FACTFILE:
GCE CHEMISTRY

5.7 AMINES

Rewarding Learning

Amines

Learning Outcomes

5.7.1 recall the molecular and structural formulae of amines with up to six carbon atoms, and refer to primary, secondary and tertiary amines;

5.7.2 refer to the effect of hydrogen bonding on boiling point and miscibility with water;

5.7.3 recall the formation of primary aliphatic amines by reduction of nitriles using lithium tetrahydridoaluminate(III) (lithal) and by the reaction of ammonia with alkyl halides;

5.7.4 explain the formation of phenylamine by reduction of nitrobenzene using tin and concentrated hydrochloric acid, to the phenylammonium salt followed by liberation of the free amine by addition of alkali;

5.7.5 recall the formation of salts by the reaction of amines with mineral acids and the liberation of amines from their salts using alkali;

5.7.6 explain the relative basic strengths of ammonia, primary, secondary, tertiary aliphatic amines and phenylamine using the availability of the lone pair on the nitrogen atom;

5.7.7 recall the reaction of amines with ethanoyl chloride and use this reaction to identify unknown amines;

5.7.8 explain the formation of benzenediazonium chloride from phenylamine and recall the coupling of diazonium ions with phenol and aniline;

5.7.9 explain the colour of compounds such as dyestuffs and indicators based on the extent of delocalisation of electrons leading to the closer proximity of electronic energy levels.

Amines

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The smell of fish is partly due to amines such as ethylamine

Amines are compounds based on ammonia, where hydrogen atoms have been replaced by alkyl or aryl (C_6H_5-) groups Amines contain the —NH_2 functional group, which is called the **amino** group. They have a fishy smell.

Naming

There are different ways of naming amines – usually just add **–ylamine**, or if there is a side group it is often more convenient to name it by using amino.

For example:

NH_2 ethylamine

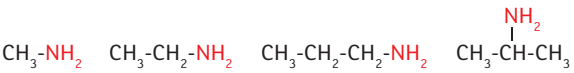
$CH_3CH_2CH_2NH_2$ proplyamine (1-aminopropane)

2-aminopropane

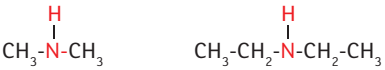
$H_2NCH_2CH_2NH_2$ 1,2–diaminiopropane

$C_6H_5NH_2$ phenylamine

A primary primary amine has only one carbon directly bonded to the nitrogen atom and therefore has the NH_2 group Examples include

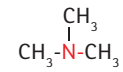


A secondary amines has two carbon atoms directly bonded to the nitrogen atom, i.e  For example:



dimethylamine diethylamine

A tertiary amine has three carbon atoms directly bonded to the nitrogen atom i.e 
For example:



trimethylamine

The easiest way to recognise a primary, secondary or tertiary amine is to count the number of H atoms bonded to the N atom.

2 H atoms bonded to N atom – Primary amine e.g. $C_2H_5NH_2$

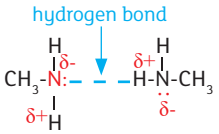
1 H atom bonded to N atom – Secondary amine e.g. $(C_2H_5)_2NH$

0 H atoms bonded to N atom – Tertiary amine e.g. $(C_2H_5)_3N$

Physical properties

1. Boiling point

Primary amines have a higher boiling point than the corresponding alkane because alkanes only have weak van der Waals' forces between molecules, but amines have strong **hydrogen bonds between the lone pair on the very electronegative nitrogen atom and the slightly positive hydrogen atom in another molecule** and so more energy is needed to break these stronger bonds and boil the amine.

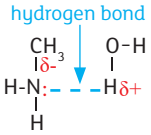


Secondary amines have lower boiling points – they still form hydrogen bonds between molecules, but each N atom only has one H atom which can form hydrogen bonds with other molecules.

In a **tertiary** amine there aren't any hydrogen atoms attached directly to the nitrogen. That means that hydrogen bonding between tertiary amine molecules is impossible, the molecules only are held together by van der Waals' forces and so the boiling points are much lower.

2. Solubility in water

Most primary amines can form hydrogen bonds with water and so are soluble in water.



Solubility decreases as the hydrocarbon chains get longer - noticeably so after about 6 carbons. The hydrocarbon chains have to force their way between water molecules, breaking hydrogen bonds between water molecules. Secondary amines are less soluble in water than primary amines and tertiary amines are less soluble than secondary amines.

