Cambridge

A2 Level

Chemistry

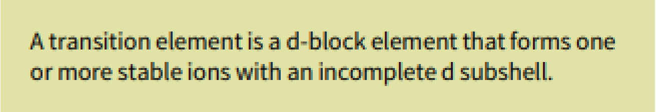
CODE: (9701)

Chapter 24 and 25

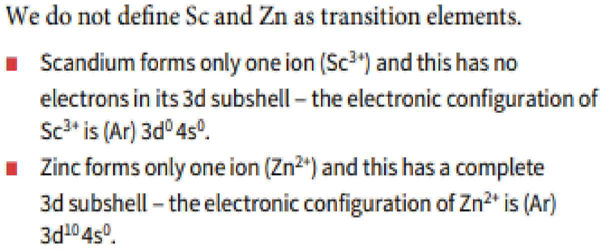
transition elements and Benzene and its compounds

What is a transition element?

The transition elements are found in the d block of the Periodic.



A transition element is a d-block element that forms one or more stable ions with an incomplete d subshell.



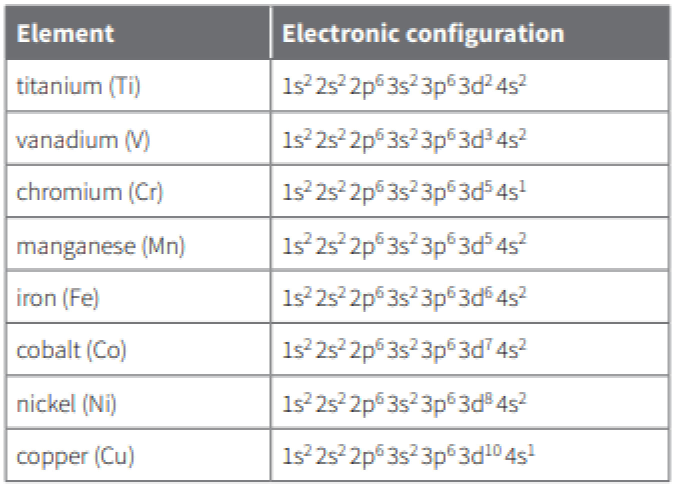
We do not define Sc and Zn as transition elements.

- Scandium forms only one ion (Sc^{3+}) and this has no electrons in its 3d subshell – the electronic configuration of Sc^{3+} is (Ar) $3d^0 4s^0$.
- Zinc forms only one ion (Zn^{2+}) and this has a complete 3d subshell – the electronic configuration of Zn^{2+} is (Ar) $3d^{10} 4s^0$.

Electronic configurations

Atoms

Table 24.1 shows the electronic configurations of the atoms in the first row of the transition elements.



Element	Electronic configuration
titanium (Ti)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
vanadium (V)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
chromium (Cr)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
manganese (Mn)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
iron (Fe)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
cobalt (Co)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
nickel (Ni)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
copper (Cu)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

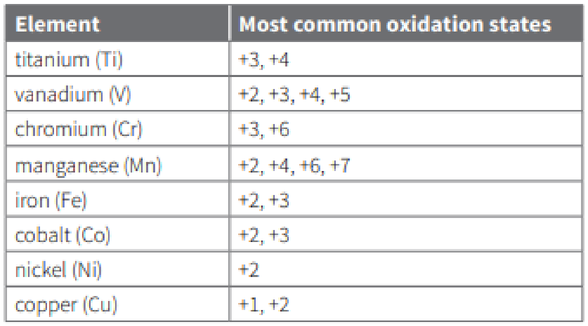
Table 24.1 Electronic configurations of the first row of transition elements.

Ions

Transition elements are metals with variable oxidation states, forming positively charged ions with different colors, such as copper's Cu^+ and Cu^{2+} ions, and losing electrons.

Table 24.2 shows the most common oxidation states of the first row of the transition elements

Figure 24.2 Vanadium and its oxidation states: **a** a solution containing VO_2^+ ions; **b** a solution containing VO^{2+} ions; **c** a solution containing V^{3+} ions; **d** a solution containing V^{2+} ions.



Element	Most common oxidation states
titanium (Ti)	+3, +4
vanadium (V)	+2, +3, +4, +5
chromium (Cr)	+3, +6
manganese (Mn)	+2, +4, +6, +7
iron (Fe)	+2, +3
cobalt (Co)	+2, +3
nickel (Ni)	+2
copper (Cu)	+1, +2

Table 24.2 Common oxidation states of the transition elements.

Variable oxidation states require compounds with transition elements to include their oxidation number. Transition elements form ions by losing electrons from the 4s subshell, followed by 3d electrons. The most common oxidation state is +2, with vanadium's maximum being +5. From iron onwards, the +2-oxidation state dominates.

Physical properties of the transition elements

The transition elements commonly have physical properties that are typical of most metals:

- They have high melting points
- They have high densities
- They are hard and rigid, and so are useful as construction materials

■They are good conductors of electricity and heat.

The first ionisation energy, the atomic radius and the ionic radius of transition elements do not vary much as we go across the first row. The data are given in Table 24.3.

Element	1st ionisation energy / kJ mol^{-1}	Atomic radius / nm	Ionic radius / nm
titanium (Ti)	661	0.132	Ti^{2+} 0.090
vanadium (V)	648	0.122	V^{3+} 0.074 or V^{2+} 0.090
chromium (Cr)	653	0.117	Cr^{3+} 0.069 or Cr^{2+} 0.085
manganese (Mn)	716	0.117	Mn^{2+} 0.080
iron (Fe)	762	0.116	Fe^{2+} 0.076
cobalt (Co)	757	0.116	Co^{2+} 0.078
nickel (Ni)	736	0.115	Ni^{2+} 0.078
copper (Cu)	745	0.117	Cu^{2+} 0.069

Table 24.3 There are comparatively small variations in 1st ionisation energy, atomic radius and ionic radius of the first-row transition elements.

The periodic properties of positively charged ions, as discussed in Chapter 10, show variations in their 1st ionisation energy, atomic radius, and ionic radius over time. The shielding effect remains constant, while the atomic and ionic radius decrease.

Comparing the transition elements with an s-block element

Calcium (Ca) is the s-block metal in Group 2 before the first row of d-block elements in the Periodic Table. Comparing its properties with the first row of transition elements reveals differences.

- the melting point of calcium (839 °C) is **lower** than that of a transition element (e.g. titanium at 1660 °C)
- the density of calcium (1.55 g cm^{-3}) is **lower** than that of a transition element (e.g. nickel at 8.90 g cm^{-3})
- the atomic radius of calcium (0.197 nm) is **larger** than that of a transition element (e.g. iron at 0.116 nm)
- the ionic radius of the calcium ion, Ca^{2+}, (0.099 nm) is **larger** than that of a transition element (e.g. Mn^{2+} at 0.080 nm)
- the first ionisation energy of calcium (590 kJ mol^{-1}) is **lower** than that of a transition element (e.g. chromium at 653 kJ mol^{-1} or cobalt at 757 kJ mol^{-1})
- the electrical conductivity of calcium is **higher** than that of a transition element (with the exception of copper).

Redox reactions

Transition elements can exist in various oxidation states, and when treated with a reagent, their oxidation state can change. Redox reactions involve electron transfer, with a species being reduced when its oxidation state is reduced and lowered when it gains electrons.

$$\underset{\text{pale yellow}}{Fe^{3+}(aq)} + e^- \longrightarrow \underset{\text{pale green}}{Fe^{2+}(aq)}$$

Fe^{3+} is reduced to Fe^{2+} by gaining one electron, acting as an oxidizing agent. Another half-equation is needed, where the reactant loses electrons, acting as a reducing agent.

Another half-equation we could consider would be:

$$\underset{\text{purple}}{MnO_4^-(aq)} + 8H^+(aq) + 5e^- \longrightarrow \underset{\text{pale pink}}{Mn^{2+}(aq)} + 4H_2O(l)$$

Both half-equations are written below as they appear in tables of data showing standard electrode potentials:

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$
$$E^\ominus = +1.52\,V$$

The study investigates the oxidation of Mn^{2+} to MnO_4^- ions in acid solution. The results show that MnO4–(aq) ions are more likely to accept electrons and change to Mn^{2+} (aq), whereas Fe^{3+} (aq) ions change to Fe^{2+} (aq). The top half-equation proceeds in the reverse direction. The Fe(III)/Fe(II) half-cell's sign changes.

The positive $E^\ominus$ value indicates a forward-directed reaction, which is utilized to calculate the amount of iron (Fe^{2+} ions) in a sample, such as an iron tablet.

