Nitrogen compounds

A-Level Chemistry

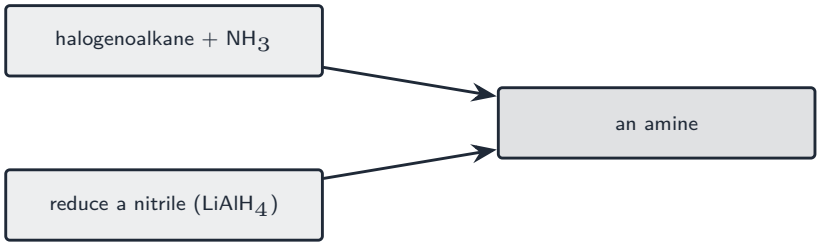
Primary and secondary amines

An **amine** 胺 has an –NH_2 (primary) or –NH (secondary) group.

A primary amine has -NH2; a secondary amine has -NH-

Making amines

- a **halogenoalkane** 卤代烷 with NH_3 in ethanol, heated under pressure → a primary amine.
- a halogenoalkane with a primary amine, heated under pressure → a secondary amine.
- **reduction** 还原 of an **amide** 酰胺 with $LiAlH_4$.
- reduction of a **nitrile** 腈 with $LiAlH_4$ or H_2/Ni.



Two routes to an amine: from a halogenoalkane, or by reducing a nitrile

An amine (or **ammonia** 氨) reacts with an acyl chloride in a **condensation** 缩合 reaction to give an amide. The reagent is an **acyl chloride** 酰氯.

Basicity of amines

The **basicity** 碱性 of an amine comes from the lone pair on its nitrogen, which can accept an H^+ from water.

Phenylamine and azo compounds

Making phenylamine

Make **phenylamine** 苯胺 from benzene in two steps: nitrate benzene to nitrobenzene, then reduce it with hot Sn and concentrated HCl, followed by NaOH(aq).

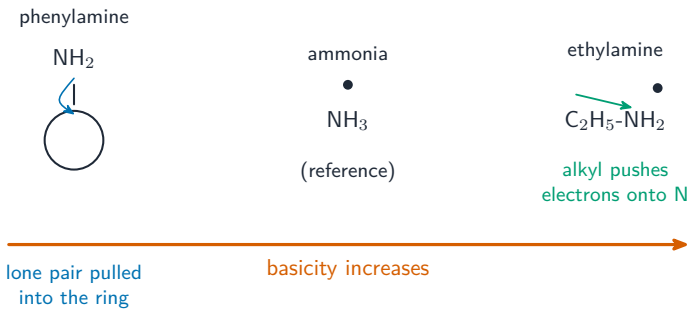
Reactions

- with bromine water at room temperature → 2,4,6-tribromophenylamine (a white precipitate). The ring is activated, like phenol.
- with HNO_2 (from $NaNO_2$ and dilute acid) below 10 °C → a diazonium salt; warming this with water gives phenol.

Relative basicity

phenylamine < ammonia < ethylamine

Ethylamine is the strongest base: its alkyl group pushes electron density onto the nitrogen, making the lone pair more available. Phenylamine is the weakest, because its lone pair is **delocalised** 离域 into the benzene ring, so it is less available to accept an H^+.



Basicity depends on the nitrogen lone pair: an alkyl group makes it more available (ethylamine strongest), a benzene ring pulls it away (phenylamine weakest)

Azo compounds

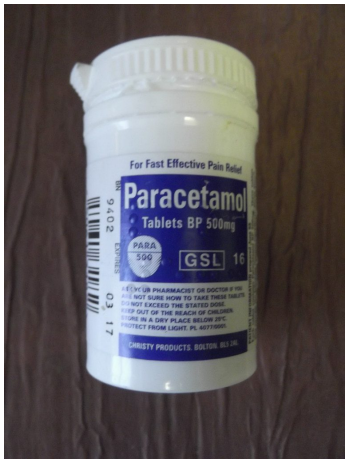
A **diazonium salt** 重氮盐 (benzenediazonium chloride) couples with **phenol** 苯酚 in NaOH(aq) to form an **azo compound** 偶氮化合物. The azo group is –N=N–. Azo compounds are brightly coloured and are often used as **dye** 染料 s; many other azo dyes are made the same way.

