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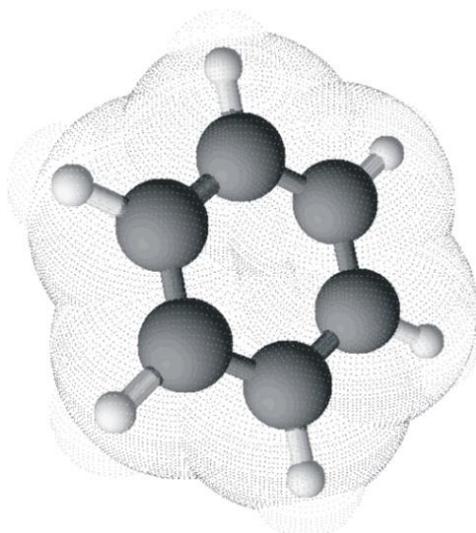
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The Chemistry of Benzene – C₆H₆

Macroconcept – Models



This booklet covers essential information concerning the chemistry of benzene, including its structure, bonding and reactions. The booklet is presented in an open learning format which students can work through at their own pace during private study or as part of a formal lesson. Contained within this booklet is a mixture of information, questions and model answers.

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Introduction

Benzene is a *hydrocarbon* (i.e. it is only composed of the two elements hydrogen and carbon) with the formula C_6H_6 . Benzene is a clear, colourless liquid at room temperature and pressure (melting point = $5.5\text{ }^\circ\text{C}$ and boiling point = $80.1\text{ }^\circ\text{C}$). Benzene is a non-polar molecule and therefore immiscible with water. It is important to note that benzene is a suspected human *carcinogen* (a chemical which causes cancer).

The Structure of Benzene

A six carbon *saturated alkane* would have the formula C_6H_{14} . Therefore benzene, with a formula of C_6H_6 , must be highly *unsaturated* (i.e. benzene must contain many carbon-to-carbon double covalent bonds). This observation is inconsistent with the chemistry of benzene. Unsaturated compounds are highly reactive but benzene is remarkably inert to many reagents. For example, it does not react with aqueous potassium manganate(VII) or with bromine water. It does not even react with cold concentrated sulphuric acid. For benzene to be so highly unsaturated, and yet so stable, it must have a very special structure.

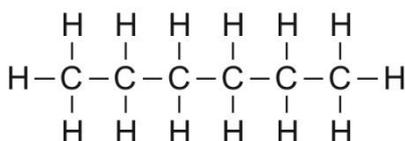


Figure 1. Hexane, C_6H_{14} , is a saturated hydrocarbon. Each carbon atom makes a single covalent bond to four separate atoms.

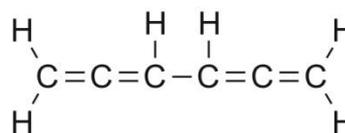


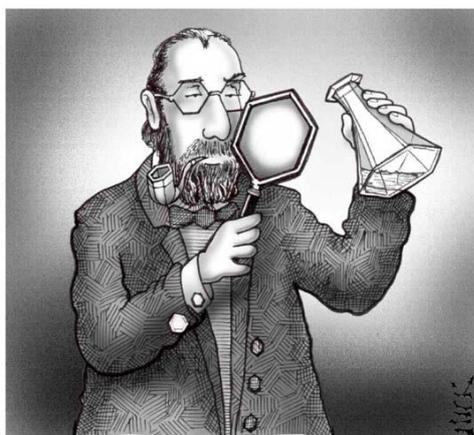
Figure 2. A possible structure for benzene. With the formula of C_6H_6 , a molecule of benzene *must* be highly unsaturated (i.e. it must contain many carbon-to-carbon double covalent bonds).

Note: This is not the real structure of benzene because it does not explain the compound's relatively unreactive nature.

Question 1: Give the systematic name of the organic compound shown in **Figure 2**.

(Answer on page 18).

Great events in Chemistry...



1865: Kekulé, moments before his brilliant insight into the structure of benzene.

Figure 3. A parody of August Kekulé's elucidation of the structure of benzene.

In 1865, the French chemist August Kekulé proposed that benzene had a *cyclic* structure. This is now recognised as the origin of the molecule's stability as the cyclic structure allows the molecule's six π -bonding electrons to *delocalise* over all six carbon atoms.

Modern analytical techniques have shown that benzene is a planar regular hexagon, with all of the bond angles equal to 120° . The carbon-to-carbon covalent bonds are all of equal length (0.139 nm) which is intermediate between the length of a carbon-to-carbon single covalent bond (0.154 nm) and a carbon-to-carbon double covalent bond (0.134 nm). **Note:** $1.0\text{ nm} = 1 \times 10^{-9}\text{ m}$.

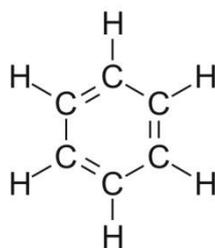


Figure 4. The cyclic structure of benzene proposed by August Kekulé—in 1865.

The structure of benzene proposed by Kekulé, with the three carbon-to-carbon double covalent bonds in localised positions, does not explain benzene's stable nature and therefore requires some modification. Modern studies have shown that the π -bonding electrons of benzene's carbon-to-carbon double covalent bonds do not have a *fixed location* in the molecule, but are actually *delocalised* around the six carbon ring. This causes benzene to be much lower in energy than expected and therefore less reactive than expected (remember that chemicals react in an attempt to lower their energy and so a chemical which is already low energy will be relatively unreactive).

Question 2: Complete the electron configurations below to show the different ways in which carbon's s and p-orbitals are *hybridised* to allow for bonding in C–C, C=C and C≡C:

	1s	2s	2p								
• Reference, carbon in its ground state:	↑↓	↑↓	↑	↑							
a) Carbon, hybridisation in C–C:	<table border="1" style="width: 100%; height: 20px;"> <tr> <td style="width: 15%;"></td> </tr> </table>										
b) Carbon, hybridisation in C=C:	<table border="1" style="width: 100%; height: 20px;"> <tr> <td style="width: 15%;"></td> </tr> </table>										
c) Carbon, hybridisation in C≡C:	<table border="1" style="width: 100%; height: 20px;"> <tr> <td style="width: 15%;"></td> </tr> </table>										

(Answer on page 18).

Question 3: Using a suitable diagram, explain what is meant by the term σ -bond:

(Answer on page 18).

Question 4: Using a suitable diagram, explain what is meant by the term π -bond:

(Answer on page 18).

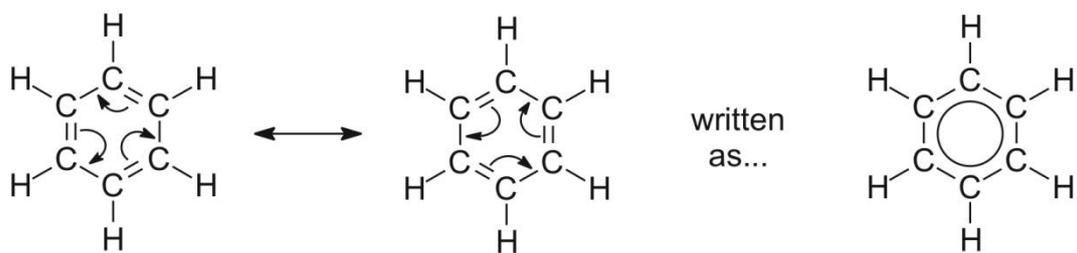


Figure 5. The six π -bonding electrons of the three C=C bonds do not have a fixed position within the molecule. Instead, evidence indicates that they are actually *delocalised* over the six carbon ring. Because the *exact* locations of the six π -bonding electrons are unknown, their *probable* location is indicated by a circle.



Figure 6. For convenience, the structure of benzene is represented by a hexagon (representing the ring of six carbon atoms) with a circle in the centre (representing the delocalised π -bonding electrons).

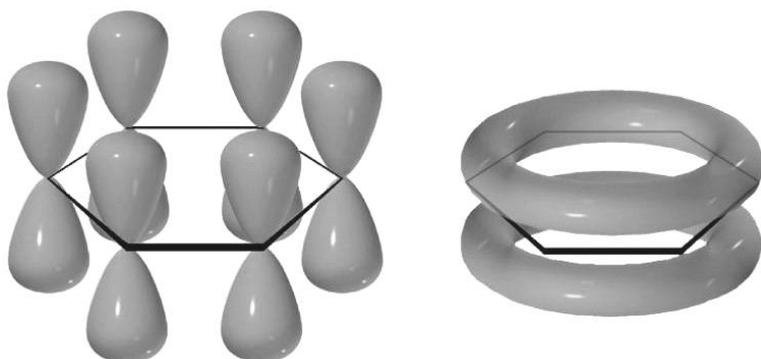


Figure 7. The overlap of the six *p-orbitals* above and below the plane of the six carbon ring results in the formation of a delocalised cloud of π -bonding electrons.

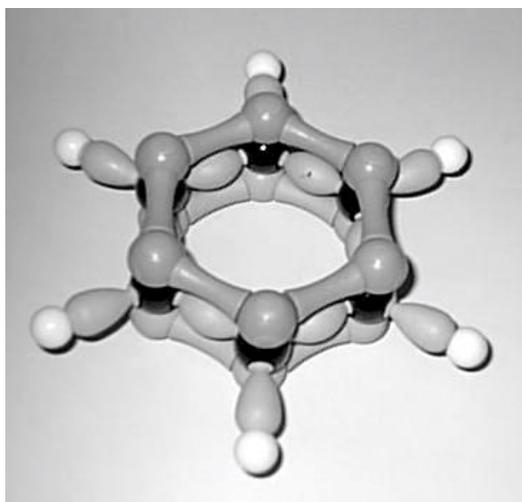


Figure 8. A model of benzene showing the σ -bonds sandwiched between the delocalised cloud of π -bonding electrons which exist above and below the plane of the six carbon ring.