- A known volume (e.g. 25 cm^3) of an unknown concentration of Fe^{2+}(aq) is placed in a conical flask.
- A solution of a known concentration of potassium manganate(VII) is put in a burette.
- The potassium manganate(VII) solution is titrated against the solution containing Fe^{2+}(aq) in the conical flask.
- The purple colour of the manganate(VII) ions is removed in the reaction with Fe^{2+}(aq). The end-point is reached when the Fe^{2+}(aq) ions have all reacted and the first permanent purple colour appears in the conical flask.

Figure 24.3 Manganate(VII) ions can be used to determine the percentage of Fe^{2+} in an iron tablet.

To accurately determine Fe^{2+} mass in a solution, dichromate (VI) ions, Cr $_2O_7$-$^{2-}$ (aq), can be used in a titration. This method requires an end-point indicator for oxidation, and the half-equation and $E^\ominus$ value for dichromate is provided.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$
$$E^\ominus = +1.33\,V$$

Ligands and complex formation

A complex ion, formed by the oxidation of Fe2+(aq) ions, is formed by six water molecules, called **ligands**, which bond to the central Fe2+ ion, forming a dative co-ordinate bond and forming an octahedral shape.

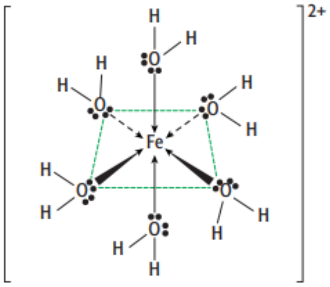


Figure 24.4 $[Fe(H_2O)_6]^{2+}$; the complex ion formed between an Fe^{2+} ion and six water molecules. It is called a hexaaquairon(II) ion.

All ligands can donate an electron pair to a central transition metal ion. The **co-ordination number** of a complex is the number of co-ordinate (dative) bonds to the central metal ion.

These are called **bidentate** ligands, as shown in Figure 24.6. Most ligands, such as water and ammonia, form just one co-ordinate bond and are called **monodentate** ligands.

Figure 24.5 shows the shape of complexes with four ligands.

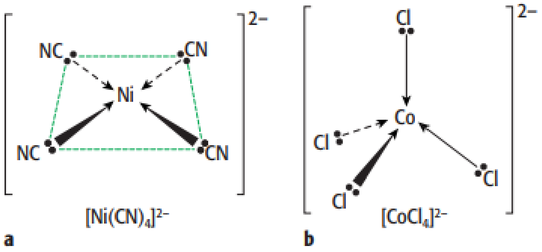


Figure 24.5 The complex ion formed between a transition metal ion and a larger ligand can only fit four ligands around the central ion. These are arranged in either a square planar shape (as in **a** $[Ni(CN)_4]^{2-}$) or a tetrahedral shape (as in **b** $[CoCl_4]^{2-}$).

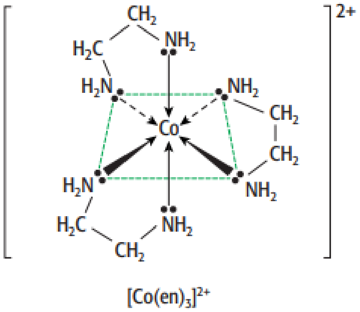


Figure 24.6 $[Co(en)_3]^{2+}$ is an example of a complex ion containing the bidentate ligand $NH_2CH_2CH_2NH_2$ (abbreviated to 'en').

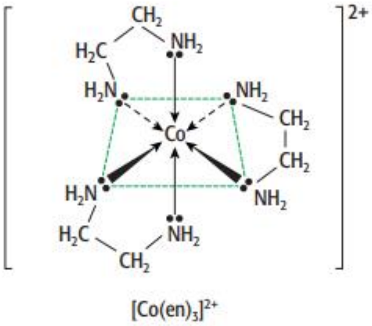


Figure 24.6 $[Co(en)_3]^{2+}$ is an example of a complex ion containing the bidentate ligand $NH_2CH_2CH_2NH_2$ (abbreviated to 'en').

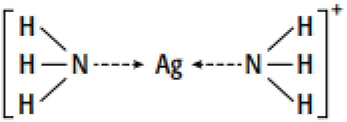


Figure 24.7 The diamminesilver(I) cation has a linear structure.

Note in Table 24.4 that the charge on a complex is simply the sum of the charges on the central metal ion and on each ligand in the complex. Some complexes will carry no charge.

Name of ligand	Formula	Example of complex	Co-ordination number	Shape of complex
water	H_2O	$[Fe(H_2O)_6]^{2+}$	6	octahedral (see Figure 24.4)
ammonia	NH_3	$[Co(NH_3)_6]^{3+}$	6	octahedral
chloride ion	Cl^-	$[CuCl_4]^{2-}$	4	tetrahedral (see Figure 24.5b)
cyanide ion	CN^-	$[Ni(CN)_4]^{2-}$	4	square planar (see Figure 24.5a)
hydroxide ion	OH^-	$[Cr(OH)_6]^{3-}$	6	octahedral
thiocyanate ion	SCN^-	$[FeSCN]^{2+}$ or $[Fe(SCN)(H_2O)_5]^{2+}$	6	octahedral
ethanedioate ion (abbreviated as 'ox' in the formulae of complexes)	$^-OOC—COO^-$	$[Mn(ox)_3]^{3-}$	6	octahedral
1,2-diaminoethane (abbreviated as 'en' in the formulae of complexes)	$NH_2CH_2CH_2NH_2$	$[Co(en)_3]^{3+}$	6	octahedral (see Figure 24.6)

Table 24.4 Some common ligands and their complexes.

Stereoisomerism in transition metal complexes

We explore two types of stereoisomerism: geometric isomerism and optical isomerism. Geometric isomerism, a type of stereoisomerism, occurs in transition metal complexes with different atom arrangements, such as cis- and trans-platin, with slightly different properties.

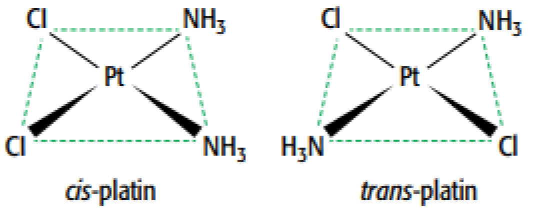


Figure 24.8 The geometrical isomers, *cis*-platin and *trans*-platin.

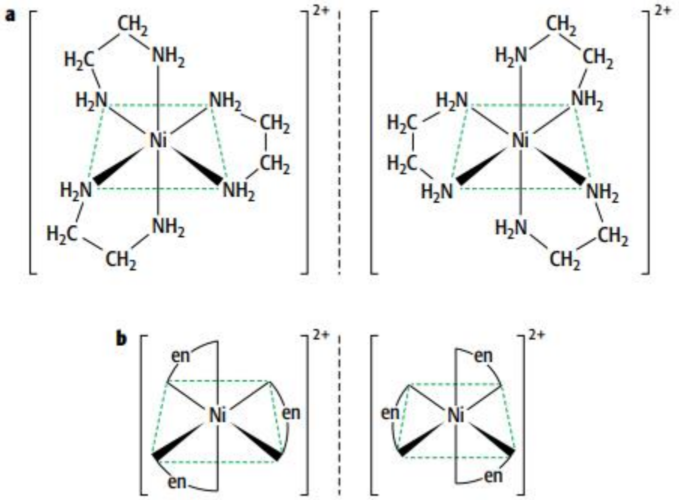


Figure 24.9 The two non-superimposable optical isomers of $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$: **a** the full structure; **b** a simplified structure with 'en' representing a molecule of 1,2-diaminoethane.

Substitution of ligands

Ligands in a complex can be exchanged for other ligands in a substitution reaction, if the new complex is more stable. Copper(II) ion complexes can demonstrate these reactions, such as copper sulfate solution and sodium hydroxide precipitate.

Two water ligands are replaced by two hydroxide ligands in the reaction:

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}(aq)} + 2OH^-(aq) \longrightarrow \underset{\text{pale blue precipitate}}{Cu(OH)_2(H_2O)_4(s)} + 2H_2O(l)$$

If you now add concentrated ammonia solution, the pale blue precipitate dissolves and we get a deep blue solution:

$$Cu(OH)_2(H_2O)_4(s) + 4NH_3(aq) \longrightarrow \underset{\text{deep blue solution}}{[Cu(H_2O)_2(NH_3)_4]^{2+}(aq)} + 2H_2O(l) + 2OH^-(aq)$$

The first reaction involves adding concentrated ammonia solution to copper sulfate solution, forming a pale blue precipitate that dissolves and forms a deep blue solution.