Methyl orange, a bright orange azo dye; the strong colour comes from the –N=N– azo group, which is why azo compounds are so widely used as dyes

Worked example. An amino acid has an isoelectric point of pH 6.0. Give its charge, and the electrode it moves towards in electrophoresis, at pH 2, at pH 6.0 and at pH 11. Compare the solution's pH with the **isoelectric point** each time. At **pH 2**, well below it, the solution is acidic, so the $–NH_2$ gains an H^+: the amino acid is **positive** and moves to the **cathode** (negative electrode). At **pH 6.0**, exactly its isoelectric point, it is the **zwitterion** with no net charge, so it does **not** move. At **pH 11**, well above it, the –COOH loses its H^+: the amino acid is **negative** and moves to the **anode**. Compare the pH with the **isoelectric point**, never with 7 - and note the zwitterion still carries both charges, it simply has no **net** charge.

Amides

An amide is made from ammonia or a primary amine with an acyl chloride at room temperature.



Paracetamol is a common painkiller that contains the amide group (–CONH–)

Its reactions:

- **hydrolysis** with aqueous acid or alkali, giving the carboxylic acid (or its salt) and the amine (or ammonium).
- **reduction** of the C=O group with $LiAlH_4$ to give an amine.

An amide is a **much weaker base** than an amine, because the nitrogen lone pair is delocalised onto the neighbouring C=O group, so it is not available to accept an H^+.

Amino acids

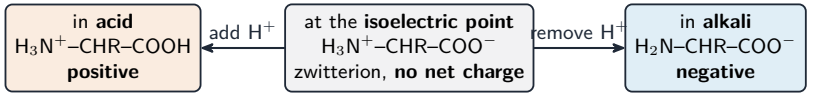
An **amino acid** 氨基酸 has both a basic $–NH_2$ group and an acidic –COOH group.

Zwitterions and the isoelectric point

The –COOH can give its H^+ to the $–NH_2$ in the same molecule, forming a **zwitterion** 两性离子 ($H_3N^+–CHR–COO^-$) — an ion with both a positive and a negative end but no overall charge.

- in acid (low pH), the amino acid gains H^+ and becomes **positive**.
- in alkali (high pH), it loses H^+ and becomes **negative**.

- at one special pH, the **isoelectric point** 等电点, it is mostly the zwitterion with no net charge.



An amino acid's charge depends on pH: positive in acid, the neutral zwitterion at the isoelectric point, negative in alkali

Peptide bonds

Two amino acids join in a condensation reaction: the –COOH of one and the $–NH_2$ of the other react, losing water and forming a **peptide bond** 肽键 (an amide link). Two amino acids give a **dipeptide** 二肽, three give a tripeptide.

$$H_2N–CHR–CO\,OH \;+\; H\,–NH–CHR'–COOH \;\downarrow\; H_2N–CHR–CO–NH–CHR'–COOH + H_2O$$

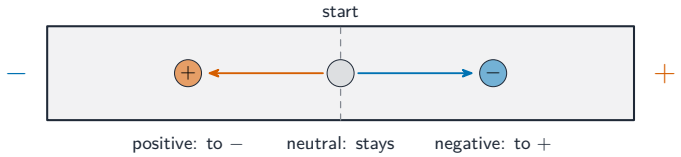
the **peptide bond** (an amide link)

Two amino acids condense: the –OH from one –COOH and the –H from the other $–NH_2$ leave as water, forming the peptide (amide) bond

Electrophoresis

In **electrophoresis** 电泳, a mixture is placed in an electric field at a chosen pH:

- above its isoelectric point, an amino acid is negative and moves to the positive electrode.
- below its isoelectric point, it is positive and moves to the negative electrode.
- at its isoelectric point, it does not move. So different amino acids separate.



at one chosen pH, amino acids with different charges separate

Electrophoresis at a chosen pH: a positive amino acid moves to the negative electrode, a negative one to the positive, and a neutral one stays — so they separate

Exam tips

- **Phenylamine** is a **weaker base** than aliphatic amines because the N lone pair delocalises into the ring.
- **Diazotisation** ($NaNO_2$/HCl, below 10 °C) then coupling gives **azo dyes** — learn the conditions and the coloured product.
- **Amino acids** are **zwitterions** (both $-NH_2$ and $-COOH$), so they are amphoteric; describe behaviour either side of the isoelectric point.