Formation of primary aliphatic amines

1. by reduction of nitriles
(nitriles contain the C≡N group)

Equation: $CH_3CH_2CN + 4\,[H] \rightarrow CH_3CH_2CH_2NH_2$

propanenitrile propylamine

Condition: [H] is lithium tetrahydridoaluminate(III) (lithal) in ether at room temp

2. by reaction of ammonia with halogenoalkanes

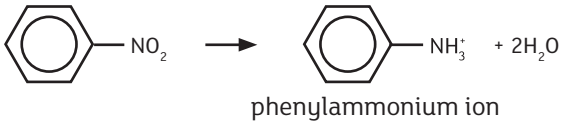
Equation: bromoethane + ammonia → ethylamine + hydrogen bromide

$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$

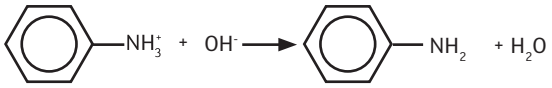
Condition: in a sealed glass tube at 100 °C with **excess** ammonia

Formation of phenylamine by reduction of nitrobenzene

The protonated form of phenylamine, the **phenylammonium ion** is first formed by the reduction of nitrobenzene with tin and concentrated hydrochloric acid. Concentrated sodium hydroxide then removes the hydrogen ion from the phenylammonium salt liberating the free amine.



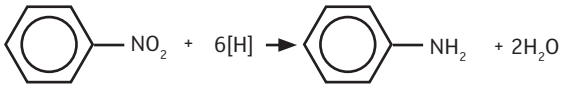
phenylammonium ion



phenylammonium ion phenylamine

Conditions: [H] is tin and concentrated hydrochloric acid. Heat under reflux, followed by addition of concentrated sodium hydroxide solution.

Overall the reduction is:

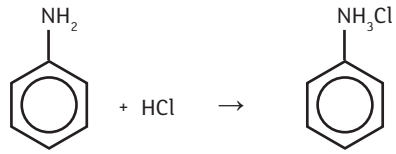


nitrobenzene phenylamine

Reactions of amines as bases
Amines are weak bases because the lone pair of electrons on the nitrogen atom can accept a proton.

amine + acid → alkylammonium salt

with dilute hydrochloric acid



phenylamine phenylammonium chloride

with dilute sulfuric acid

$2CH_3CH_2NH_2 + H_2SO \rightarrow (CH_3CH_2NH_3)_2\,SO_4$

ethylamine ethylammonium sulphate

Conditions: room temp

To liberate the free amine from an amine salt add alkali and heat

Relative basic strengths
Usually compounds with a NH_2 group are basic because the lone pair of electrons on the nitrogen atom can combine with a hydrogen ion (a proton) from some other source - it acts as a base (lone pair donor/proton acceptor)

tertiary aliphatic amine

secondary aliphatic amine

primary aliphatic amine

ammonia

primary aromatic amine

amides

basic strength decreases

Primary aliphatic amines are stronger bases than ammonia because of the alkyl group attached to the nitrogen. The alkyl group is said to be **electron donating** – it releases electrons meaning there is slightly more electron density on the nitrogen atom. As a result the **lone pair is more available** and so has an increased ability to accept a proton. Aliphatic amines generally increase in base strength as the number of alkyl groups attached to the nitrogen atom increases.

Primary aromatic amines are weaker bases than ammonia because nitrogen's lone pair of electrons can overlap with the delocalised pi electrons in the benzene ring. The lone pair is delocalised into the pi system, the electron density on the nitrogen is decreased and the **lone pair is less available** for accepting a proton.
Amides are weaker bases than primary aromatic amines (see 5.8)

Reactions of Amines

With ethanoyl chloride

ethanoyl chloride + propylamine→
N-propylethanamide + hydrogen chloride

$CH_3COCl + CH_3CH_2CH_2NH_2 \rightarrow +CH_3CONHCH_2CH_2CH_3 + HCl$

Conditions: room temp.

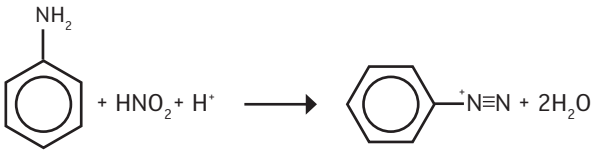
The N in N-propylethanamide indicates that the propyl group is bonded to the nitrogen.

Use of this reaction.
This reaction produces crystalline solids so the

reaction is used to identify an amine, by finding the melting point of the solid produced (after recrystallisation) and comparing to data books.

