# Nitrogen compounds

A-Level Chemistry

## Primary and secondary amines

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

### 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.

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).

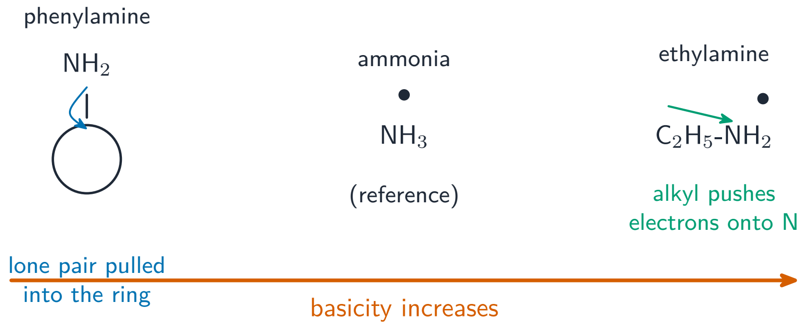
### Reactions

- 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

$$\text{phenylamine} < \text{ammonia} < \text{ethylamine}$$

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*

Image: Ben Mills, Public domain (commons.wikimedia.org)

## 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 $H^+$.

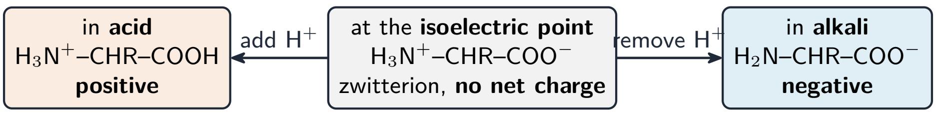
# Amino acids

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.

$$H_2N\text{–}CHR\text{–}CO\ \ OH \quad + \quad H\ \ \text{–}NH\text{–}CHR'\text{–}COOH$$

$$\downarrow$$

$$H_2N\text{–}CHR\text{–}CO\text{–}NH\text{–}CHR'\text{–}COOH \ + \ H_2O$$

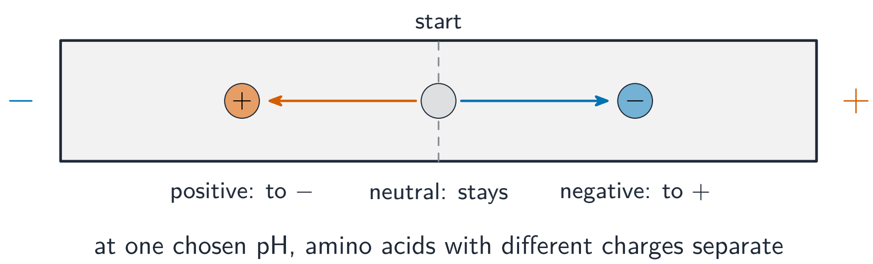
the **peptide bond** (an amide link)

*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.




*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*