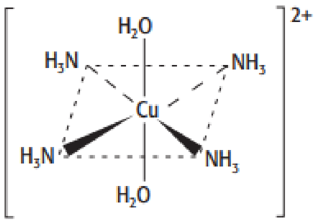
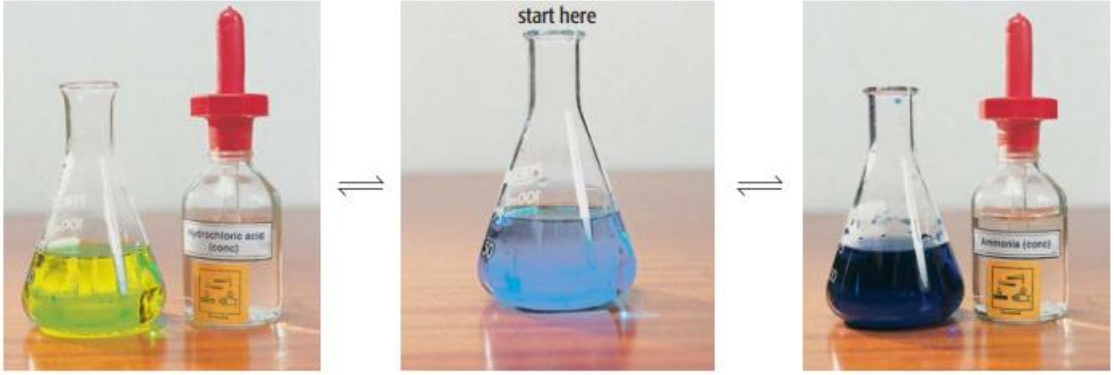


Figure 24.10 The structure of $[Cu(H_2O)_2(NH_3)_4]^{2+}(aq)$.

Water ligands in $[Cu(H_2O)_6]^{2+}$ can also be exchanged for chloride ligands if we add concentrated hydrochloric acid drop by drop. A yellow solution forms, containing the complex ion $[CuCl_4]^{2-}$ (Figure 24.11):



$[CuCl_4]^{2-}$
this yellow complex forms
on adding concentrated HCl

$[Cu(H_2O)_6]^{2+}$
the well-known blue Cu^{2+}
complex with water

$[Cu(H_2O)_2(NH_3)_4]^{2+}$
this dark blue complex forms
on adding concentrated NH_3

Figure 24.11 The equations for the changes are:
$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$ and $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$.

$$\underset{\text{blue solution}}{[Cu(H_2O)_6]^{2+}(aq)} + 4Cl^-(aq) \longrightarrow \underset{\text{yellow solution}}{[CuCl_4]^{2-}(aq)} + 6H_2O(l)$$

Cobalt(II) compounds form complex ions, giving aqueous solutions pink color. When sodium hydroxide is added, a blue precipitate forms, turning red when heated. Water ligands can be exchanged for ammonia ligands.

$$[Co(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \longrightarrow [Co(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

Drops of concentrated hydrochloric acid are added to an aqueous solution of cobalt(II) ions, resulting in the formation of a blue solution containing the tetrahedral complex $[CoCl^4]^{2-}$ (aq).

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \longrightarrow [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

Stability constants

Transition element ions in aqueous solutions are complex ions with water as a ligand, forming different complexes with varying stabilities, like when adding concentrated ammonia to copper(II) sulfate.

$$[Cu(H_2O)_6]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+}(aq) + H_2O(l)$$

$$[Cu(NH_3)(H_2O)_5]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+}(aq) + H_2O(l)$$

As we increase the concentration of ammonia, this process continues until four of the water molecules are replaced by ammonia to form a deep blue solution. The overall process is:

$$[Cu(H_2O)_6]^{2+} + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

The stability of a complex is determined by the equilibrium constants for ligand displacement, known as the stability constant. The more stable complex, such as a complex with ammonia, is more stable. Diluting the complex with water shifts the equilibrium position, forming a complex with more water molecules. The **stability constant** is typically expressed as K_{stab}, a stepwise constant.

$$[Cu(H_2O)_6]^{2+} + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

the expression is:

$$K_{stab} = \frac{[[CuCl_4]^{2-}(aq)]}{[[Cu(H_2O)_6]^{2+}]\,[Cl^-(aq)]^4}$$

Note:

- water does not appear in the equilibrium expression because it is in such a large excess that its concentration is regarded as being constant

- the units for the stability constant are worked out in the same way as for the units of K_c (see page 124). For example, in the above case:

$$K_{stab} = \frac{[[CuCl_4]^{2-}(aq)]}{[[Cu(H_2O)_6]^{2+}]\,[Cl^-(aq)]^4} \quad \frac{\cancel{(mol\,dm^{-3})}}{\cancel{(mol\,dm^{-3})} \times (mol\,dm^{-3})^4}$$

$$= dm^{12}\,mol^{-4}$$

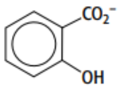
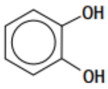
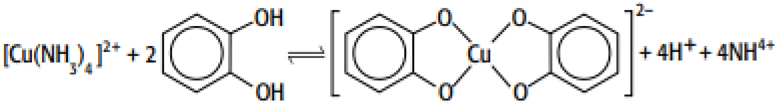
Ligand	$\log_{10} K_{stab}$
chloride, Cl^-	5.6
ammonia, NH_3	13.1
2-hydroxybenzoate 	16.9
1,2-dihydroxybenzene 	25.0

Table 24.5 The stability constants of some complexes of copper.

Stability constants, expressed on a log10 scale, measure the stability of complexes relative to their aqueous ions, with higher values indicating more stability. Table 24.5 provides values for various copper(II) complexes.

The table reveals that complexes with bidentate ions (2-hydroxybenzoate and 1,2-dihydroxybenzene) have higher stability constants than those with monodentate ligands. These constants can be used to predict the effect of adding different ligands to complex ions, such as adding excess ammonia to a dark blue solution or 1,2-dihydroxybenzene to a green complex.



The colour of complexes

The striking colours of complexes containing transition metal ions are due to the co-ordinate bonding between ligands and the transition metal ion. The five d orbitals in an isolated transition metal atom or ion are **degenerate**, but in the presence of ligands, they split into two sets of **non-degenerate** orbitals at slightly different energy levels. In a complex with six ligands, the lone pairs in the d_{x2-y2} and d_{z2} orbitals repel electrons more than in the other three orbitals, resulting in a slightly higher energy level.

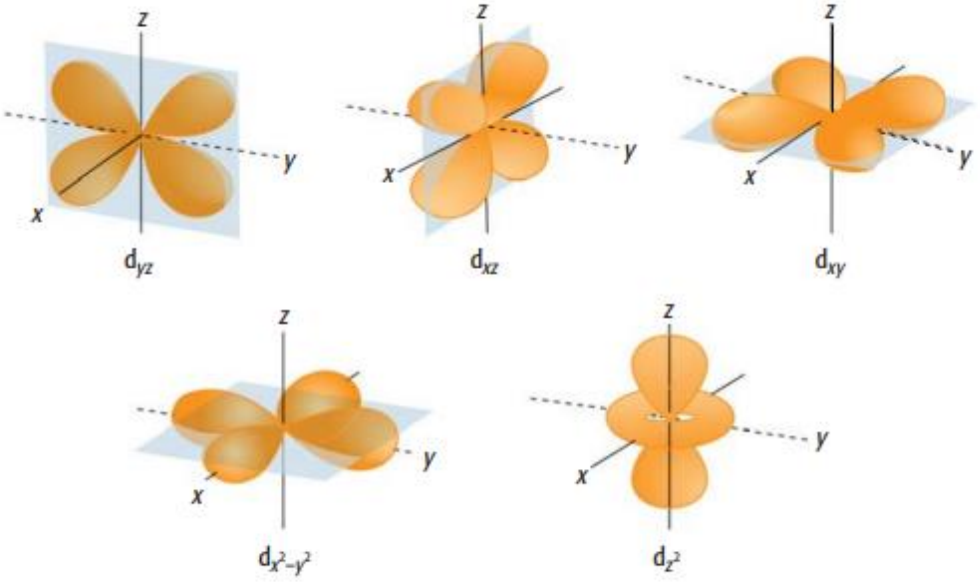


Figure 24.13 The degenerate d orbitals in a transition metal atom.

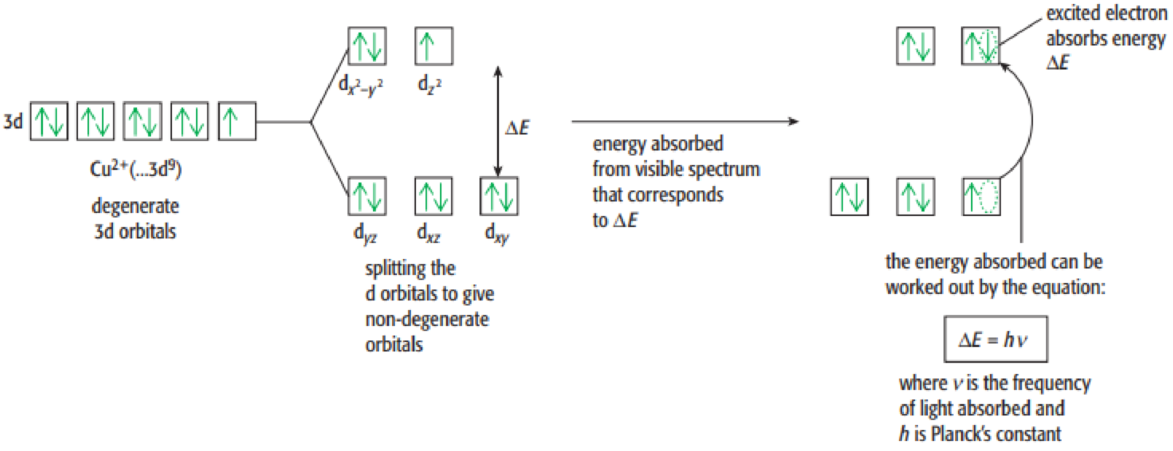


Figure 24.14 The splitting of the 3d orbitals in a $Cu(H_2O)_6^{2+}$ complex ion.