Evidence for the Delocalised Structure and Extra Stability of Benzene

• Bond Length:

If Kekulé's structure for benzene were correct, then the benzene ring should have the shape of an *irregular hexagon*, with sides alternating in length between 0.154 nm (the length of a carbon-to-carbon single covalent bond) and 0.134 nm (the length of a carbon-to-carbon double covalent bond). This structure is shown in **Figure 9**. In reality, X-ray diffraction confirms that all of the carbon-to-carbon covalent bonds in benzene are 0.139 nm in length (see **Figure 9**). The carbon-to-carbon *single* covalent bond in ethane is 0.154 nm long while the carbon-to-carbon *double* covalent bond in ethene is 0.134 nm long. Therefore, at 0.139 nm, the carbon-to-carbon bond length in benzene is midway between the length of a carbon-to-carbon single covalent bond and a carbon-to-carbon double covalent bond. This indicates that all six carbon-to-carbon bonds in benzene are identical in nature. This infers that the six π -bonding electrons are delocalised over the whole molecule rather than being fixed in position between just three pairs of carbon atoms.

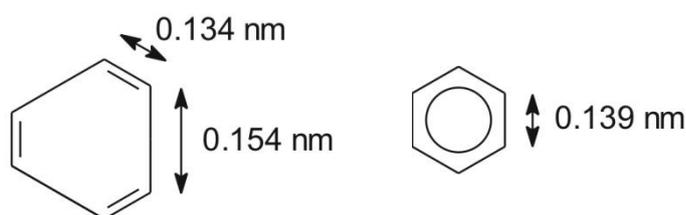


Figure 9. If the π -bonding electrons of benzene were *not* delocalised then the benzene ring would be an *irregular hexagon* with sides of *different length*. Because the π -bonding electrons are delocalised in benzene, the carbon-to-carbon covalent bonds are all identical in nature and are therefore all the *same length*.

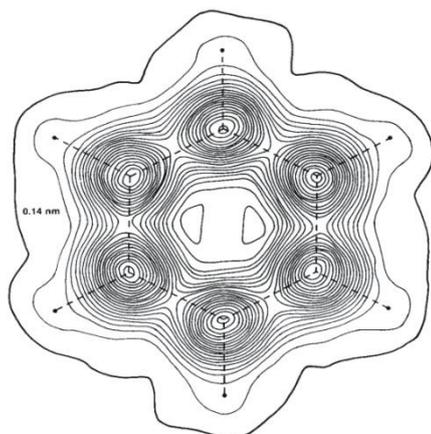


Figure 10. An electron density contour map of benzene (obtained by X-ray diffraction) shows that all of the carbon-to-carbon covalent bonds are the same length. In addition, the data shows that the electron density is spread evenly over the whole molecule.

• Thermodynamic Evidence:

Thermochemical cycles can be used to compare the stability of *real* benzene (in which the π -bonding electrons are delocalised over the six carbon ring) with that of the *theoretical* Kekulé type structure of benzene (in which the π -bonding electrons are localised between three pairs of carbon atoms).

Part A – Enthalpy Change of Hydrogenation:

Figure 11 shows the catalytic hydrogenation of cyclohexene:

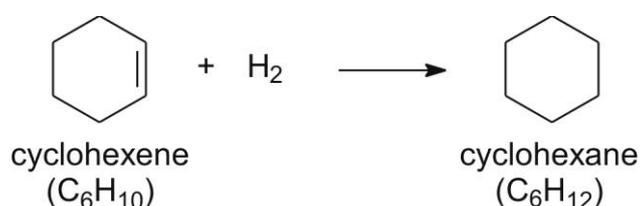
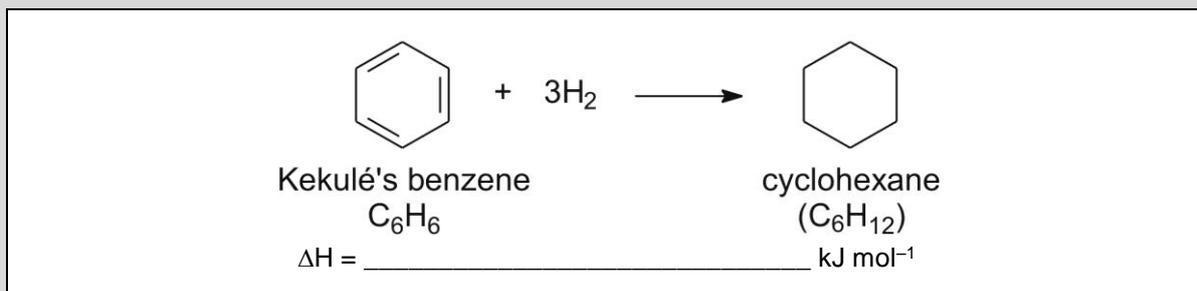


Figure 11. The enthalpy change for the catalytic hydrogenation of cyclohexene is -120 kJ mol^{-1} .

Question 5: If the enthalpy change for the catalytic hydrogenation of cyclohexene is -120 kJ mol^{-1} , calculate the enthalpy change for the catalytic hydrogenation of the *theoretical* Kekulé type structure of benzene:



(Answer on page 19).

Figure 12 shows the catalytic hydrogenation of *real* benzene with a delocalised π -bonding electron system:

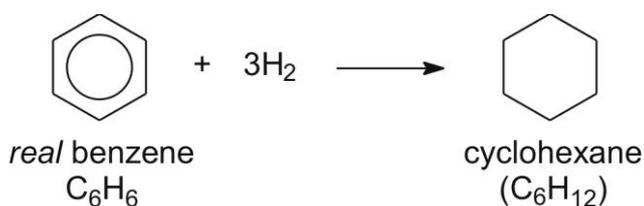
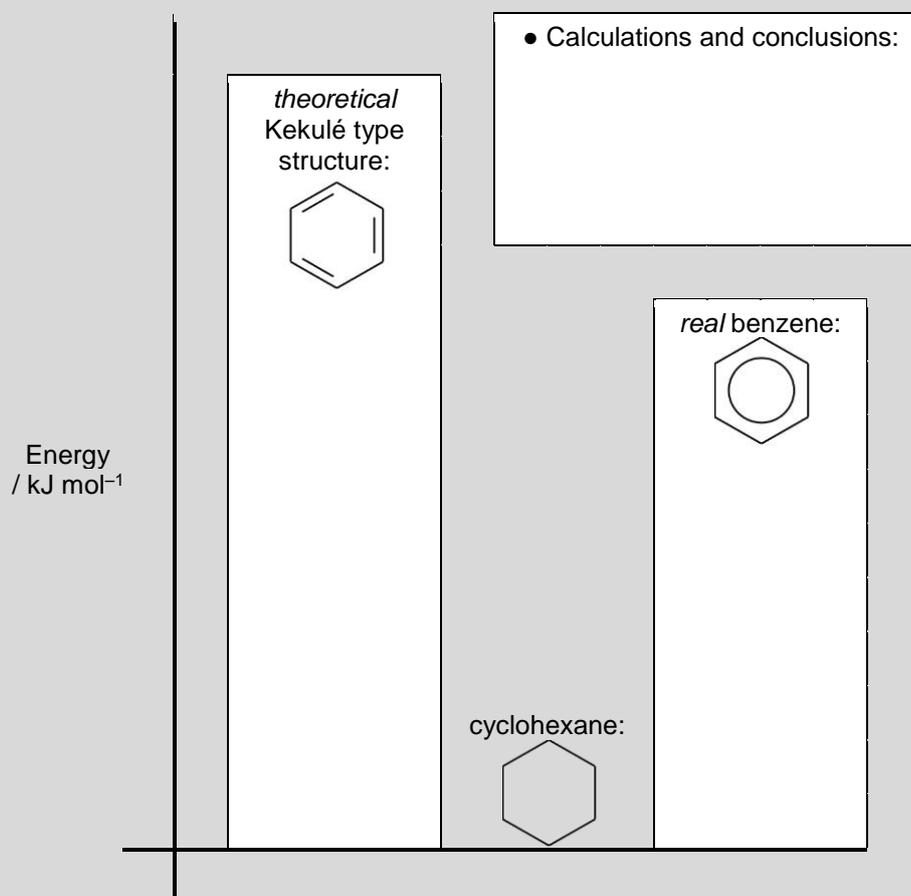


Figure 12. The enthalpy change for the catalytic hydrogenation of *real* benzene is -208 kJ mol^{-1} .

Question 6: Using the answer that you calculated to **Question 5**, complete the enthalpy diagram below. Calculate the difference between the enthalpy change for the hydrogenation of *real* benzene and the enthalpy change for the hydrogenation of the *theoretical* Kekulé type structure. Mark this energy value on the enthalpy diagram:



(Answer on page 19).

