A-LEVEL CHEMISTRY • EXERCISE SHEET

34.1 Primary and secondary amines

Name: _____ Class: _____ Date: _____ **Total: 23 marks**

KEY WORDS amine 胺 • amide 酰胺 • basicity 碱性 • ammonia 氨 • reduction 还原

Objective

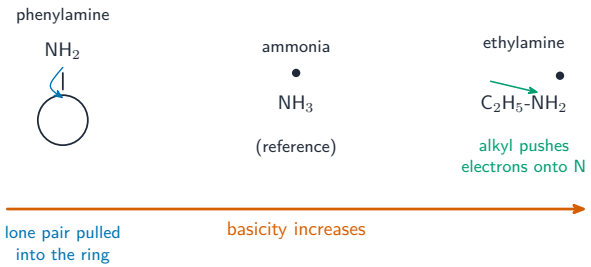
Build the skills to answer exam questions on **primary and secondary amines** 胺 — how they are made, and the trends in **basicity** 碱性.

You must be able to:

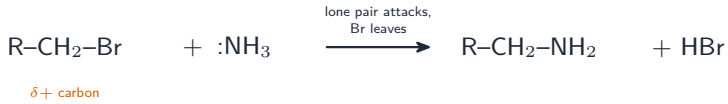
- give the reagents to make amines (from halogenoalkanes, amides, nitriles)
- explain why amines are basic
- explain and compare the basicity of ammonia, an aliphatic amine and phenylamine

1 Worked examples

Basicity



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



Routes to primary and secondary amines

- amines are basic because the **N lone pair** can accept an H^+.
- **basicity:** phenylamine < ammonia < ethylamine.
  - ethylamine: alkyl group pushes electrons onto N → lone pair more available → strongest.
  - phenylamine: lone pair delocalised into the ring → less available → weakest.
- **make a primary amine:** halogenoalkane + excess NH_3 in ethanol, heat under pressure; or reduce a nitrile/amide with $LiAlH_4$.

2 Practice

2.1 State why an amine is able to act as a base. [1]

2.2 Give the reagents to convert bromoethane into ethylamine. [2]

3 Exam-style questions

3.1 Which is the **strongest** base? [1]

- **A** phenylamine
- **B** ammonia
- **C** ethylamine
- **D** they are equal

3.2 Reduction of a nitrile, CH_3CN, with $LiAlH_4$ gives: [1]

- **A** ethylamine
- **B** ethanamide
- **C** ethanoic acid
- **D** ethanenitrile

3.3 Explain why ethylamine is a stronger base than ammonia. [2]

3.4 Explain why phenylamine is a much weaker base than ethylamine. [3]

3.5 Three bases are compared: ammonia, ethylamine and phenylamine.

(a) Place the three in order of increasing basicity and explain the order in terms of the availability of the nitrogen lone pair. [4]

(b) Ethylamine can be made from bromoethane and excess ethanolic ammonia. Write the equation, name the mechanism, and explain why an **excess** of ammonia is used. [4]

(c) Phenylamine is made from nitrobenzene. Give the reagents and conditions, and write the equation using [H] for the reducing agent. [3]

(d) Write the equation for ethylamine reacting with dilute hydrochloric acid, and name the salt. [2]

Solutions

2.1 the nitrogen lone pair can accept (donate to) an H^+.

2.2 excess ammonia, NH_3, in ethanol; heat under pressure.

3.1 C. Ethylamine — the alkyl group makes the lone pair most available.

3.2 A. $LiAlH_4$ reduces the nitrile to a primary amine, ethylamine.

3.3 the ethyl group pushes electron density onto the nitrogen (positive inductive effect); this makes the lone pair more available to accept an H^+, so ethylamine is a stronger base than ammonia.

3.4 in phenylamine the nitrogen lone pair overlaps with / is delocalised into the benzene ring; so it is less available to accept an H^+; whereas in ethylamine the lone pair is fully available (and the alkyl group pushes electrons onto N), so phenylamine is much weaker.

3.5 (a) phenylamine < ammonia < ethylamine. A base donates the nitrogen lone pair, so the more available that pair, the stronger the base. In ethylamine the ethyl group **releases** electron density inductively towards the nitrogen, making the lone pair more available; in phenylamine the lone pair is delocalised into the benzene ring, so it is much less available.
(b) $CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$; the mechanism is **nucleophilic substitution**; an excess of ammonia makes it more likely that ammonia — not the ethylamine already made — attacks the next bromoethane, which limits further substitution to secondary and tertiary amines.
(c) Tin and concentrated hydrochloric acid, heated under reflux, then made alkaline with sodium hydroxide; $C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$.
(d) $CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+Cl^-$; **ethylammonium chloride**.