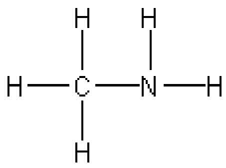
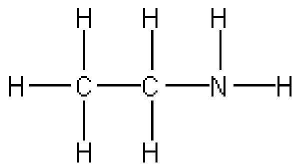
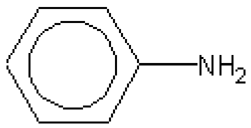
<u>Topic 9 – Nitrogen compounds</u>
<u>Revision Notes</u>

1) <u>Amines - introduction</u>

- 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, $C_6H_5NH_2$







- In amines, the N has 3 bonding pairs and 1 lone pair so shape is pyramidal, bond angle = 107°

2) <u>Amines as bases</u>

- 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	**CH_3NH_2 + HCl →** Methylamine	**$CH_3NH_3^+$ + Cl^-** methylammonium chloride
with water	**$CH_3CH_2NH_2$ + H_2O** Ethylamine	**$CH_3CH_2NH_3^+$ + OH^-** ethylammonium hydroxide

- N now has 4 bonding pairs so its shape is tetrahedral, bond angle 109.5°

3) <u>Preparation of amines</u>

a) Reduction of nitrobenzene to make phenylamine

Here, reduction means gain of hydrogen

$C_6H_5NO_2$ + 6[H] → Nitrobenzene	**$C_6H_5NH_2$ + $2H_2O$** phenylamine

Reagents Tin (Sn) and concentrated hydrochloric acid
Conditions Reflux

b) Substitution of halogenoalkanes

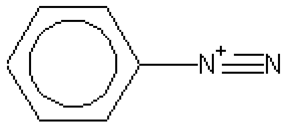
CH_3CH_2Cl + NH_3 → Chloroethane	**$CH_3CH_2NH_2$ + HCl** ethylamine

Reagents excess ammonia
Conditions dissolved in ethanol

4) Synthesis of azo dyes

- o Azo dyes contain the azo functional group -N=N-
- o Azo dyes are brightly coloured and bond well to fabrics
- o Phenylamine can be converted into an azo dye by a two stage process
- o Stage 1 – phenylamine to diazonium salt

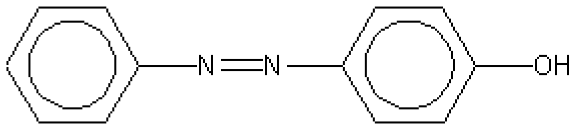
$C_6H_5NH_2$ + HNO_2 + HCl →	**C_6H_5N⌒N^+ + Cl^- + $2H_2O$**
Phenylamine	benzenediazonium chloride



Reagents	HNO_2/HCl (nitrous acid/HCl) or $NaNO_2$/HCl (sodium nitrite/HCl)
Conditions	<10°C (to prevent the diazonium salt decomposing)

- o Stage 2 – coupling with phenol under alkaline conditions

C_6H_5N⌒N^+ + C_6H_5OH + OH^- → $C_6H_5N{=}NC_6H_4OH$ + H_2O

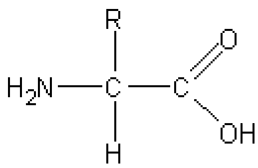


Reagents	phenol/NaOH
Conditions	<10°C

- o These reactions are used in formation of dyestuffs (soluble substances used for staining or colouring fabrics)

5) Amino acids - introduction

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

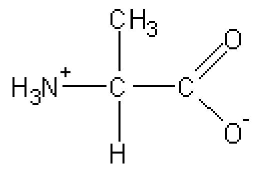


- Amino acids contain an acidic functional group (-COOH) and a basic functional group ($-NH_2$). This means they can act as both acids and bases (they are amphoteric)
- Technically, these are ¯-amino acids because the $-NH_2$ is on the C next to the –COOH. ¯-amino acids have the $-NH_2$ on the next but 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 glycine is 2-aminopropanoic acid
- All amino acids, apart from glycine, show optical isomerism as the central C has four different groups attached to it

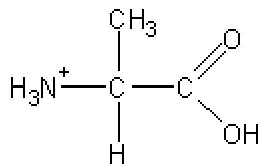
- There are 20 different amino acids in the human body

6) Effect of pH

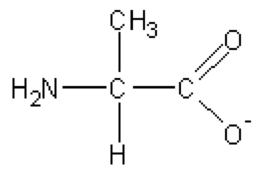
- At a pH value called the isoelectric point, amino acids exist as zwitter ions (zwitter is a German word whose English equivalent is hybrid). These ions contain a full positive charge and a full negative charge
- The –COOH has lost H^+ and the $–NH_2$ has gained H^+
- Amino acids exist in this form in the solid state and have high melting points because there are strong ion-ion forces between the zwitter ions
- Different R groups in α-amino acids result in different isoelectric points



- At a pH lower than the isoelectric point the amino acid has the form shown below. The amino acid is in acidic conditions and the NH_2 will gain H^+ to become NH_3^+

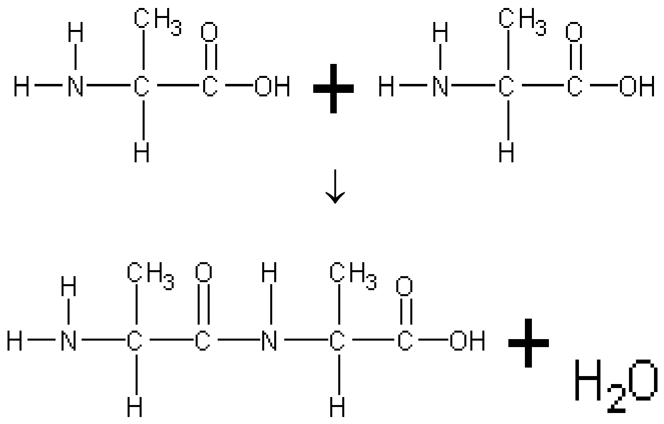


- At a pH higher than the isoelectric point the amino acid has the form shown below. The amino acid is in alkaline conditions and the COOH will lose H^+ to become COO^-



7) Dipeptides, polypeptides and proteins

- Amino acids can join together to form dipeptides
- This uses the –COOH group of one amino acid and the $–NH_2$ group of another amino acid (see equation on next page)
- The link between the two amino acids is called a peptide link (-CONH-)
- This is a condensation reaction (a small molecule, like water, is produced when a link is made)
- Three amino acids joined together make a tripeptide. Several amino acids in a chain are a polypeptide
- Proteins are long chains of amino acids. 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



- If the 2 amino acids are not the same, 2 different dipeptides can be formed e.g.

HOOC-CHR¹-NHCO-CHR²-NH₂	**HOOC-CHR²-NHCO-CHR¹-NH₂**
R¹ nearest COOH	R¹ nearest NH₂

- A peptide link can be split up by hydrolysis
- Acid hydrolysis with HCl(aq) produces amino acids (COOH groups)
- Alkaline hydrolysis with NaOH(aq) produces carboxylates (COO^- groups)