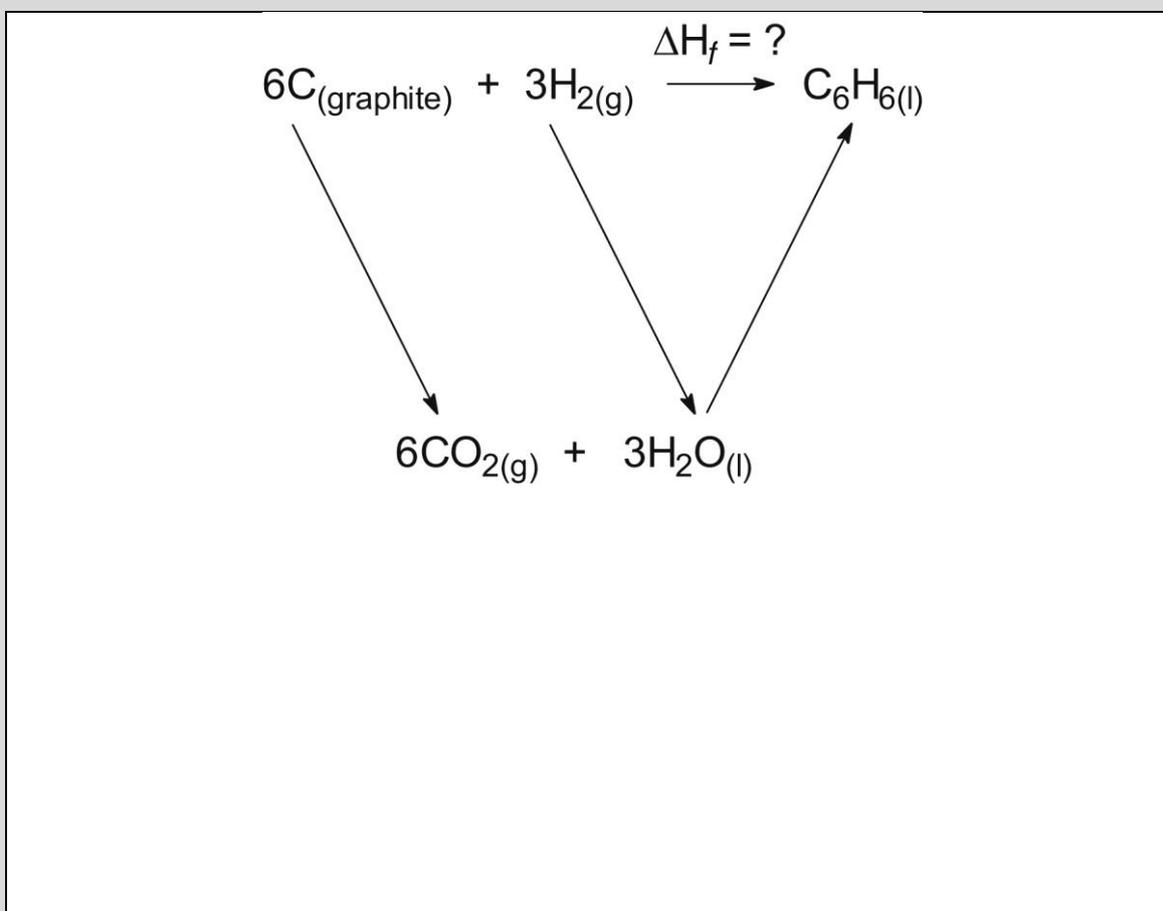
The answer to **Question 6** should demonstrate that *real* benzene (with a delocalised π -bonding electron system) is significantly lower in energy, and therefore more stable, than the *theoretical* Kekulé type structure of benzene (in which the six π -bonding electrons are localised between three pairs of carbon atoms). The difference between the two energy values used in **Question 6** is often referred to as the *resonance energy* of benzene. It is a measure of the stability that is conferred upon the molecule due to the ability of the six π -bonding electrons to delocalise over the six carbon ring.

Part B – Enthalpy Change of Formation:

Question 7: Use the following data to calculate the enthalpy change for the formation of *real* benzene. The calculation should be carried out by completing the Hess cycle given below.

Data:

- The enthalpy change for the combustion (ΔH_c) of carbon (as graphite) = -394 kJ mol^{-1} .
- The enthalpy change for the combustion (ΔH_c) of hydrogen gas = -286 kJ mol^{-1} .
- The enthalpy change for the combustion (ΔH_c) of *real* benzene = $-3273 \text{ kJ mol}^{-1}$.



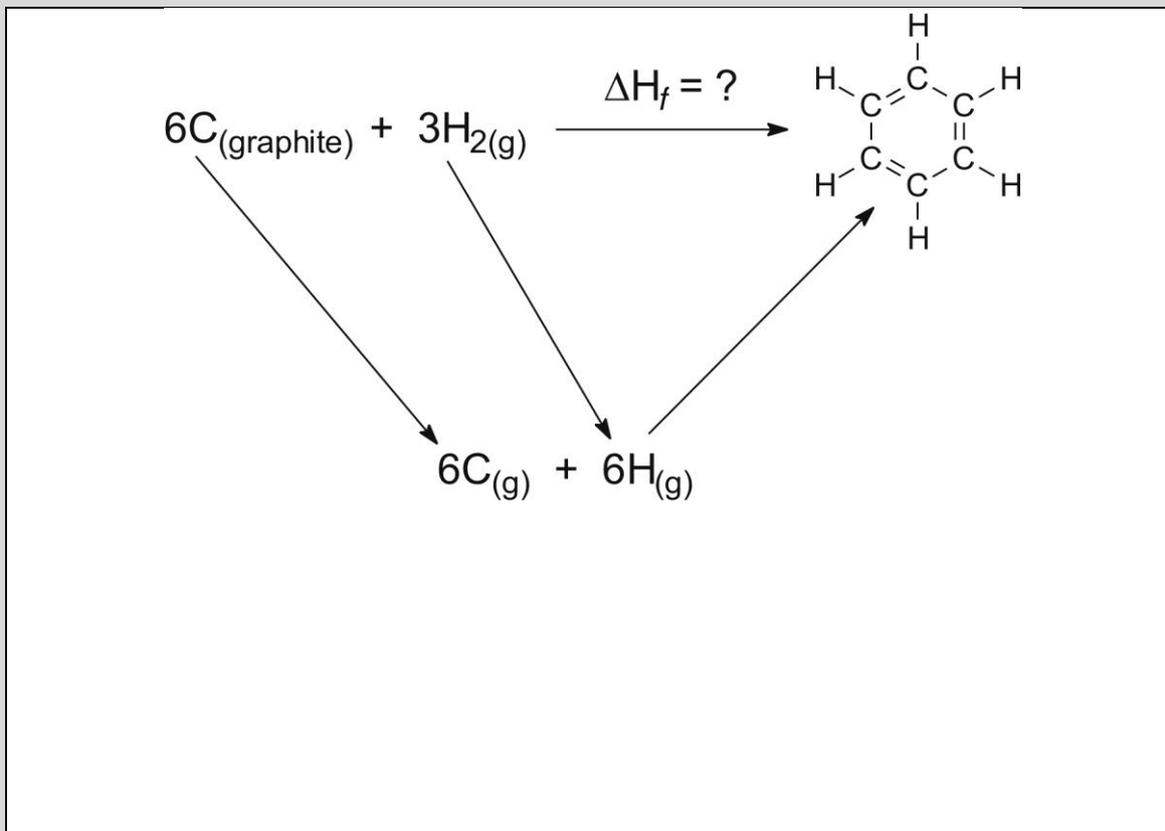
The enthalpy change for the formation (ΔH_f) of *real* benzene measured by experiment is $+49 \text{ kJ mol}^{-1}$ (this information can be found in most chemistry data books). Compare this value to the value that you have calculated.

(Answer on page 19).

Question 8: Use the following data to calculate the enthalpy change for the formation (ΔH_f) of the *theoretical* Kekulé type structure of benzene. The calculation should be carried out by completing the Hess cycle given below.

Data:

- The enthalpy change for the atomisation (ΔH_a) of $C_{(\text{graphite})} = +715 \text{ kJ mol}^{-1}$ of $C_{(\text{g})}$ formed.
- The enthalpy change for the atomisation (ΔH_a) of $\frac{1}{2}H_{(\text{g})} = +218 \text{ kJ mol}^{-1}$ of $H_{(\text{g})}$ atoms formed.
 - The average C–C bond enthalpy = 348 kJ mol^{-1} .
 - The average C=C bond enthalpy = 612 kJ mol^{-1} .
 - The average C–H bond enthalpy = 412 kJ mol^{-1} .



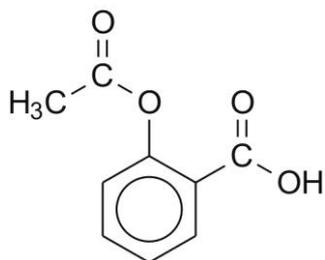
Compare the answer to **Question 7** (ΔH_f of *real* benzene) with the answer to **Question 8** (ΔH_f of *theoretical* Kekulé type structure of benzene). The calculations should once again demonstrate that *real* benzene (with a delocalised π -bonding electron system) is lower in energy, and therefore more stable, than the *theoretical* Kekulé type structure of benzene (in which the six π -bonding electrons are localised between three pairs of carbon atoms).

(Answer on page 20).

Question 9: Describe how *models* have been employed in deducing and understanding the structure of benzene. In which other areas of science are *models* used to good effect?

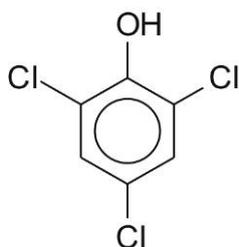
(Answer on page 20).

Examples of Important Compounds that Contain a Benzene Ring



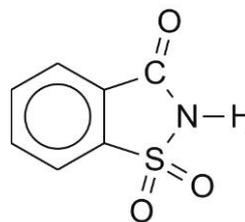
aspirin

Analgesic, anti-pyretic and anti-inflammatory drug.



