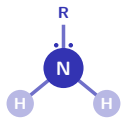
Nitrogen Compounds

A-Level Chemistry ▪ Topic 34

A-Level Chemistry



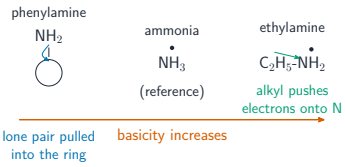
What we will cover

1. Amines & basicity
2. Phenylamine & azo dyes
3. Amides
4. Zwitterions
5. Peptide bonds
6. Electrophoresis

azo compounds are dyes

1 Amines

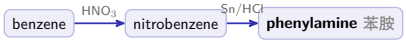
Amines and basicity



An **amine** 胺's **basicity** 碱性 comes from its N lone pair accepting H^+.

Order: **phenylamine** 苯胺 < ammonia < ethylamine. An alkyl group pushes electrons in; a ring pulls the lone pair away.

Phenylamine and azo dyes

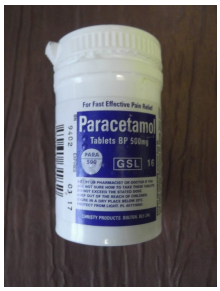


A **diazonium salt** 重氮盐 (made below 10 °C) couples with phenol to form a brightly coloured **azo compound** 偶氮化合物 (−N=N−) – used as a **dye** 染料.

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.

Amides



An **amide** 酰胺 is made from ammonia or an amine with an acyl chloride.

- **hydrolysis** 水解 → the acid + the amine
- **reduction** 还原 ($LiAlH_4$) → an amine

It is a much weaker base than an amine (lone pair delocalised onto C=O).

2 Amino acids

Zwitterions

in **acid**	at the **isoelectric point**	in **alkali**
H_3N^+–CHR–$COOH$	H_3N^+–CHR–COO^-	H_2N–CHR–COO^-
positive	zwitterion, **no net charge**	**negative**

add H^+ ← → remove H^+

An **amino acid** 氨基酸 has a basic $-NH_2$ & an acidic $-COOH$.

It forms a **zwitterion** 两性离子 (both charges, no net). It is positive in acid, negative in alkali, and neutral at the **isoelectric point** 等电点.

Peptide bonds

Two amino acids **condense** 缩合: the $-OH$ and $-H$ leave as water, forming a **peptide bond** 肽键 (an amide link). Two give a **dipeptide** 二肽, three a tripeptide.

$$H_2N\text{–}CHR\text{–}CO\,\cancel{OH}\;\cancel{H}\;\text{–}NH\text{–}CHR'\text{–}COOH$$

$$\downarrow$$

$$H_2N\text{–}CHR\text{–}CO\text{–}NH\text{–}CHR'\text{–}COOH + \cancel{H}\,\cancel{OH} = H_2O$$

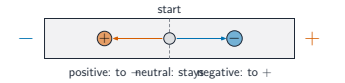
the **peptide bond** (an amide link)

Zwitterions, and how electrophoresis separates them

a zwitterion	at intermediate pH an amino acid has a positive $-NH_3^+$ and a negative $-COO^-$, with no net charge
in acid	low pH: it gains H^+ and becomes positive
in alkali	high pH: it loses H^+ and becomes negative
the isoelectric point	the pH at which the net charge is zero – and it differs between amino acids
electrophoresis 电泳	a mixture is placed in an electric field at a chosen pH
what happens	each amino acid moves toward the electrode its charge *at that pH* attracts – and one at its isoelectric point does not move at all

The chosen pH is the whole technique. Change it and the same mixture separates differently, because each component's charge changes.

Electrophoresis



positive: to – neutral: stays negative: to +

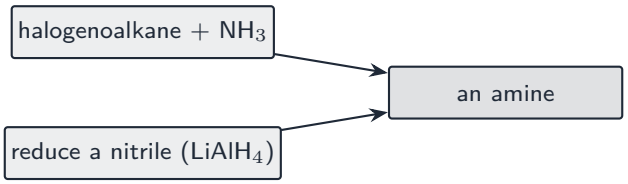
at one chosen pH, amino acids with different charges separate

In **electrophoresis** 电泳 at a chosen pH:

- positive amino acid → the – electrode
- negative → the + electrode
- neutral (isoelectric) → stays put

So they separate.

Making amines



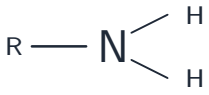
Two routes to an amine: from a halogenoalkane, or by reducing a nitrile

Making phenylamine, and the azo route

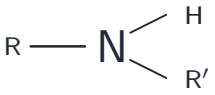
step 1	nitrate benzene: concentrated HNO_3 and H_2SO_4, giving nitrobenzene
step 2	reduce it with hot tin and concentrated HCl, then add alkali – giving **phenylamine** 苯胺
diazotisation	phenylamine with HNO_2 (from $NaNO_2$ and HCl) below $10\,^{\circ}C$ gives a diazonium salt
why cold	the diazonium salt decomposes above about $10\,^{\circ}C$
coupling	the diazonium salt with phenol in NaOH(aq) gives an azo dye
the colour	comes from the extended delocalisation across the $-N{=}N-$ bridge joining two rings

Two steps to phenylamine, then two more to the dye. Naming the temperature of the diazotisation is a marked condition, not a detail.

Primary and secondary amines



primary ($-NH_2$)



secondary ($-NH-$)

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

Exam tips

- **Phenylamine** is a **weaker base** than aliphatic amines because the N lone pair delocalises into the ring.
- **Diazotisation** ($NaNO_2$/HCl, below $10\,^{\circ}C$) 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.

3 Recap

Worked example – why is phenylamine a weak base?

Explain why phenylamine is a much weaker base than ethylamine.

- Base strength depends on how available the N lone pair is to accept H^+.
- In phenylamine the lone pair overlaps with the ring's delocalised π system.
- It is drawn into the ring, so it is far less available.
- In ethylamine the alkyl group pushes density onto N – the opposite effect.
- Order: ethylamine $>$ ammonia $>$ phenylamine.

Lone pair delocalised into a ring $\Rightarrow$ weak base.
Lone pair pushed at by alkyl groups $\Rightarrow$ strong base.

Topic 34 – key takeaways

1 Basicity

phenylamine $<$ ammonia $<$ ethylamine

2 Azo dyes

diazonium + phenol $\rightarrow$ coloured $-N{=}N-$

3 Amino acids

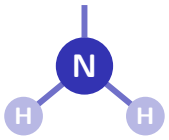
zwitterion; isoelectric point

4 Peptides

condense to form peptide bonds; electrophoresis

Check yourself

1. Which is the strongest base of the three amines?
2. What group makes azo dyes coloured?
3. What is an amino acid at its isoelectric point?
4. What bond joins two amino acids?



Answers **1.** ethylamine **2.** the azo group $-N{=}N-$ **3.** a neutral zwitterion **4.** a peptide bond