The benzene ring

The benzene ring, a hexagonal group of six carbon atoms, is a crucial functional group in many organic compounds, including medicines, dyes, and plastics. These compounds are known as **arenes**, **aryl compounds**, or aromatic compounds. Friedrich August Kekulé proposed a hexagonal ring structure in 1865, which reflects the name benzene, which has the same ending as alkenes.

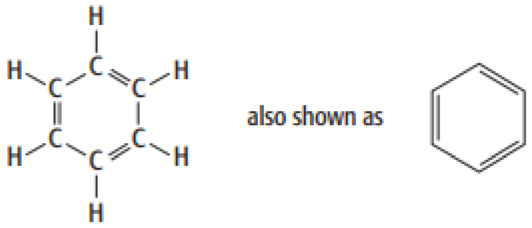


Figure 25.2 Kekulé's structure of benzene.

Analytical techniques revealed that benzene molecule is a planar, perfectly symmetrical molecule with a distorted hexagonal shape, unlike Kekulé's structure, which suggests three double and three single C -- C bonds.

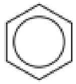
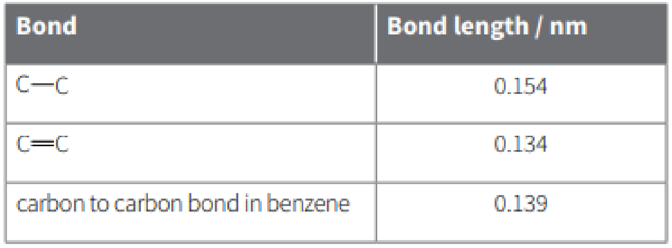


Figure 25.3 The skeletal formula of benzene. It can also be used in displayed formulae of aryl compounds, as on the previous page showing the structure of vanillin.

Table 25.1 shows that the bond length of the carbon– carbon bonds in benzene lie between the values for C-- C single bonds and C= C double bonds.



Bond	Bond length / nm
C—C	0.154
C=C	0.134
carbon to carbon bond in benzene	0.139

Table 25.1 Comparing bond lengths.

The actual structure of benzene can be explained by considering the bonding in the molecule. Each carbon atom in the hexagonal ring is sp^2 hybridised sharing.

- ■ One pair of electrons with one of its neighbouring carbon atoms
- ■ One pair of electrons with its other neighbouring carbon atom
- ■ One pair of electrons with a hydrogen atom.

σ (sigma) bonds are covalent bonds between atoms, with each carbon atom forming three bonds. This leaves one electron spare on each carbon atom, contributing to a π (pi) bond. In benzene, π bonds are **delocalised** and spread over all six carbon atoms in a hexagonal ring. The molecule must be planar to achieve maximum overlap.

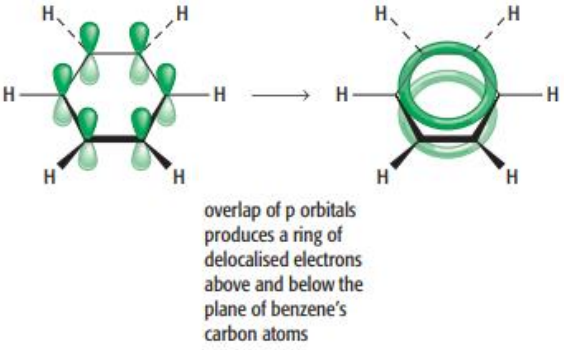


Figure 25.4 The π bonding in benzene. The three bond angles around each of the sp^2 hybridised carbon atoms are 120°.

Naming aryl compounds

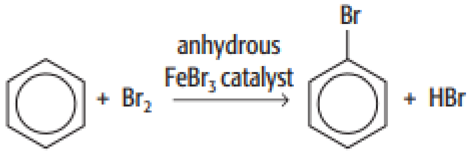
You saw how to name aryl compounds with alkyl sidechains on page 193. Some aryl compounds have functional groups that are substituted directly into the benzene ring in place of a hydrogen atom. You need to know the names of the compounds in Table 25.2.

Reactions of arenes

Benzene reactions typically preserve the stable delocalised ring of π bonding electrons by substituting an atom for hydrogen atoms, typically by an electrophile attracted to the high electron density.

Electrophilic substitution with chlorine or bromine

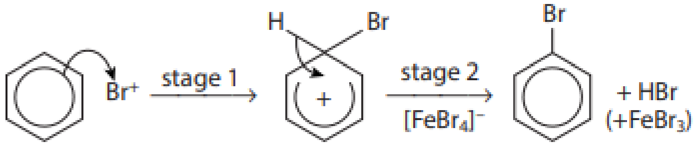
Benzene reacts with bromine using an anhydrous iron(III) bromide catalyst, which can be created by adding iron filings to the benzene and bromine.

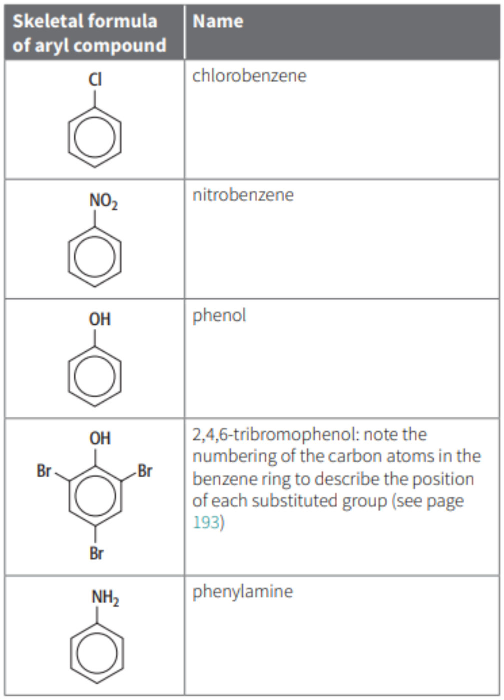


We can think of the electrophile as a Br^+ cation:

$$\overset{\delta+}{Br} \longrightarrow \overset{\delta-}{Br}\ \ FeBr_3 \longrightarrow Br^+ + [FeBr_4]^-$$

The Br+ cation and the 'electron-rich' benzene ring are attracted, as shown by the movement of a pair of electrons in the diagram.

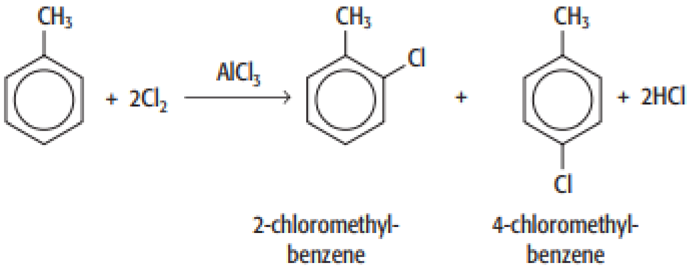




Skeletal formula of aryl compound	Name
Cl	chlorobenzene
NO2	nitrobenzene
OH	phenol
OH Br Br Br	2,4,6-tribromophenol: note the numbering of the carbon atoms in the benzene ring to describe the position of each substituted group (see page 193)
NH2	phenylamine

Table 25.2 The names of some aryl compounds. The phenyl group can be written as C_6H_5; e.g. the structural formula of phenylamine is $C_6H_5NH_2$.

Chlorine gas is bubbled through benzene at room temperature with a catalyst like iron(III) chloride or aluminium chloride, producing chlorobenzene and hydrogen chloride. Halogen carriers, $FeBr_3$, $AlCl_3$, and $FeCl_3$, are used in these reactions. Halogenation activates benzene ring positions 2 or 4, resulting in phenol and phenylamine.