2,4,6-trichlorophenol (TCP)

Antiseptic.

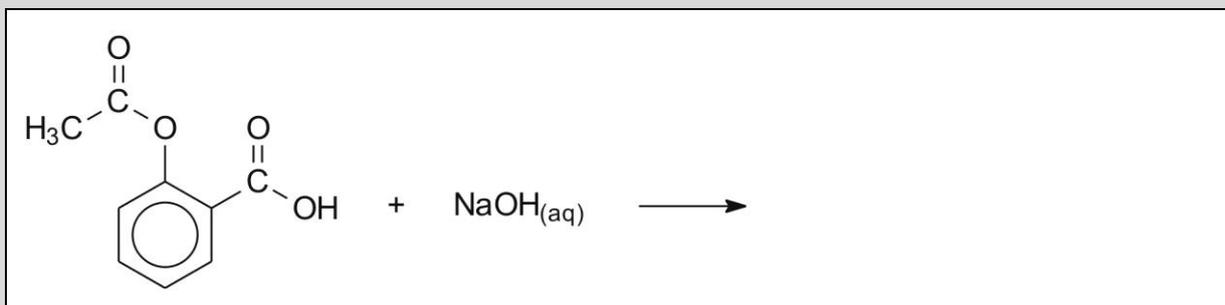


saccharin

Artificial sweetener.

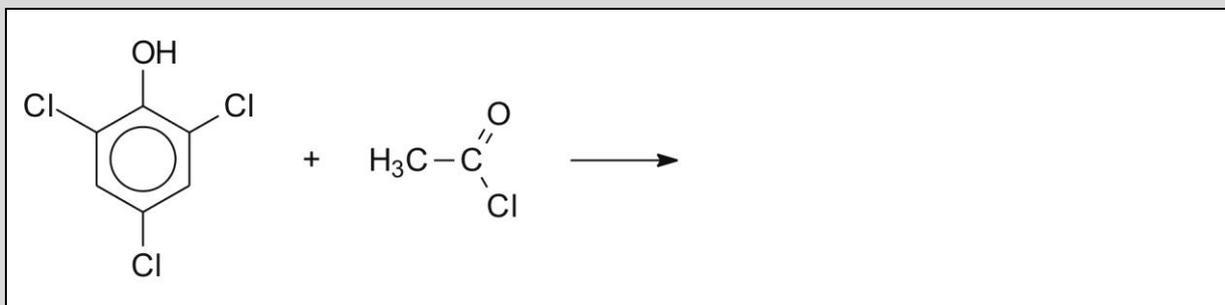
Figure 13. Some examples of important compounds that contain a benzene ring.

Question 10: What organic reaction product will be formed when aspirin is refluxed with an aqueous solution of sodium hydroxide?



(Answer on page 20).

Question 11: What organic reaction product will be formed when 2,4,6-trichlorophenol is treated with ethanoyl chloride?



(Answer on page 20).

The Reaction Mechanism of Benzene

The homologous series of alkenes contain a carbon-to-carbon double covalent bond as the functional group. The alkenes react by an *electrophilic addition* mechanism, which results in loss of the carbon-to-carbon double covalent bond, forming a saturated reaction product (see **Figure 14**).

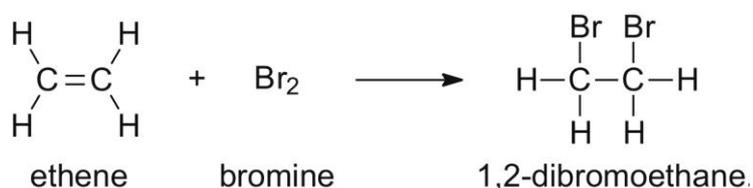


Figure 14. Electrophilic addition to an alkene results in loss of the carbon-to-carbon double covalent bond.

Electrophilic addition is *not* the favoured reaction mechanism of benzene. This is because the loss of one carbon-to-carbon double covalent bond will result in the remaining carbon-to-carbon double covalent bonds becoming *localised* within the molecule. Consequential loss of the delocalised π -electron system will result in the loss of stability that it confers upon the molecule. In turn, this will result in the undesired formation of a relatively high energy and unstable reaction product, *i.e.* an *endothermic* reaction will have taken place. In summary, if benzene were to undergo an electrophilic addition reaction, it would be in conflict with the Second Law of Thermodynamics, from which it can be inferred that a spontaneous chemical change will only take place when the reaction product is of *lower energy* and consequently more stable than the original reactant (see **Figure 15**).

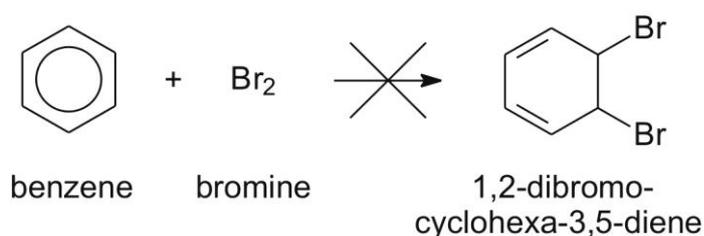


Figure 15. Benzene does *not* react by electrophilic addition because this would result in loss of the delocalised π -bonding electron system and the stability that it confers upon the molecule.

Benzene is susceptible to attack by electrophiles due to the high density of negatively charged π -bonding electrons which exist above and below the plane of the six carbon ring (see **Figure 7** and **Figure 8**). However, the electrophile does not *add* to the benzene ring but instead *substitutes* for one of the six hydrogen atoms. This allows benzene to react while retaining its delocalised π -bonding electron system and the stability that is associated with it. Therefore *benzene reacts by electrophilic substitution*. An outline of the electrophilic substitution reaction mechanism is given in **Figure 16**.

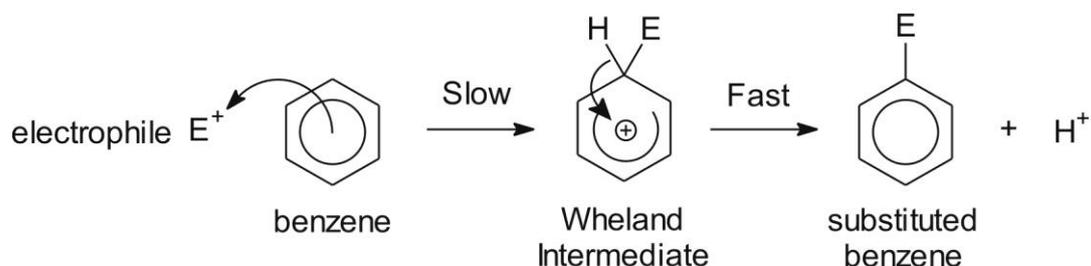


Figure 16. The electrophile (usually a cation) is attracted to the benzene ring by the cloud of delocalised π -bonding electrons which exist above and below the plane of the ring. The electrophile adds to the benzene ring to form a short lived intermediate (*Wheland* intermediate) in which the entering electrophile and leaving hydrogen ion are both bonded to the ring. The positive charge contributed by the electrophile is distributed over the ring. The Wheland intermediate rapidly loses a hydrogen ion, restoring the stability of the benzene ring.

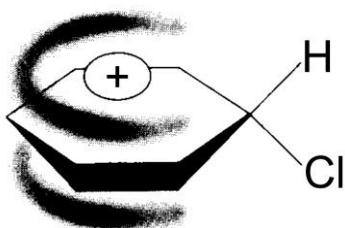


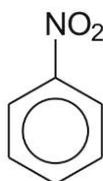
Figure 17. This figure shows the distribution of the π -bonding electrons in the Wheland intermediate. Note that the electrophile used to generate this intermediate was Cl^+ .

Examples of Electrophilic Substitution Into Benzene

Three important electrophilic substitution reactions will be studied in this booklet:

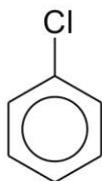
- Nitration
- Halogenation
- Alkylation

Nitration: Introduction of the nitro group, $-\text{NO}_2$, into a benzene ring is known as *nitration*. To synthesise nitrobenzene, NO_2^+ is used as the electrophile.

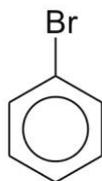


nitrobenzene

Halogenation: Introduction of a Group VII element into a benzene ring is known as *halogenation*. To synthesise chlorobenzene and bromobenzene, the cations Cl^+ and Br^+ are used respectively.



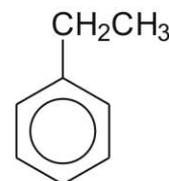
chlorobenzene



bromobenzene



methylbenzene



ethylbenzene

Figure 18. Derivatives of benzene; nitrobenzene, chlorobenzene, bromobenzene, methylbenzene and ethylbenzene.

• Nitration (the preparation of nitrobenzene):

The substitution of a hydrogen atom by the nitro group ($-\text{NO}_2$) is called *nitration*. To obtain nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) benzene is refluxed at 60°C with a *nitrating mixture* as shown in **Figure 19**.

