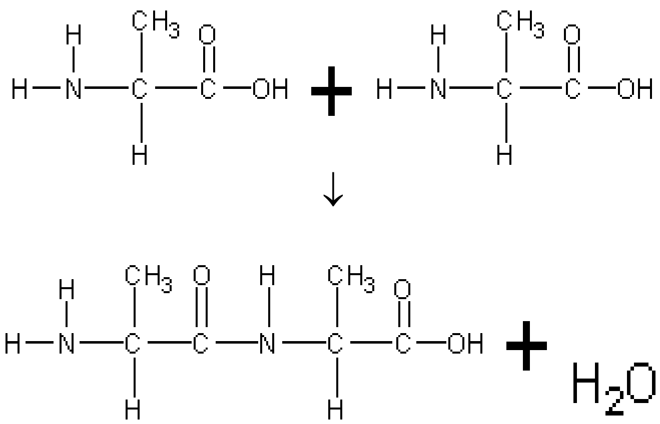


- At high pH/in alkaline solution (one that contains OH^-) the amino acid has the following form



7) <u>**Proteins**</u>

- Amino acids can join together via peptide links (-CONH-). This uses the –COOH group of one amino acid and the $–NH_2$ group of another amino acid. A molecule of water is produced when the peptide link is formed e.g.



- Two amino acids join to make a dipeptide. If the amino acids are not the same, two different dipeptides can be formed (one using COOH of amino acid 1 and NH_2 of amino acid 2 and the other using NH_2 of amino acid 1 and the COOH of amino acid 2)
- Proteins are sequences of amino acids joined by peptide links
- A protein can be split up into its constituent amino acids by heating with HCl(aq). This is called hydrolysis
- Mixtures of amino acids can be separated by chromatography
- Protein chains are held in one of two basic shapes by hydrogen bonds between the N-H of one amino acid and the C=O of another amino acid
- These basic shapes (α-helix and a β-pleated sheet) are called secondary protein structures