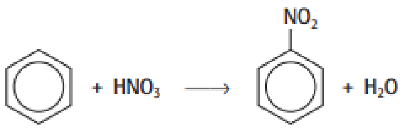


Excess chlorine gas can form 1-methyl-2,4-dichlorobenzene, 1-methyl-2,6-dichlorobenzene, and 1-methyl-2,4,6-trichlorobenzene. The carbon-halogen bond in halogenoarenes is stronger due to a partial double bond character. Chlorine reacts with alkanes in the presence of UV light or strong sunlight, resulting in a free radical substitution reaction.

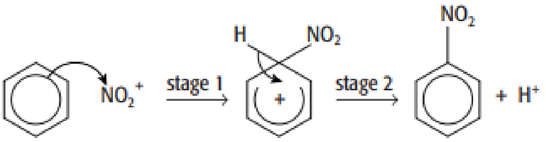
Nitration is an electrophilic substitution where the NO_2 group is introduced into a molecule, creating the nitronium ion from a mixture of concentrated nitric and sulfuric acids.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

This 'nitrating mixture' is refluxed with benzene at about 55 °C to make nitrobenzene:



The mechanism of the electrophilic substitution is:

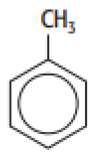


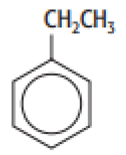
Alkylation (or acylation) of benzene (Friedel–Crafts reaction)

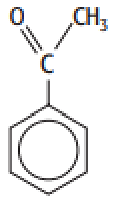
Friedel–Crafts reactions, named after the chemists who first discovered them, are a third example of electrophilic **substitution** into the benzene ring.

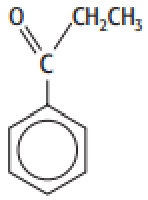
The same type of reaction can also be used to introduce an acyl group into a benzene ring. An acyl group contains an alkyl group and a carbonyl (C= O) group.

> Friedel–Crafts reactions result in **the introduction of a side-chain** into a benzene ring.
> They are also called alkylation or acylation reactions.


methylbenzene

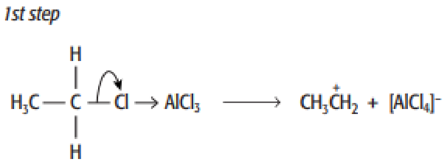

ethylbenzene


phenylethanone

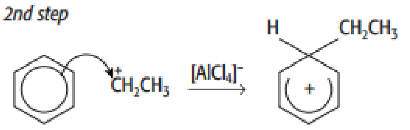

phenylpropanone

The reactions involve attack on the benzene ring by an **electrophile** carrying a positive charge on a carbon atom, i.e. a carbocation.

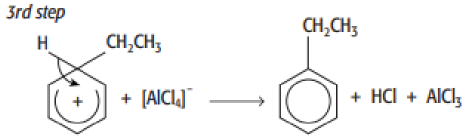
The electrophile is often formed by adding an aluminium chloride catalyst to a halogenoalkane. This creates the carbocation electrophile:



The carbocation electrophile then attacks the benzene ring:



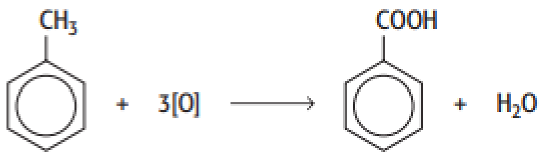
The aluminium chloride catalyst is regenerated in the final step:



Further alkylation of the benzene ring can take place as the reaction proceeds.

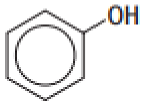
Oxidation of the side-chain in arenes

The benzene ring in alkylarenes like methylbenzene influences their side-chain reactions, forming carboxylic acids when oxidized with chemical agents like potassium manganate(VII) or acidified with sulfuric acid or potassium dichromate(VI).



Phenol

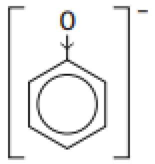
Phenol, C_6H_5OH, is a crystalline solid that melts at 43 °C. It is used to manufacture a wide range of products (Figure 25.5). Its structure is:



Phenol's high melting point due to hydrogen bonding makes it slightly soluble in water, and its non-polar benzene ring makes it weakly acidic.

$$C_6H_5OH(aq) \rightleftharpoons \underset{\text{phenoxide ion}}{C_6H_5O^-(aq)} + H^+(aq)$$

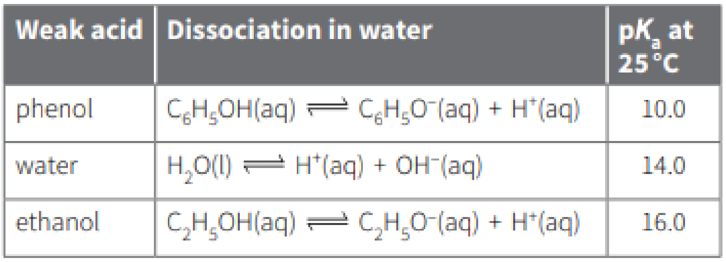
Phenol is more acidic than water, with ethanol being the least acidic. This is due to conjugate bases formed in Table 25.3, where the phenoxide ion has a negative charge.



phenoxide ion, with negative charge spread over the whole ion

$CH_3CH_2 \rightarrow O^-$

ethoxide ion, with negative charge concentrated on the oxygen



Weak acid	Dissociation in water	pK_a at 25 °C
phenol	$C_6H_5OH(aq) \rightleftharpoons C_6H_5O^-(aq) + H^+(aq)$	10.0
water	$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$	14.0
ethanol	$C_2H_5OH(aq) \rightleftharpoons C_2H_5O^-(aq) + H^+(aq)$	16.0

Table 25.3 Comparing the acidity of phenol, water and ethanol.

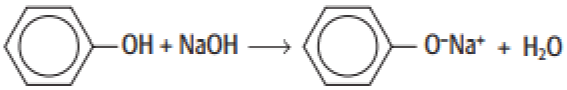
Delocalisation reduces the charge density of the negative charge on phenoxide ions, making H+(aq) ions less attracted to them. This makes phenoxide ions less likely to form undissociated molecules. The greater acidity of phenol can be explained by its ionisation to form a more stable negative ion, resulting in a higher equilibrium position. Ethanol's weaker acidity favors undissociated molecules.

Reactions of phenol

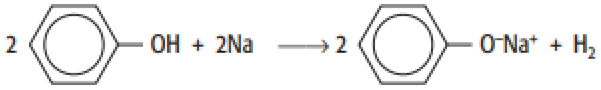
We can divide the reactions of phenol into those involving the hydroxyl group, OH, and those involving substitution into the benzene ring.

Breaking of the OH bond in phenol

Although phenol is only slightly soluble in water, it dissolves well in an alkaline solution. As you have just learnt, phenol is a weak acid so it will react with an alkali to give a salt plus water:

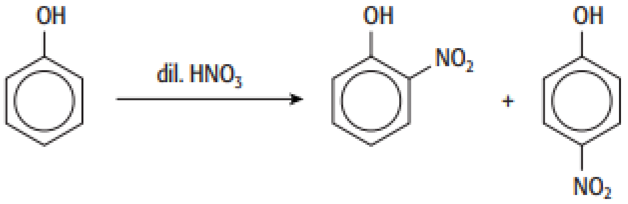


The salt formed, sodium phenoxide, is soluble in water. Phenol also reacts vigorously with sodium metal, giving off hydrogen gas and again forming sodium phenoxide:

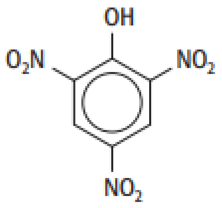


Substitution into the benzene ring of phenol

Phenol reacts more readily with electrophiles than benzene due to the increased electron density of the benzene ring. This activation, particularly at positions 2, 4, and 6, occurs between phenol and chlorine or iodine. This activation is also evident in nitration, which can occur with dilute nitric acid at room temperature.



If we use concentrated nitric acid we get 2,4,6-trinitrophenol formed, shown below:



Chapter 25 – Benzene and its compounds

The benzene ring

The benzene ring, a hexagonal group of six carbon atoms, is a crucial functional group in many organic compounds, including medicines, dyes, and plastics. These compounds are known as **arenes**, **aryl compounds**, or aromatic compounds. Friedrich August Kekulé proposed a hexagonal ring structure in 1865, which reflects the name benzene, which has the same ending as alkenes.

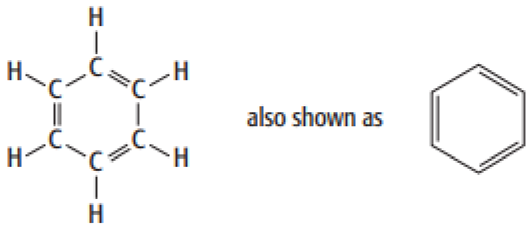


Figure 25.2 Kekulé's structure of benzene.

Analytical techniques revealed that benzene molecule is a planar, perfectly symmetrical molecule with a distorted hexagonal shape, unlike Kekulé's structure, which suggests three double and three single C -- C bonds.