Formation of benzene diazonium chloride

Phenylamine reacts with nitrous acid to form benzene diazonium ion.
Ionic equation:



benzene diazonium ion

Full equation:
$C_6H_5NH_2 + HNO_2 + HCl \longrightarrow C_6H_5N_2^+ + Cl^- + 2H_2O$

Conditions: Nitrous acid (HNO_2) decomposes very readily and is always made in situ from hydrochloric acid and sodium nitrite solution.

$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

The temperature must be less than 5°C

In the benzene diazonium ion, make sure the + charge is placed on the nitrogen atom with four covalent bonds – it uses 4 electrons in forming 4 covalent bonds and so has lost one electron (N atom should have 5 electrons) and has a positive charge.

Note benzene diazonium chloride is unstable when warmed and it reacts to form phenol.

$C_6H_5N_2Cl + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$

Aliphatic amines react with nitrous acid to produce an alcohol and nitrogen – this is because aliphatic diaszonium ions are too unstable at any temperature.

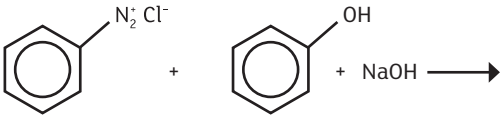
$CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O$

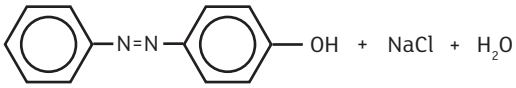
ethylamine ethanol

Coupling reaction of diazonium ions with phenol and aniline

A coupling reaction is a reaction in which two benzene rings are linked together through an azo (-N=N-) group

<u>With phenol</u> (C_6H_5OH)



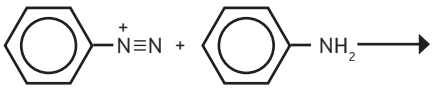


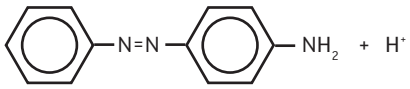
Conditions: cold NaOH

The dyes formed are called AZO DYES they are **yellow precipitates** and often used as dyes or indicators. The one above is called **4-hydroxyazobenzene.**

<u>With aniline (phenylamine)</u>

A yellow azo dye is produced.





Why are dyestuffs and indicators coloured?

For a compound to be coloured it has to remove (absorb) one or more colours from white light.
If a molecule has a conjugated system or an extended delocalised electron system – dyes and indicators do - this means that the energy levels are closer together and as a result less energy is needed to cause an electron to be raised to a higher level. Hence the energy absorbed is less (longer wavelength) and in the visible region; this removes light of a particular frequency and colour and the colour remaining produces the resulting colour of the dye.

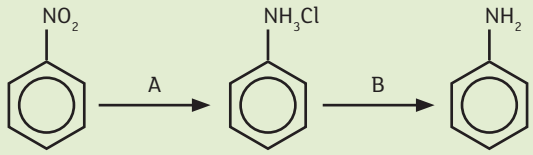
Revision Questions

1 Which one of the following lists the compounds in order of increasing base strength?

A ethanamide, methylamine, phenylamine
B ethanamide, phenylamine, methylamine
C methylamine, ethanamide, phenylamine
D phenylamine, ethanamide, methylamine [1]

2 Phenylamine is involved in the manufacture of azo-compounds which can be used as dyestuffs.

(a) Phenylamine can be prepared from nitrobenzene according to the following flow scheme:



Name the reagents for Steps A and B.

Step A _____ [1]

Step B _____ [1]

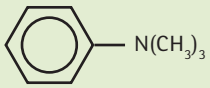
(b) Phenylamine is then converted to benzenediazonium chloride. Name the reagents and state the condition required to convert phenylamine to benzenediazonium chloride.

_____

_____

_____ [2]

(c) Benzenediazonium chloride forms a yellow dye when coupled with dimethylaminobenzene.



dimethylaminobenzene

Write the equation for the reaction and circle the azo group.

_____ [3]

3 Putrescine is a foul smelling liquid produced by the breakdown of amino acids in dead organisms.

$H_2N(CH_2)_4NH_2$

putrescine

(i) Suggest the synthetic name for putrescine.

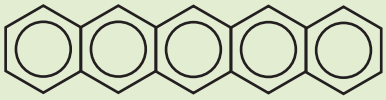
_____ [1]

(ii) State why putrescine is soluble in water.

_____

_____ [1]

4 Benzene is colourless but the solid pentacene is red.



pentacene

Explain why pentacene is coloured and benzene is not.

_____

_____

_____

_____ [4]