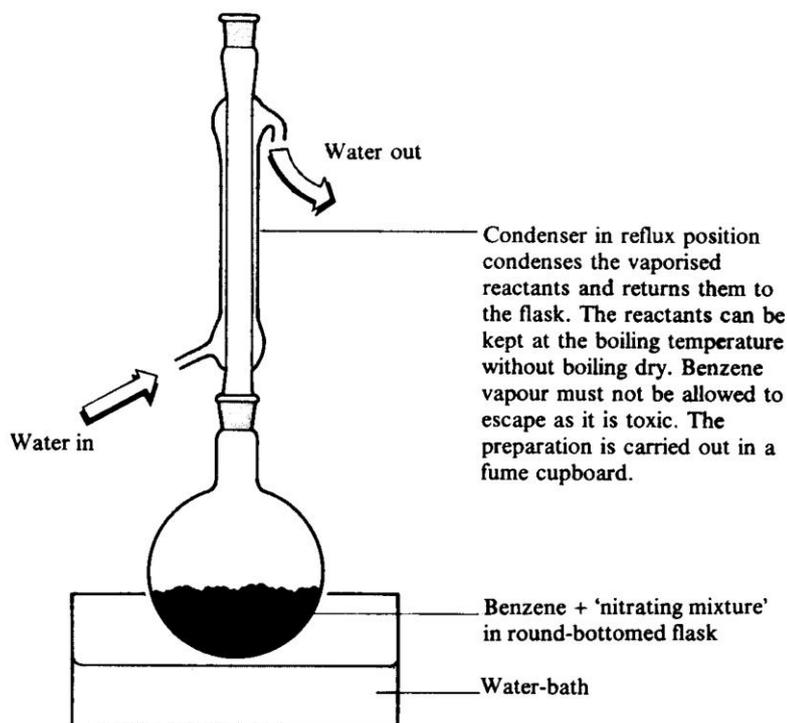


Figure 19. Nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) is prepared by refluxing benzene with conc. HNO_3 and conc. H_2SO_4 at 60°C .

The nitrating mixture is prepared by adding concentrated nitric acid and concentrated sulphuric acid together at 0°C in an ice bath. While the mixture of concentrated acids is still at 0°C, benzene is carefully added. The reaction mixture is allowed to reach room temperature and is then refluxed at 60°C in a thermostatically controlled water bath.

The nitrobenzene produced by this reaction is a pale yellow liquid which can be separated from benzene by distillation under reduced pressure (b.p. benzene = 80.1°C and b.p. nitrobenzene = 211°C). **Figure 20** shows the typical apparatus used for a distillation.

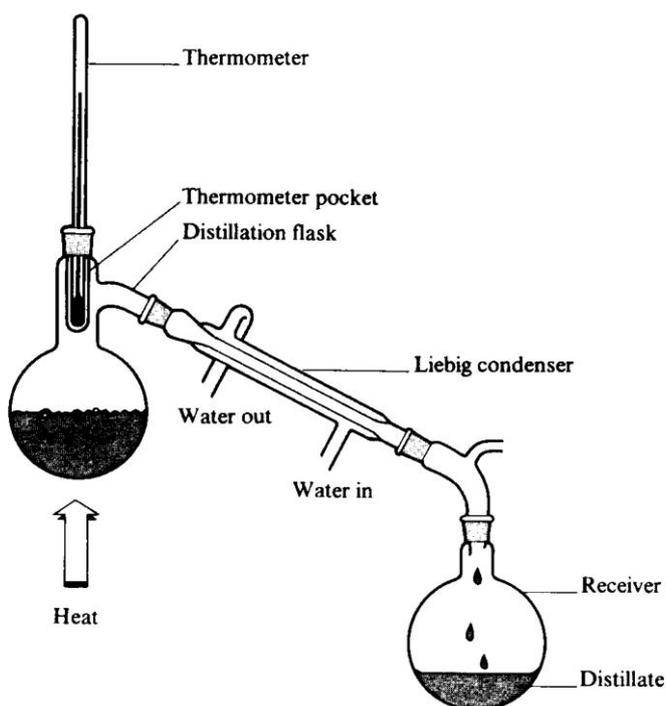
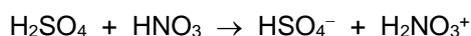


Figure 20. Typical distillation apparatus that might be used to separate nitrobenzene (b.p. = 211°C) from benzene (b.p. = 80.1°C).

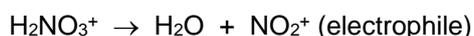
Question 12: What is the distillate and what is the residue in this system? What temperature will the thermometer read during the distillation?

(Answer on page 21).

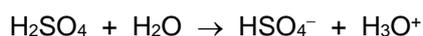
When the concentrated sulphuric acid and concentrated nitric acid are added together the sulphuric acid donates a hydrogen ion to the nitric acid. This happens because sulphuric acid is a stronger acid than nitric acid. In this reaction the nitric acid is acting as a base (a hydrogen ion acceptor):



The protonated nitric acid splits up to form a molecule of water and the NO_2^+ cation, which is called the *nitryl cation*:



The molecule of water is protonated by a second molecule of sulphuric acid:

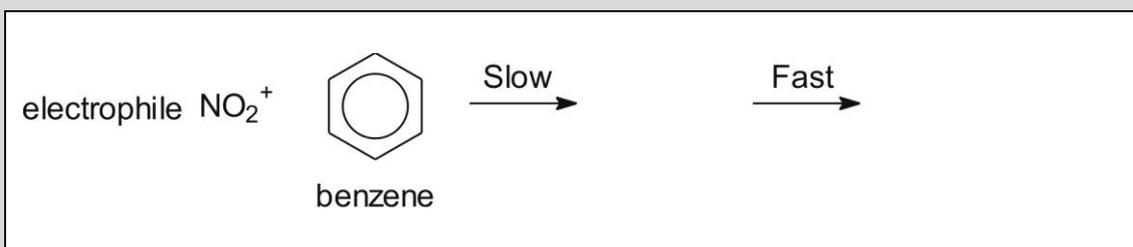


Combining the three reactions gives:



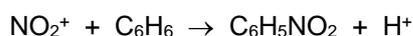
The nitryl cation is an electrophile and attacks the benzene ring according to the mechanism given on page 10.

Question 13: Complete the reaction mechanism below to show electrophilic substitution of NO_2^+ into the benzene ring:

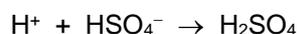


(Answer on page 21).

This reaction mechanism can be summarised as:



The hydrogen ion produced by this reaction is immediately accepted by the hydrogensulphate ion:



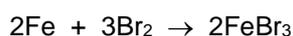
The overall rate of reaction is determined by the slowest step in the reaction sequence. For this reaction the slowest step is the rate at which the C–NO₂ bond is formed in the Wheland intermediate.

• **Halogenation** (the preparation of chlorobenzene and bromobenzene):

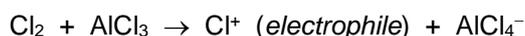
To substitute chlorine or bromine into a benzene ring the electrophilic Cl^+ or Br^+ cations must be formed. To generate these cations, a catalyst is required. The catalyst is called a *Friedel-Crafts* catalyst and varies in nature depending upon the halogen which is to be substituted into the benzene ring:

- Aluminium chloride (AlCl_3) is the Friedel-Crafts catalyst used to substitute chlorine into the benzene ring.
- Iron(III) bromide (FeBr_3) is the Friedel-Crafts catalyst used to substitute bromine into the benzene ring.

Note: the iron(III) bromide catalyst is freshly prepared at the start of the reaction by adding bromine to iron filings:



Benzene can be halogenated at room temperature by treating it with the desired halogen in the presence of a Friedel-Crafts catalyst. The Friedel-Crafts catalyst acts as a Lewis acid (an electron pair acceptor) and the halogen acts as a Lewis base (an electron pair donor). To chlorinate benzene, and thus synthesise chlorobenzene, an aluminium chloride catalyst is treated with chlorine in order to produce the desired electrophilic Cl^+ cation:



which may be considered as:



Once the electrophile has been generated, electrophilic substitution into the benzene ring takes place according to the mechanism on page 10. The mechanism for the electrophilic substitution of chlorine into the benzene ring is given in **Figure 21**.

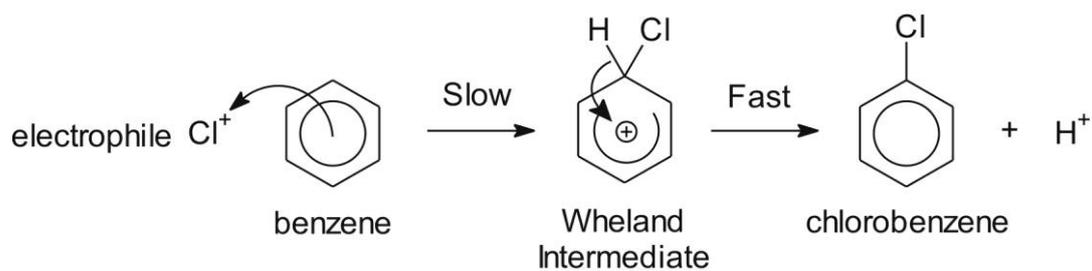
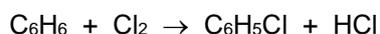


Figure 21. Electrophilic substitution of the Cl^+ cation into benzene, producing chlorobenzene as the substituted reaction product.

The hydrogen ion reacts with the AlCl_4^- to form HCl and AlCl_3 . The catalyst is therefore regenerated:



The overall reaction for the electrophilic substitution of chlorine into benzene may therefore be written as:

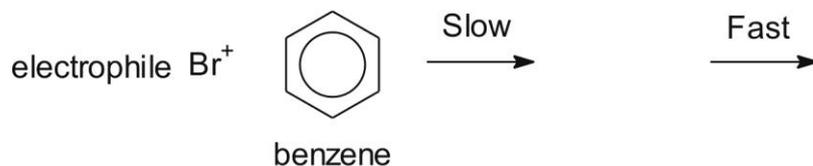


Question 14: Complete the reaction mechanism below to show how bromine and iron(III) bromide react to produce the electrophilic Br^+ cation. In the reaction, identify which chemical species is behaving as the Lewis acid and which chemical species is behaving as the Lewis base.



