A-LEVEL CHEMISTRY • EXERCISE SHEET

34.2 Phenylamine and azo compounds

Name: _____ Class: _____ Date: _____ **Total: 32 marks**

KEY WORDS phenylamine 苯胺 • azo compound 偶氮化合物 • phenylamine and azo compounds 苯胺与偶氮化合物 • phenol 苯酚 • dye 染料

Objective

Build the skills to answer exam questions on **phenylamine and azo compounds** 苯胺与偶氮化合物 — making phenylamine, diazonium salts, and azo dye coupling.

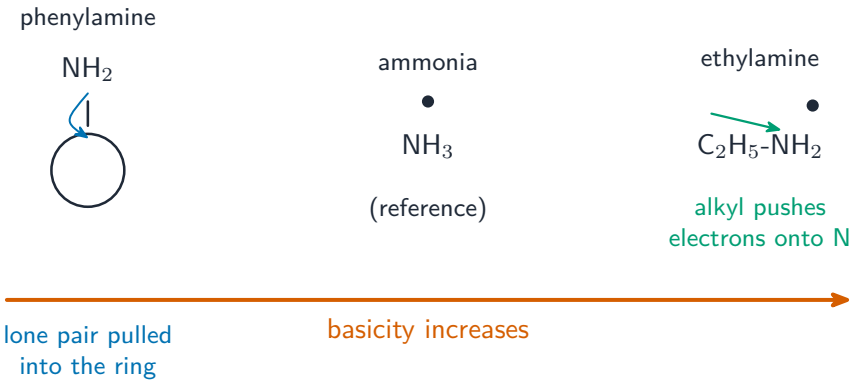
You must be able to:

- give the two-step route from benzene to phenylamine
- describe the formation of a diazonium salt and its conditions
- describe azo coupling and why azo compounds are coloured dyes

1 Worked examples

Diazonium salts and azo dyes

The strong colour of an azo dye comes from the –N=N– azo group joining two aromatic rings



Phenylamine is a weaker base than aliphatic amines

- **make phenylamine:** benzene → (nitrate) → nitrobenzene → (Sn / conc. HCl, then NaOH) → phenylamine.
- **diazonium salt:** phenylamine + $NaNO_2$ + dilute acid, **below 10 °C** → benzenediazonium chloride.
- **azo coupling:** diazonium salt + phenol in NaOH(aq) → a coloured **azo compound** (a dye); the –N=N– group links two rings.

Benzene to an azo dye, in three named steps

Step 1 — nitration. $C_6H_6 \rightarrow C_6H_5NO_2$ with concentrated HNO_3 and concentrated H_2SO_4 at 55 °C.

Step 2 — reduction to phenylamine 苯胺. $C_6H_5NO_2 \rightarrow C_6H_5NH_2$ with **tin and concentrated hydrochloric acid**, then **excess NaOH** to liberate the free amine from its salt. Both halves are marks; stopping at the tin/HCl step leaves you with the ammonium salt, not the amine.

Step 3 — diazotisation. $NaNO_2$ with dilute acid (which makes HNO_2 in situ) at **below 10 °C**, giving the **diazonium salt** 重氮盐 $C_6H_5N_2^+Cl^-$. The temperature is the mark: above about 10 °C the diazonium ion decomposes to phenol and nitrogen gas.

Step 4 — coupling. The diazonium salt is added to an alkaline solution of **phenol** (or another activated ring) to give an **azo compound** 偶氮化合物, an intensely coloured solid.

Why azo dyes are coloured. The two rings are joined through the $-N=N-$ **azo group**, which extends the **delocalised** system across the whole molecule. A larger delocalised system means a **smaller** energy gap between the levels, so the molecule absorbs light in the **visible** region, and the colour seen is the complement of what is absorbed. Changing the groups attached to the rings changes the gap, which is how a dye's colour is tuned.

Phenylamine is a weaker base than ethylamine — a favourite comparison. The nitrogen's lone pair is **delocalised into the benzene ring**, so it is less available to accept a proton. In ethylamine the alkyl group is electron-releasing and pushes

electron density onto the nitrogen, making the lone pair more available. Order: ethylamine > ammonia > phenylamine.

2 Practice

2.1 Give the reagents to reduce nitrobenzene to phenylamine. [2]

2.2 State the temperature needed to make a stable diazonium salt. [1]

2.3 Give the reagents and conditions for converting nitrobenzene into phenylamine. [3]

2.4 State why the diazotisation must be carried out below 10 °C. [2]

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

3 Exam-style questions

3.1 A diazonium salt is made from phenylamine using: [1]

A	B
C	D

A $NaNO_2$ + dilute acid, below 10 °C
B conc. HNO_3 + conc. H_2SO_4
C Br_2 water
D $LiAlH_4$

3.2 The colour of an azo dye is due to the: [1]

A	B
C	D

A –OH group
B $-NH_2$ group
C –N=N– group
D benzene ring alone

3.3 Outline the two-step synthesis of phenylamine from benzene, giving the reagents for each step. [3]

3.4 A benzenediazonium salt is coupled with phenol in alkaline solution.

(a) State the type of compound formed. [1]

(b) State **one** common use of such compounds. [1]

3.5 An azo dye is made from benzene in four steps.

(a) Give the reagents and conditions for step 1, the conversion of benzene into nitrobenzene, and name the mechanism. [3]

(b) Give the reagents for step 2 and explain why a second reagent is needed after the reduction. [3]

(c) Give the reagents and conditions for the formation of the diazonium salt, and write its formula. [3]

(d) The diazonium salt is coupled with phenol in alkaline solution. Draw the structure of the azo compound formed. [2]

(e) Explain, in terms of electrons, why azo compounds are coloured. [3]