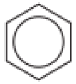
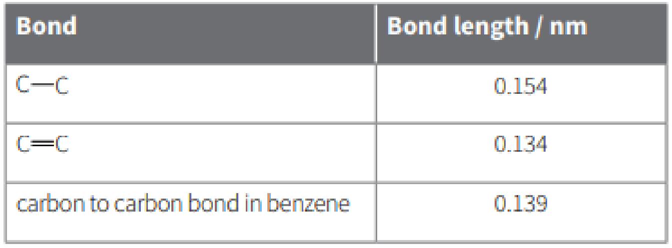


Figure 25.3 The skeletal formula of benzene. It can also be used in displayed formulae of aryl compounds, as on the previous page showing the structure of vanillin.

Table 25.1 shows that the bond length of the carbon– carbon bonds in benzene lie between the values for C-- C single bonds and C= C double bonds.



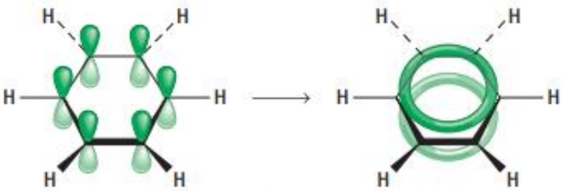
Bond	Bond length / nm
C—C	0.154
C=C	0.134
carbon to carbon bond in benzene	0.139

Table 25.1 Comparing bond lengths.

The actual structure of benzene can be explained by considering the bonding in the molecule. Each carbon atom in the hexagonal ring is sp^2 hybridised sharing.

- ■ One pair of electrons with one of its neighbouring carbon atoms
- ■ One pair of electrons with its other neighbouring carbon atom
- ■ One pair of electrons with a hydrogen atom.

σ (sigma) bonds are covalent bonds between atoms, with each carbon atom forming three bonds. This leaves one electron spare on each carbon atom, contributing to a π (pi) bond. In benzene, π bonds are **delocalised** and spread over all six carbon atoms in a hexagonal ring. The molecule must be planar to achieve maximum overlap.



overlap of p orbitals produces a ring of delocalised electrons above and below the plane of benzene's carbon atoms

Figure 25.4 The π bonding in benzene. The three bond angles around each of the sp^2 hybridised carbon atoms are 120°.

Naming aryl compounds

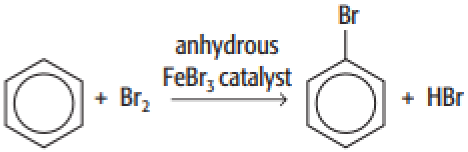
You saw how to name aryl compounds with alkyl sidechains on page 193. Some aryl compounds have functional groups that are substituted directly into the benzene ring in place of a hydrogen atom. You need to know the names of the compounds in Table 25.2.

Reactions of arenes

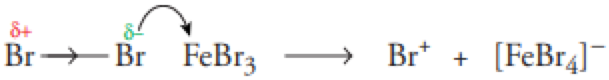
Benzene reactions typically preserve the stable delocalised ring of π bonding electrons by substituting an atom for hydrogen atoms, typically by an electrophile attracted to the high electron density.

Electrophilic substitution with chlorine or bromine

Benzene reacts with bromine using an anhydrous iron(III) bromide catalyst, which can be created by adding iron filings to the benzene and bromine.

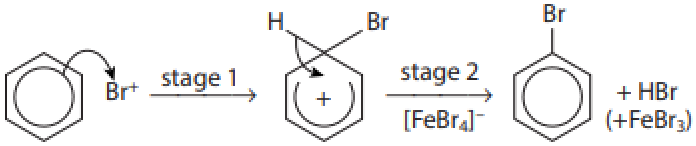


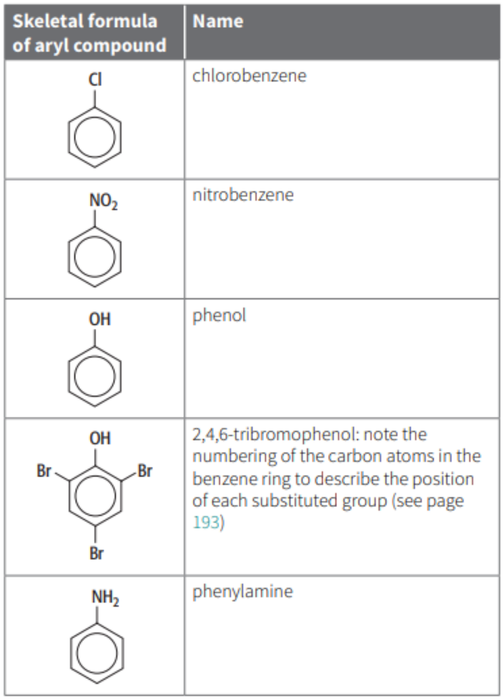
We can think of the electrophile as a Br^+ cation:



$$\overset{\delta+}{Br} \longrightarrow \overset{\delta-}{Br}\ FeBr_3 \longrightarrow Br^+ + [FeBr_4]^-$$

The Br+ cation and the 'electron-rich' benzene ring are attracted, as shown by the movement of a pair of electrons in the diagram.

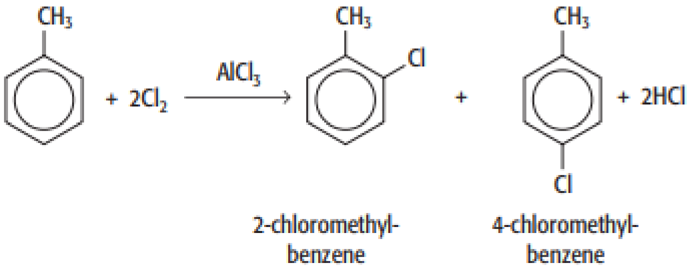




Skeletal formula of aryl compound	Name
Cl	chlorobenzene
NO_2	nitrobenzene
OH	phenol
OH Br Br Br	2,4,6-tribromophenol: note the numbering of the carbon atoms in the benzene ring to describe the position of each substituted group (see page 193)
NH_2	phenylamine

Table 25.2 The names of some aryl compounds. The phenyl group can be written as C_6H_5; e.g. the structural formula of phenylamine is $C_6H_5NH_2$.

Chlorine gas is bubbled through benzene at room temperature with a catalyst like iron(III) chloride or aluminium chloride, producing chlorobenzene and hydrogen chloride. Halogen carriers, $FeBr_3$, $AlCl_3$, and $FeCl_3$, are used in these reactions. Halogenation activates benzene ring positions 2 or 4, resulting in phenol and phenylamine.

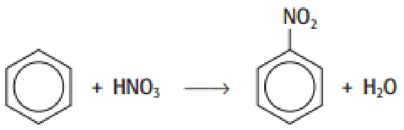


Excess chlorine gas can form 1-methyl-2,4-dichlorobenzene, 1-methyl-2,6-dichlorobenzene, and 1-methyl-2,4,6-trichlorobenzene. The carbon-halogen bond in halogenoarenes is stronger due to a partial double bond character. Chlorine reacts with alkanes in the presence of UV light or strong sunlight, resulting in a free radical substitution reaction.

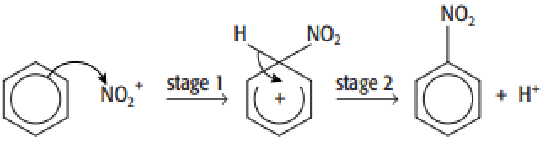
Nitration is an electrophilic substitution where the NO_2 group is introduced into a molecule, creating the nitronium ion from a mixture of concentrated nitric and sulfuric acids.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

This 'nitrating mixture' is refluxed with benzene at about 55 °C to make nitrobenzene:

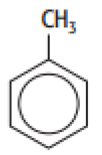


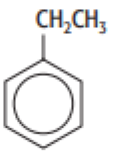
The mechanism of the electrophilic substitution is:

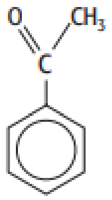


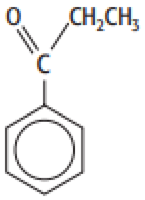
Alkylation (or acylation) of benzene (Friedel–Crafts reaction)

Friedel–Crafts reactions, named after the chemists who first discovered them, are a third example of electrophilic **substitution** into the benzene ring.


methylbenzene


ethylbenzene


phenylethanone


phenylpropanone

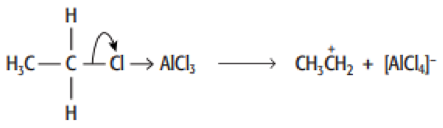
The same type of reaction can also be used to introduce an acyl group into a benzene ring. An acyl group contains an alkyl group and a carbonyl (C= O) group.

> Friedel–Crafts reactions result in **the introduction of a side-chain** into a benzene ring.
> They are also called alkylation or acylation reactions.

