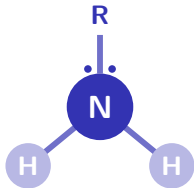


# Nitrogen Compounds

A-Level Chemistry ■ Topic 34

A-Level Chemistry



# What we will cover

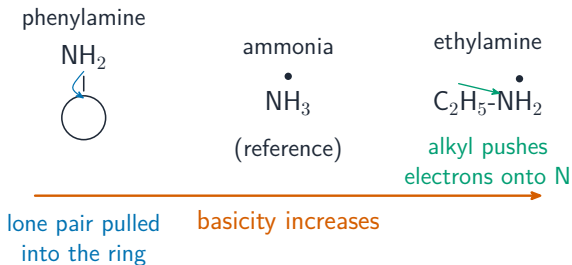
- 1 Amines & basicity
- 2 Phenylamine & azo dyes
- 3 Amides
- 4 Zwitterions
- 5 Peptide bonds
- 6 Electrophoresis



*azo compounds are dyes*



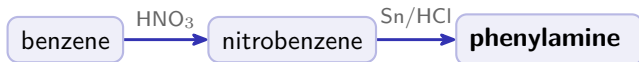
# Amines and basicity



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

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

## Phenylamine and azo dyes



A **diazonium salt** (made below  $10^{\circ}\text{C}$ ) couples with phenol to form a brightly coloured **azo compound** ( $-\text{N}=\text{N}-$ ) – used as a **dye** .

# Reactions

- with bromine water at room temperature  $\rightarrow$  2,4,6-tribromophenylamine (a white precipitate). The ring is activated, like phenol.
- with  $\text{HNO}_2$  (from  $\text{NaNO}_2$  and dilute acid) below  $10^\circ\text{C}$   $\rightarrow$  a diazonium salt; warming this with water gives phenol.

# Amides



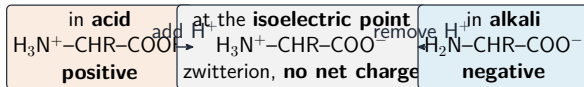
An **amide** is made from ammonia or an amine with an acyl chloride.

- **hydrolysis** → the acid + the amine
- **reduction** ( $\text{LiAlH}_4$ ) → an amine

It is a much **weaker base** than an amine (lone pair delocalised onto  $\text{C}=\text{O}$ ).



# Zwitterions



An **amino acid** has a basic  $-\text{NH}_2$  & an acidic  $-\text{COOH}$ .

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

## Peptide bonds

Two amino acids **condense** : the  $\text{—OH}$  and  $\text{—H}$  leave as water, forming a **peptide bond** (an amide link). Two give a **dipeptide** , three a tripeptide.



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

# Zwitterions, and how electrophoresis separates them

## a zwitterion

at intermediate pH an amino acid has a **positive**  $-\text{NH}_3^+$  and a **negative**  $-\text{COO}^-$ , with no net charge

## in acid

low pH: it gains  $\text{H}^+$  and becomes **positive**

## in alkali

high pH: it **loses**  $\text{H}^+$  and becomes **negative**

## the isoelectric point

the pH at which the net charge is zero – and it differs between amino acids

## electrophoresis

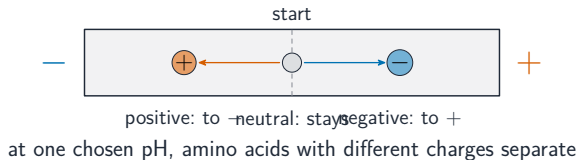
a mixture is placed in an electric field **at a chosen pH**

## 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

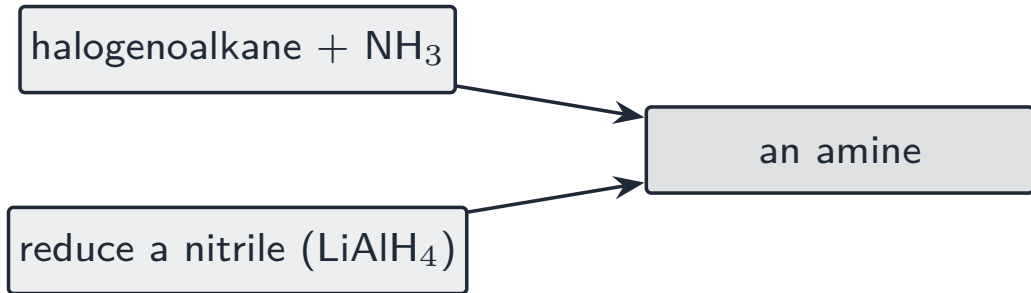


In **electrophoresis** at a chosen pH:

- 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  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , giving nitrobenzene

## step 2

**reduce** it with hot tin and concentrated  $\text{HCl}$ , then add alkali – giving **phenylamine**

## diazotisation

phenylamine with  $\text{HNO}_2$  (from  $\text{NaNO}_2$  and  $\text{HCl}$ ) below  $10^\circ\text{C}$  gives a diazonium salt

## why cold

the diazonium salt decomposes above about  $10^\circ\text{C}$

## coupling

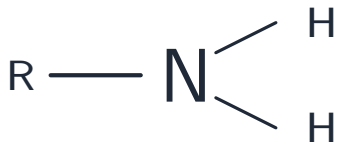
the diazonium salt with phenol in  $\text{NaOH(aq)}$  gives an **azo dye**

## the colour

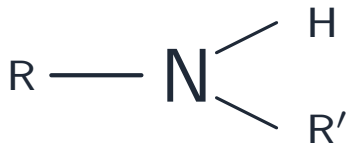
comes from the extended delocalisation across the  $-\text{N}=\text{N}-$  bridge joining two rings

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 ( $-\text{NH}_2$ )



secondary ( $-\text{NH}-$ )

A primary amine has  $-\text{NH}_2$ ; a secondary amine has  $-\text{NH}-$

## Exam tips

- **Phenylamine** is a **weaker base** than aliphatic amines because the N lone pair delocalises into the ring.
- **Diazotisation** ( $\text{NaNO}_2/\text{HCl}$ , below  $10\text{ }^\circ\text{C}$ ) then coupling gives **azo dyes** – learn the conditions and the coloured product.
- **Amino acids** are **zwitterions** (both  $-\text{NH}_2$  and  $-\text{COOH}$ ), so they are amphoteric; describe behaviour either side of the isoelectric point.



## 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  $\text{H}^+$ .
- In phenylamine the lone pair **overlaps with the ring's delocalised  $\pi$  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  
 $-\text{N}=\text{N}-$

3

### Amino acids

zwitterion; isoelectric point

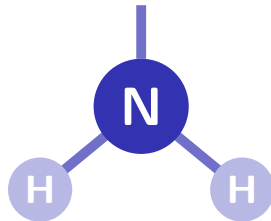
4

### 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  $\text{—N=N—}$  3. a neutral zwitterion 4. a peptide bond