(Answer on page 21).

Question 15: Complete the reaction mechanism below to show electrophilic substitution of Br^+ into the benzene ring:



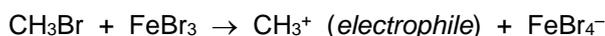
(Answer on page 21).

Chlorobenzene and bromobenzene are both liquids at room temperature and pressure and may therefore be purified by distillation (b.p. chlorobenzene = 132°C and b.p. bromobenzene = 156°C). The distillation apparatus is shown in **Figure 20**.

• **Alkylation** (the preparation of methylbenzene and ethylbenzene):

Alkylation of benzene requires the introduction of a methyl group (–CH₃) or ethyl group (–CH₂CH₃) into the benzene ring. To introduce a methyl group into benzene requires formation of the electrophilic CH₃⁺ carbocation and introduction of an ethyl group into benzene requires formation of the electrophilic CH₃CH₂⁺ carbocation.

The carbocations CH₃⁺ and CH₃CH₂⁺ can be generated by treating a suitable halogenoalkane with a Friedel-Crafts catalyst. For example, the halogenoalkane bromomethane (CH₃Br) may be treated with the Friedel-Crafts catalyst iron(III) bromide (FeBr₃):



A more detailed view of the reaction looks like this:



The Friedel-Crafts catalyst is acting as a Lewis acid (an electron pair acceptor) while the halogenoalkane is acting as a Lewis base (an electron pair donor).

Once the electrophilic carbocations have been generated, electrophilic substitution into the benzene ring takes place according to the mechanism on page 10. For example, if the electrophile was the CH₃⁺ carbocation, the reaction mechanism would be:

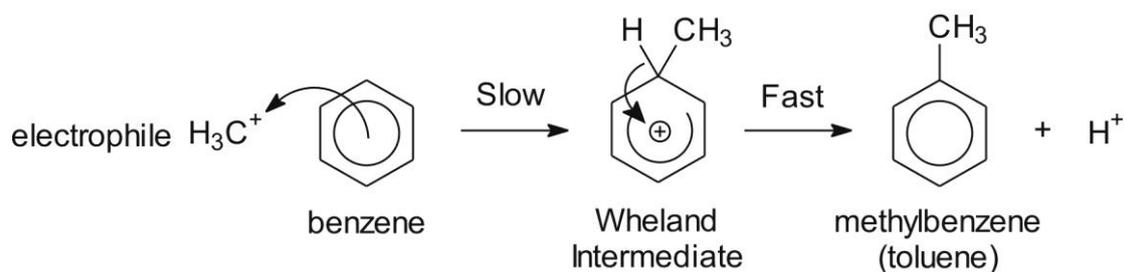
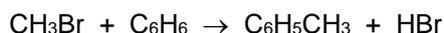


Figure 22. Electrophilic substitution of the H₃C⁺ cation into benzene, producing methylbenzene as the substituted reaction product.

The hydrogen ion reacts with FeBr₄[–] to regenerate the iron(III) bromide catalyst and form HBr:



The overall reaction between bromomethane and benzene can therefore be written as:



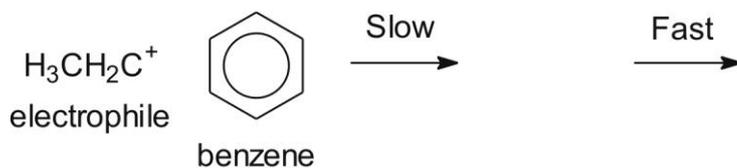
To carry out this reaction in the laboratory the liquid halogenoalkane would be mixed with benzene in the presence of the Friedel-Crafts catalyst and warmed slightly above room temperature using a thermostatically controlled water bath. The reaction product would be purified by distillation (b.p. methylbenzene = 111°C).

Question 16: Complete the reaction mechanism below to show how chloroethane and aluminium chloride react to produce the electrophilic $\text{H}_3\text{CH}_2\text{C}^+$ cation. In the reaction, identify which chemical species is behaving as the Lewis acid and which chemical species is behaving as the Lewis base.



(Answer on page 21).

Question 17: Complete the reaction mechanism below to show electrophilic substitution of $\text{H}_3\text{CH}_2\text{C}^+$ into the benzene ring.



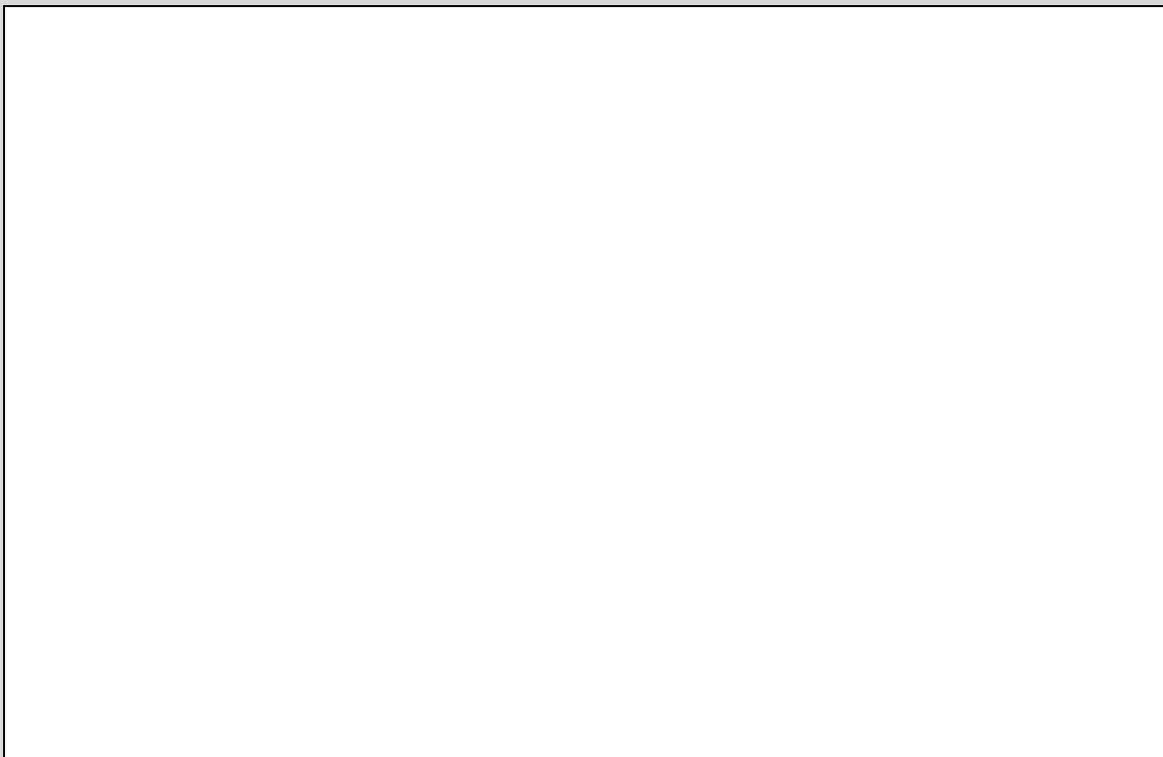
(Answer on page 21).

Question 18: With reference to the physical properties of methylbenzene, predict the boiling point of ethylbenzene.

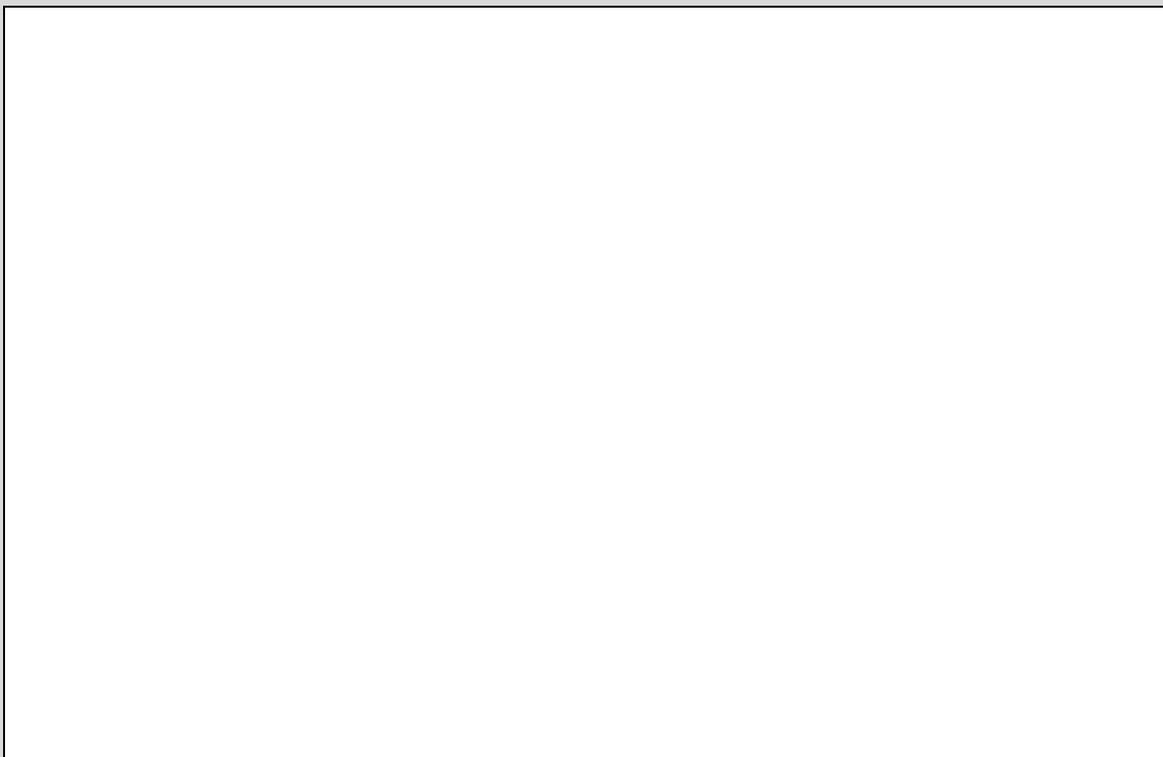
(Answer on page 22).