The reactions involve attack on the benzene ring by an **electrophile** carrying a positive charge on a carbon atom, i.e. a carbocation.

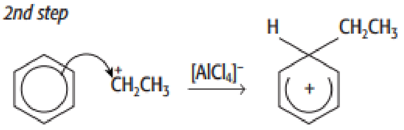
The electrophile is often formed by adding an aluminium chloride catalyst to a halogenoalkane. This creates the carbocation electrophile:

1st step



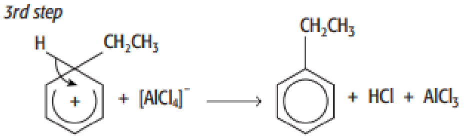
The carbocation electrophile then attacks the benzene ring:

2nd step



The aluminium chloride catalyst is regenerated in the final step:

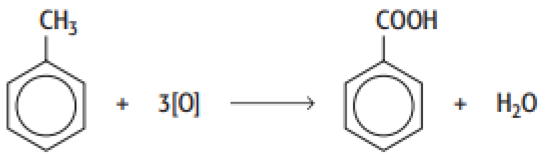
3rd step



Further alkylation of the benzene ring can take place as the reaction proceeds.

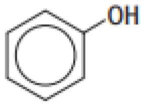
Oxidation of the side-chain in arenes

The benzene ring in alkylarenes like methylbenzene influences their side-chain reactions, forming carboxylic acids when oxidized with chemical agents like potassium manganate(VII) or acidified with sulfuric acid or potassium dichromate(VI).



Phenol

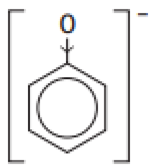
Phenol, C_6H_5OH, is a crystalline solid that melts at 43 °C. It is used to manufacture a wide range of products (Figure 25.5). Its structure is:



Phenol's high melting point due to hydrogen bonding makes it slightly soluble in water, and its non-polar benzene ring makes it weakly acidic.

$$C_6H_5OH(aq) \rightleftharpoons \underset{\text{phenoxide ion}}{C_6H_5O^-(aq)} + H^+(aq)$$

Phenol is more acidic than water, with ethanol being the least acidic. This is due to conjugate bases formed in Table 25.3, where the phenoxide ion has a negative charge.



phenoxide ion, with negative charge spread over the whole ion

ethoxide ion, with negative charge concentrated on the oxygen

Weak acid	Dissociation in water	pK_a at 25 °C
phenol	$C_6H_5OH(aq) \rightleftharpoons C_6H_5O^-(aq) + H^+(aq)$	10.0
water	$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$	14.0
ethanol	$C_2H_5OH(aq) \rightleftharpoons C_2H_5O^-(aq) + H^+(aq)$	16.0

Table 25.3 Comparing the acidity of phenol, water and ethanol.

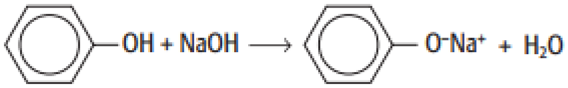
Delocalisation reduces the charge density of the negative charge on phenoxide ions, making H+(aq) ions less attracted to them. This makes phenoxide ions less likely to form undissociated molecules. The greater acidity of phenol can be explained by its ionisation to form a more stable negative ion, resulting in a higher equilibrium position. Ethanol's weaker acidity favors undissociated molecules.

Reactions of phenol

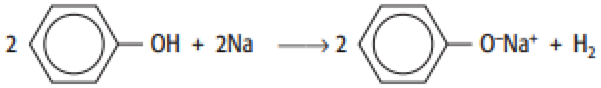
We can divide the reactions of phenol into those involving the hydroxyl group, OH, and those involving substitution into the benzene ring.

Breaking of the OH bond in phenol

Although phenol is only slightly soluble in water, it dissolves well in an alkaline solution. As you have just learnt, phenol is a weak acid so it will react with an alkali to give a salt plus water:

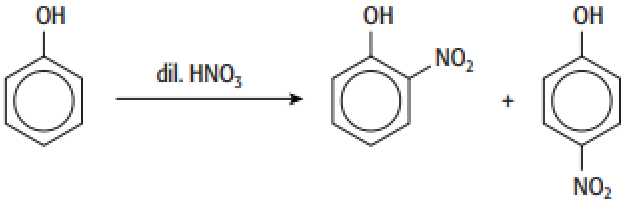


The salt formed, sodium phenoxide, is soluble in water. Phenol also reacts vigorously with sodium metal, giving off hydrogen gas and again forming sodium phenoxide:

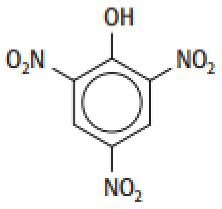


Substitution into the benzene ring of phenol

Phenol reacts more readily with electrophiles than benzene due to the increased electron density of the benzene ring. This activation, particularly at positions 2, 4, and 6, occurs between phenol and chlorine or iodine. This activation is also evident in nitration, which can occur with dilute nitric acid at room temperature.

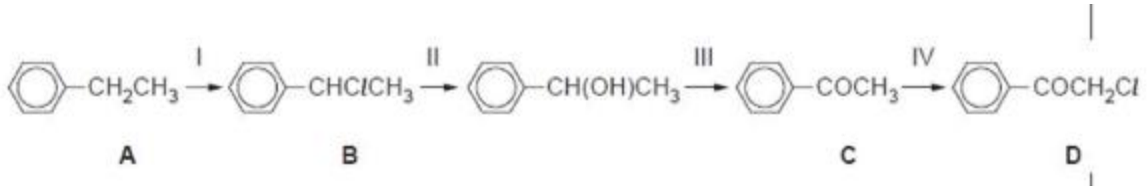


If we use concentrated nitric acid we get 2,4,6-trinitrophenol formed, shown below:



Revision questions

1)Chloroacetophenone (compound D, below) was formerly the most widely used tear gas, under the codename CN. It was used in warfare and in riot control. It can be synthesised from ethylbenzene, A, by the following route.



(a) Suggest reagents and conditions for step I.

(b) Suggest reagents and conditions for converting ethylbenzene into compound E, an isomer of B.

E

(c) Draw the structure of the product obtained by heating ethylbenzene with $KMnO_4$

(d) Describe a test (reagents and observations) that would distinguish compound C from compound F.

F

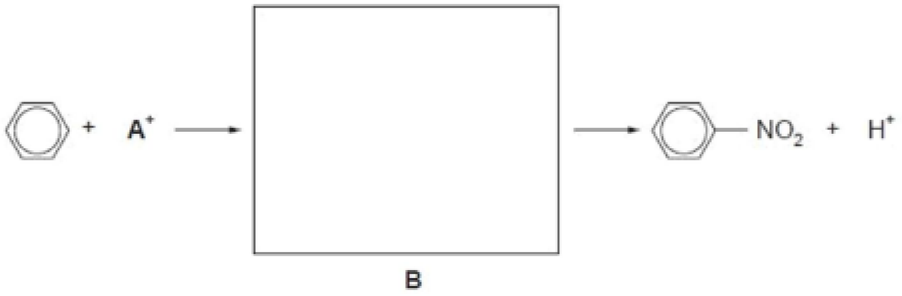
2)(a) State the reagents and conditions needed to convert benzene into

(i) chlorobenzene,

(ii) bromobenzene,

(iii) nitrobenzene.

(b) The nitration of benzene is a two-step reaction that can be represented as follows.

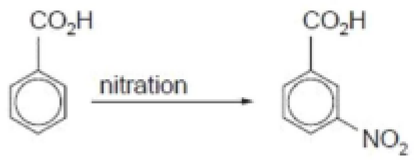


(i) Identify the cation A^+

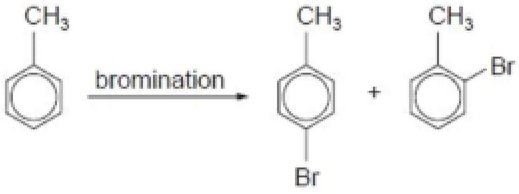
(ii) Draw the structure of the intermediate B in the box

(c) The position of substitution during the electrophilic substitution of arenes is determined by the nature of the group already attached to the ring.

Electron-withdrawing groups such as $-CO_2H$ or $-NO_2$ direct the incoming group to the 3-position.

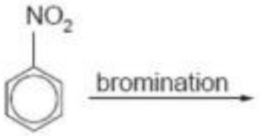


On the other hand, electron-donating groups such as -CH_3 or -NH_2 direct the incoming group to the 2- or 4- positions.

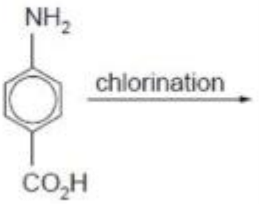


Use this information to suggest a likely structure for the organic product of each of the following reactions.

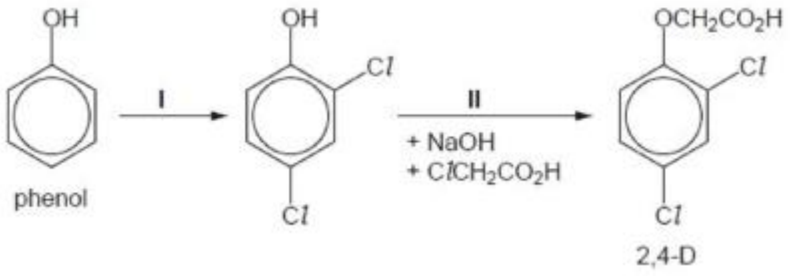
(i)



(ii)



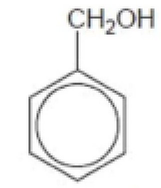
3)The acid $ClCH_2CO_2H$ features in the industrial synthesis of the important weedkiller 2,4-D.



(i) Suggest a possible reagent for reaction I.

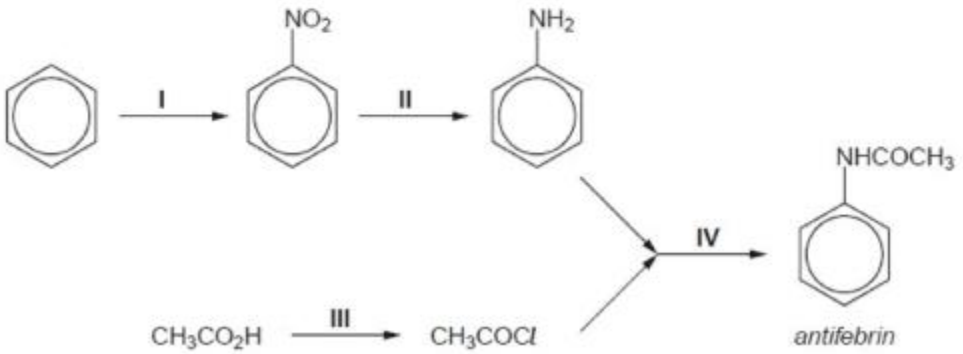
(ii) What type of reaction is

reaction I,
reaction II?
(iii) Describe a test (reagents and observations) that would distinguish phenol from compound A.

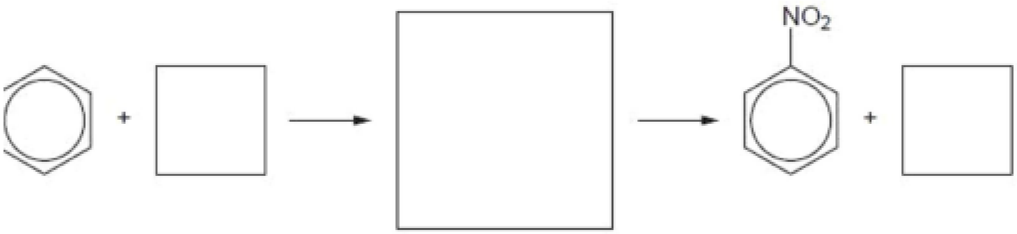


compound **A**

4)The antipyretic (fever-reducing) drug antifebrin can be made from benzene and ethanoic acid by the following route.



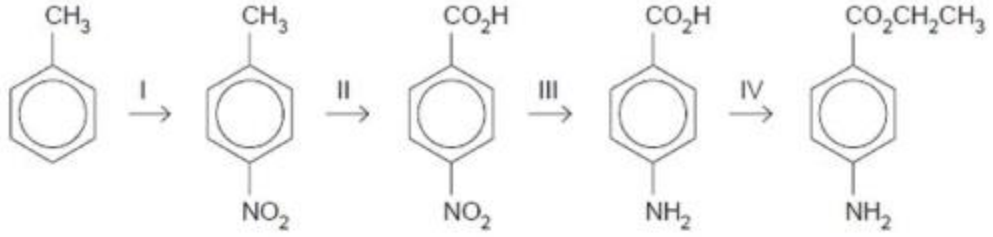
(a) (i) What type of reaction is reaction I?
(ii) Suggest the reagents and conditions for reaction I.
(iii) Complete the following scheme showing the mechanism of reaction I, by drawing appropriate formulae in the three boxes.



(b) (i) What type of reaction is reaction II?
(ii) Suggest the reagents and conditions for reaction II.

(c) Suggest the reagents and conditions for reaction III.
(d) (i) Apart from the benzene ring, name the functional group in antifebrin.
(ii) What reagents and conditions are needed to hydrolyse antifebrin?

5)Benzocaine is an important local anaesthetic used in skin creams for sprains and other muscular pains. It can be made by the following route.

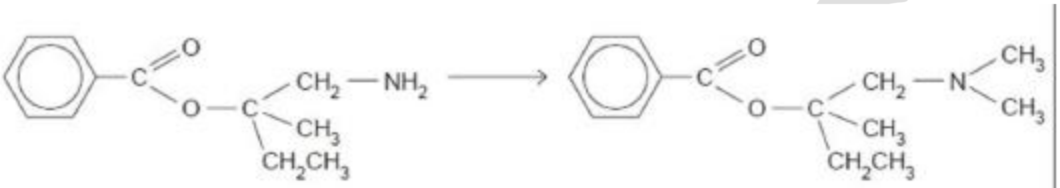


benzocaine

a)suggest regents and conditions for each of the above 4 reactions.

(b) Draw steps to show the mechanism of reaction I.

(c) Another local anaesthetic is amylocaine, which can be made from compound X.



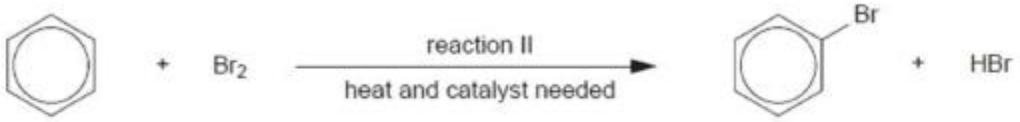
X amylocaine

(i) Apart from the benzene ring, name two functional groups in the molecule of compound X.

(ii) Explain whether compound X would be more or less basic than benzocaine.

6) Both ethene and benzene react with bromine, but the mechanisms and the types of products of the two reactions are different.

$$H_2C{=}CH_2 \quad + \quad Br_2 \xrightarrow[\text{no heat, no light, no catalyst needed}]{\text{reaction I}} BrCH_2CH_2Br$$



(a) State the *type of reaction* undergone in each of reactions I and II.

(a) State the type of reaction undergone in each of reactions I and II.

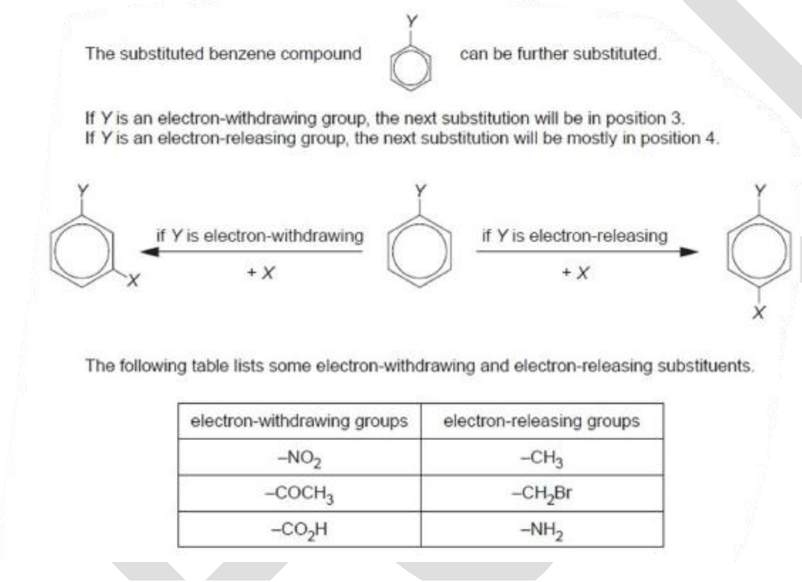
reaction I

reaction II

(b) In each of reactions I and II, the intermediate is a bromine-containing cation. In each of the following boxes, draw the intermediate and use curly arrows to show how it is converted into the product.

(c) Why do ethene and benzene differ in their reaction with bromine?

7)



The substituted benzene compound can be further substituted.

If *Y* is an electron-withdrawing group, the next substitution will be in position 3.
If *Y* is an electron-releasing group, the next substitution will be mostly in position 4.

The following table lists some electron-withdrawing and electron-releasing substituents.

electron-withdrawing groups	electron-releasing groups
$-NO_2$	$-CH_3$
$-COCH_3$	$-CH_2Br$
$-CO_2H$	$-NH_2$

Use the above information to draw relevant structural formulae in the boxes in the schemes below.