Assessment of Learning

Question 1: Phenylethanone, $C_6H_5(CO)CH_3$, can be prepared by reacting benzene with a second organic compound in the presence of a suitable catalyst. Write balanced chemical equations and reaction mechanisms to clearly show how phenylethanone can be synthesised from benzene in the laboratory.



Question 2: Sketch the energy profile to represent the energy change that occurs when an electrophile, E-Z, substitutes into a benzene ring. You should include the stability that is conferred on the reaction by the Wheland Intermediate as well as the possible outcome of an addition product being formed.



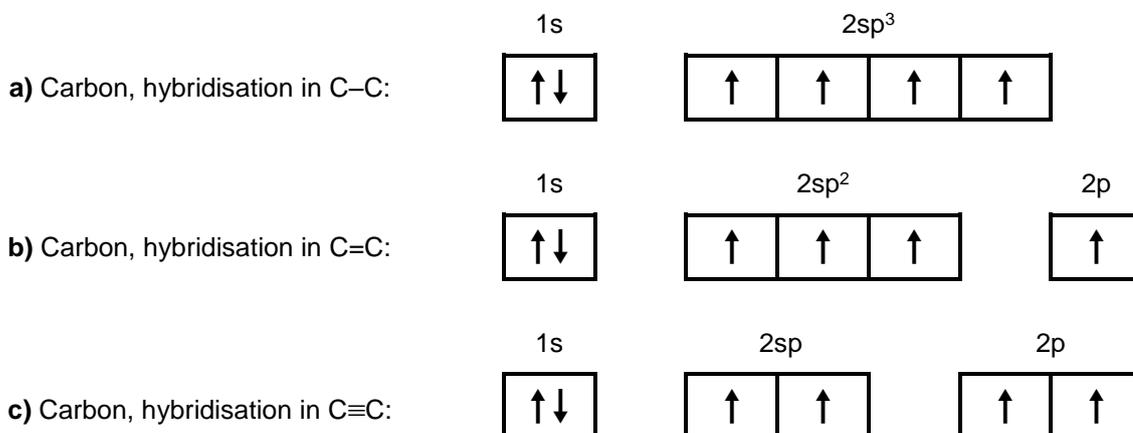
(Answers on page 22).

Answers to Questions

Question 1:

Hexa-1,2,4,5-tetraene.

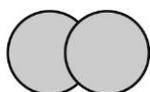
Question 2:



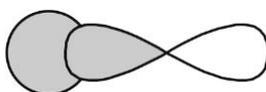
Question 3:

A σ -bond (called a *sigma-bond*) could be formed by either the overlap of two s-orbitals, the overlap of an s-orbital and a p-orbital, or the overlap of two p-orbitals. The region of orbital overlap and the nuclei of the two bonding atoms all exist on the same single straight line.

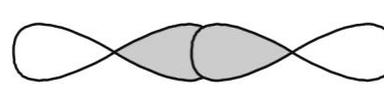
Various ways in which σ -bonds can be formed:



Overlap of two s-orbitals.



Overlap of an s-orbital and a p-orbital.

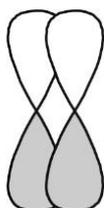


Overlap of two p-orbitals.

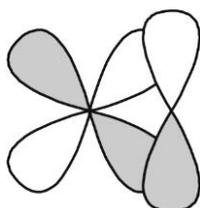
Question 4:

A π -bond (called a *pi-bond*) is most commonly formed when two p-orbitals overlap. The two p-orbitals must be arranged *parallel* to each other. As a consequence, the p-orbitals overlap in *two separate regions*, on opposite sides of a single straight line that connects the nuclei of the two bonding atoms.

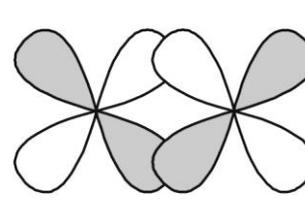
Various ways in which π -bonds can be formed:



Overlap of two p-orbitals.



Overlap of a d-orbital and a p-orbital.

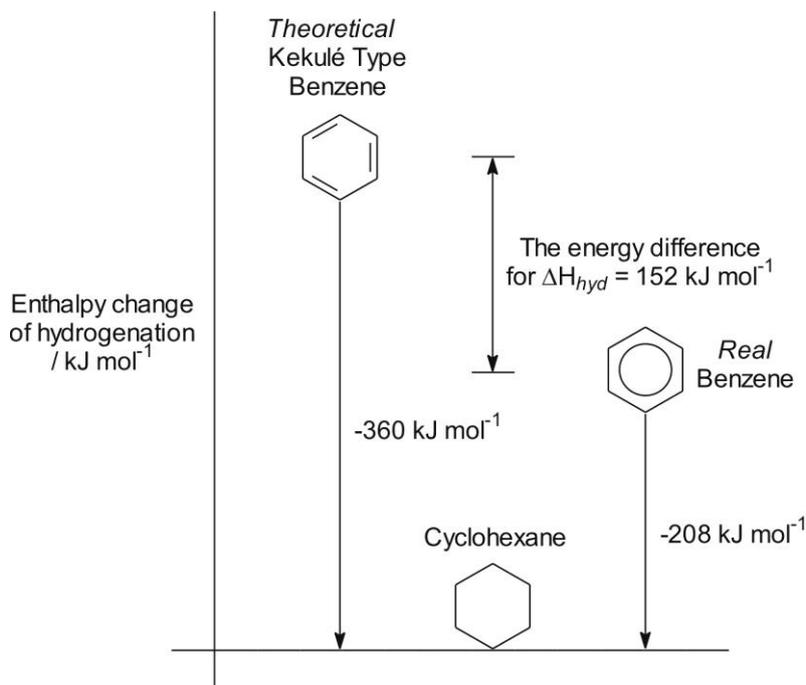


Overlap of two d-orbitals.

Question 5.

The enthalpy change of hydrogenation for the *theoretical* Kekulé type benzene = $3 \times (-120) = \underline{-360 \text{ kJ mol}^{-1}}$

Question 6:



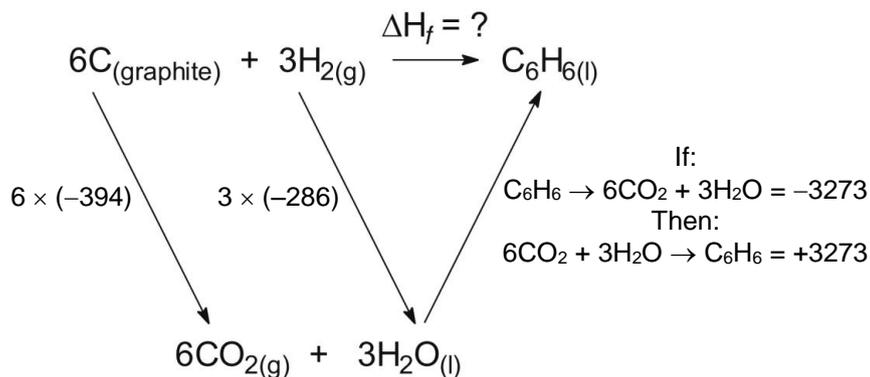
The enthalpy change of hydrogenation for the *theoretical* Kekulé type benzene = -360 kJ mol^{-1} .

The enthalpy change of hydrogenation for *real* benzene = -208 kJ mol^{-1} .

$$(-208) - (-360) = \underline{152 \text{ kJ mol}^{-1}}$$

The difference between these energy values is 152 kJ mol^{-1} . Due to its delocalised electron system, *real* benzene is 152 kJ mol^{-1} more stable than expected. The stability that is conferred on benzene by its delocalised electron system is known as *resonance energy*.

Question 7:

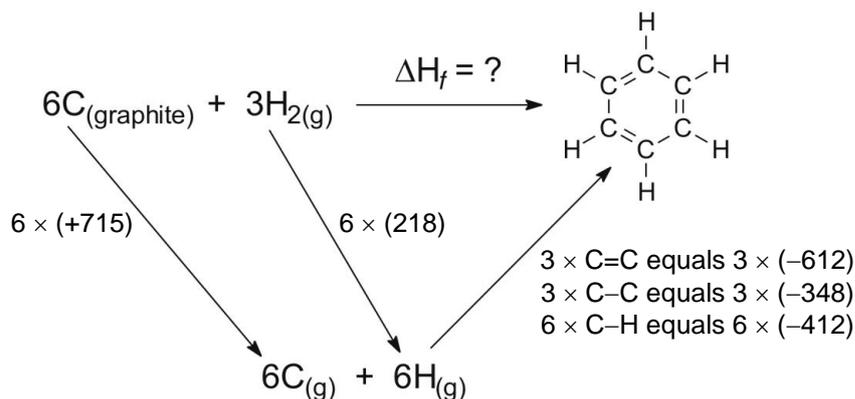


Adding up the figures gives:

$$[6 \times (-394)] + [3 \times (-286)] + 3273 = \Delta H_f \text{ benzene}$$

$$(-2364) + (-858) + 3273 = \Delta H_f \text{ benzene}$$

$$\Delta H_f \text{ Benzene} = \underline{+51 \text{ kJ mol}^{-1}} \text{ (compared with the data book value of } +49 \text{ kJ mol}^{-1}\text{).}$$

Question 8:

Remember that the enthalpy change for atomisation is *endothermic* (+ ΔH) and that bond formation is *exothermic* (- ΔH).

Adding up the figures gives:

$$[6 \times (+715)] + [6 \times (+218)] + [3 \times (-612)] + [3 \times (-348)] + [6 \times (-412)] = \Delta H_f \text{ benzene}$$

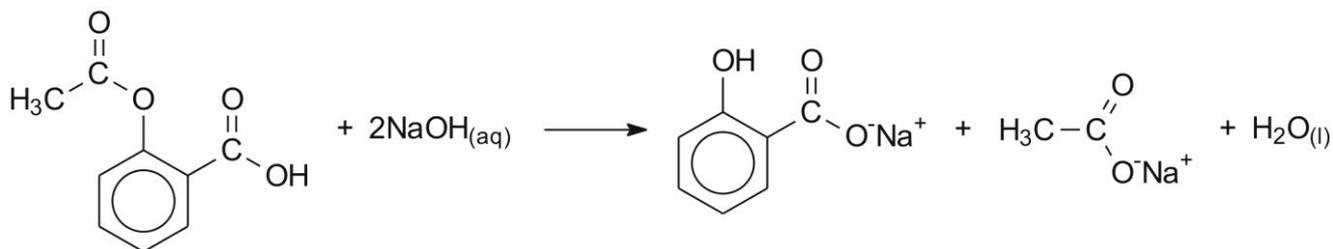
$$4290 + 1308 + (-1836) + (-1044) + (-2472) = \Delta H_f \text{ benzene}$$

$$\Delta H_f \text{ Benzene} = +246 \text{ kJ mol}^{-1}$$

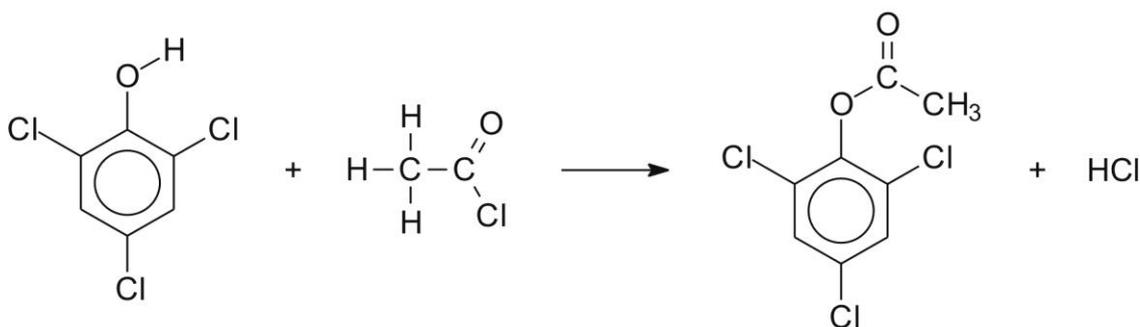
Comparing the answers to **Question 7** (ΔH_f *real* benzene) and **Question 8** (ΔH_f *theoretical* Kekulé type benzene) demonstrates that *real* benzene is more stable than expected.

Question 9:

Acceptable answers should include generalisations about models, *i.e.* models facilitate testing and prediction. Models can be physical, conceptual or mathematical. Models have limitations.

Question 10:

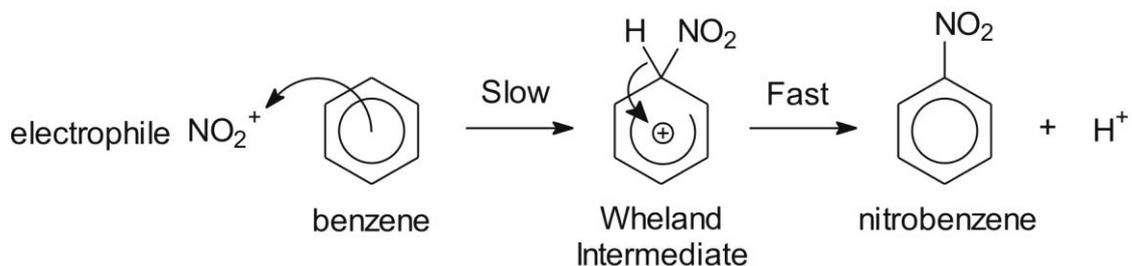
aspirin + sodium hydroxide → 2-hydroxy sodium benzoate + sodium ethanoate + water

Question 11:

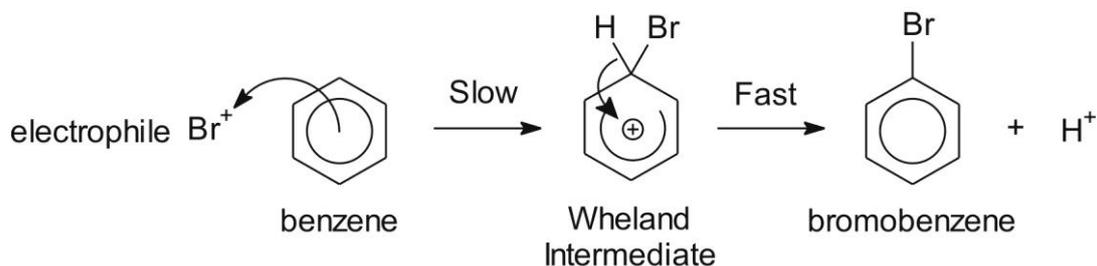
2,4,6-trichlorophenol + ethanoyl chloride → 2,4,6-trichlorophenyl ethanoate + hydrogen chloride

Question 12:

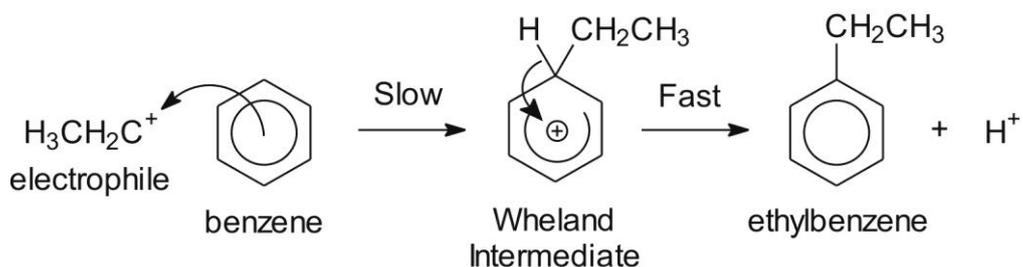
Benzene (b.p. = 80.1°C) will be the distillate while nitrobenzene (b.p. = 211°C) will be the residue. During the distillation, the thermometer will have a temperature reading of 80.1°C.

Question 13:**Question 14:**

The bromine is the Lewis base (electron pair donor).
The iron(III) bromide is the Lewis acid (electron pair acceptor).

Question 15:**Question 16:**

The chloroethane is the Lewis base (electron pair donor).
The aluminium chloride is the Lewis acid (electron pair acceptor).

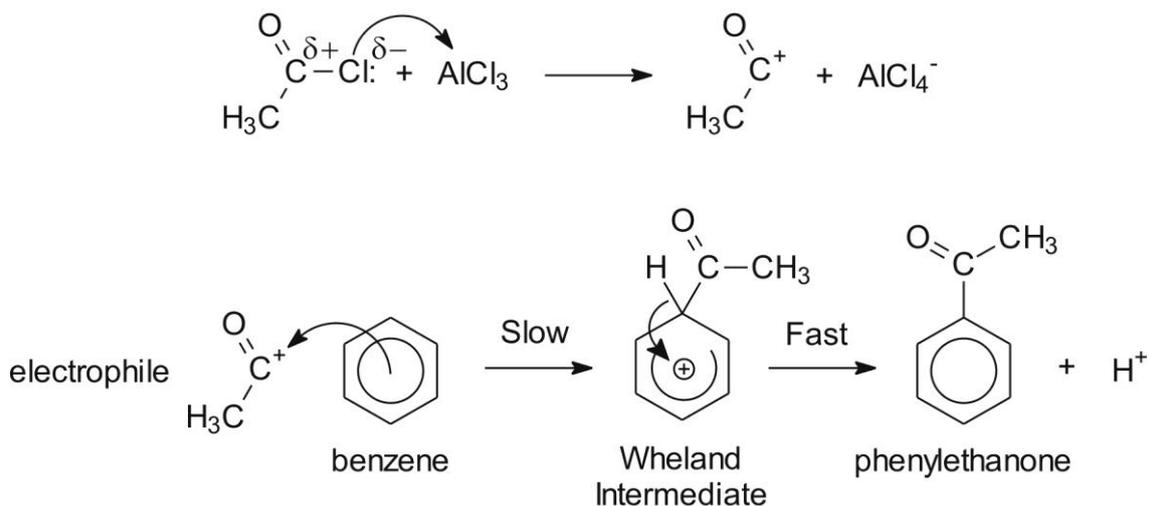
Question 17:

Question 18:

Ethylbenzene will have a higher boiling point than methylbenzene. This is due to ethylbenzene's greater relative molecular mass and greater surface area over which *van der Waals* intermolecular forces of attraction can operate. The actual boiling point of ethylbenzene = 136°C.

Answer to Question – Assessment of Learning

Question 1:



Question 2:

