Tuesday 11 June 2019 – Afternoon

A Level Chemistry B (Salters)

H433/02 Scientific literacy in chemistry

Time allowed: 2 hours 15 minutes

You must have:
- the Insert (inserted)
- the Data Sheet for Chemistry B (Salters) (sent with general stationery)

You may use:
- a scientific or graphical calculator

Please write clearly in black ink. **Do not write in the barcodes.**

Centre number						Candidate number				

First name(s) ____________________

Last name ____________________

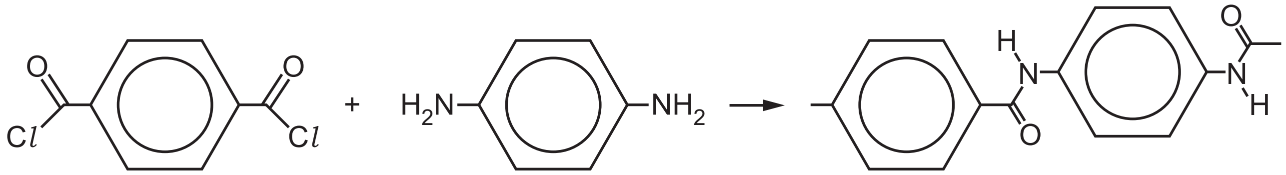
INSTRUCTIONS
- The Insert will be found inside this document.
- Use black ink. You may use an HB pencil for graphs and diagrams.
- Answer **all** the questions.
- Where appropriate, your answers should be supported with working. Marks may be given for a correct method even if the answer is incorrect.
- Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.

INFORMATION
- The total mark for this paper is **100**.
- The marks for each question are shown in brackets **[ ]**.
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **20** pages.

Answer **all** the questions.

1 Twaron™ is a polymer used to make body armour.

The polymer strands are made using the reaction in **Fig. 1.1**.



compound **A** compound **B** polymer strand of Twaron

Fig. 1.1

(a) Name the **functional groups** in compounds **A** and **B**.

A ....

B .... **[2]**

(b) Suggest the $O{=}\hat{C}{-}Cl$ bond angle in compound **A**.

Explain your answer.

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.... **[3]**

(c) Compound **A** can be made by the reaction in **Fig. 1.2**.

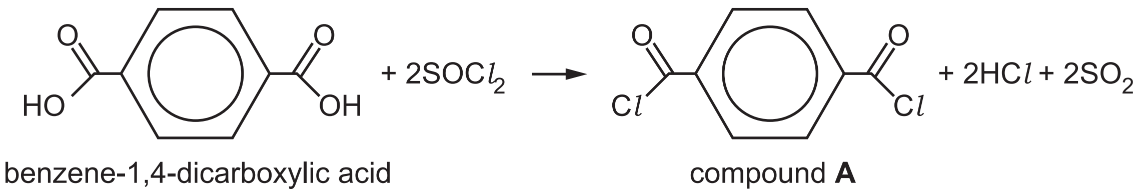


Fig. 1.2

Calculate the mass of compound **A** that can be made from 32 g of benzene-1,4-dicarboxylic acid if the yield is 67%.

Give your answer to the nearest whole number.

mass of compound **A** = ... g **[2]**

(d) A synthetic route for making compound **B** is shown in **Fig. 1.3**.

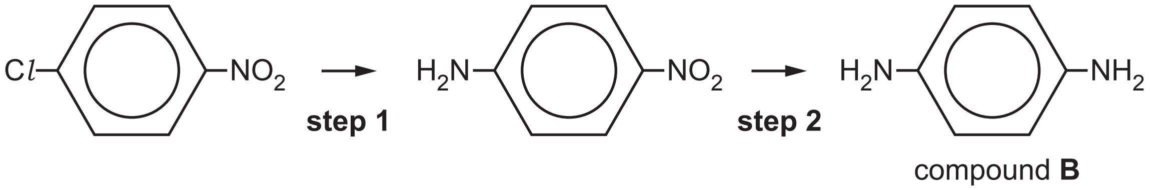


Fig. 1.3

Use your chemical knowledge and the Data Sheet to suggest possible reagents for **steps 1** and **2**.

Step 1 ....

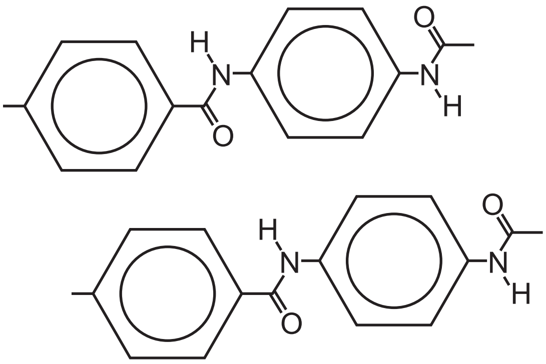
Step 2 ....
[2]

(e) The polymer strands link together by intermolecular bonds when they are spun to form Twaron. This gives the fabric its tough quality.

(i) Name the strongest intermolecular bonds that can form between the chains.

.... **[1]**

(ii) Mark the positions of the intermolecular bonds by drawing dotted lines on the diagram below.



[1]

(f) A Twaron polymer strand is hydrolysed.

(i) State the conditions that could be used to hydrolyse the polymer.

.... **[1]**

(ii) Draw the formulae of the **two** organic products of hydrolysis in the boxes.

[2]

2 Strontium carbonate is used in fireworks to colour the flames red.

(a) The red colour comes from lines of specific frequency in the atomic emission spectrum of strontium.

Explain how these lines are formed.

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....

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....

.... **[3]**

(b) Strontium carbonate decomposes to give strontium oxide when heated.

$SrCO_3 \rightarrow SrO + CO_2$

(i) 12.0 g of $SrCO_3$ are heated.

Calculate the volume of CO_2 (in cm^3) that would be collected at 290 K and 155 kPa.

Give your answer to an **appropriate** number of significant figures.

volume of CO_2 = ... cm^3 **[4]**

(ii) A student says 'Strontium ions are larger than calcium ions, so the attraction to carbonate ions is weaker. This means that strontium carbonate has a lower thermal stability than calcium carbonate.'

Discuss the student's statement, giving the correct chemistry where necessary.

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.... **[4]**

(c) A sample of strontium metal has the isotopic composition shown in the table.

Mass number	84	86	87	88
Abundance / %	0.56	9.86	7.00	82.58

(i) How many neutrons are there in an atom of ^{84}Sr?

number of neutrons = ... **[1]**

(ii) Use the data to calculate the relative atomic mass of the strontium sample.

Give your answer to **2** decimal places.

relative atomic mass = ... **[2]**

(d)* Strontium oxide reacts with water to form strontium hydroxide, $Sr(OH)_2$.

The solubility of strontium hydroxide in water at room temperature is around 10 g dm^{-3}.

A student is given a saturated solution of strontium hydroxide, normal titration equipment and a variety of different concentrations of hydrochloric acid.

The student wishes to find an accurate value for the concentration of the solution in mol dm^{-3}.

Describe in full a suitable procedure and indicate how the result would be calculated. **[6]**

Additional answer space if required

(e) **(i)** Write the equation for the equilibrium that occurs between solid strontium hydroxide and its ions in solution.

Use your equation to write the expression for the solubility product of strontium hydroxide.

Equation with state symbols:

Ksp = **[2]**

(ii) At 0 °C, the solubility of strontium hydroxide in water is 3.4×10^{-2} mol dm^{-3}.

Calculate the solubility product of strontium hydroxide at this temperature.

Give the units in your answer.

solubility product = ... units ....**[3]**

(iii) Explain how the solubility of strontium hydroxide in aqueous NaOH at 0 °C compares with 3.4×10^{-2} mol dm^{-3}.

Use the idea of solubility product in your answer.

....

....

.... **[2]**

(f) The melting point of strontium is higher than the melting point of rubidium.

(i) To which block of the Periodic Table do these elements belong?

.... **[1]**

(ii) Explain the difference in melting point.

....

....

....

....

.... **[2]**

3 Chlorine is made by electrolysing sodium chloride solution.

Sodium chlorate(V) is made by letting the chlorine react with the hydroxide ions that are also produced.

(a) When chlorine reacts with hot hydroxide ions, part of the chlorine is oxidised to chlorate(V) and the rest of the chlorine is reduced to chloride.

Use oxidation states to balance the equation for the reaction.

$$\ldots\ldots Cl_2 + \ldots\ldots OH^- \longrightarrow \ldots\ldots ClO_3^- + \ldots\ldots Cl^- + \ldots\ldots H_2O$$ **[2]**

(b) ClO_2 can be made by reacting ClO_3^- with concentrated hydrochloric acid.

$2ClO_3^- + 4H^+ + 2Cl^- \rightleftharpoons 2ClO_2 + 2H_2O + Cl_2$ **Equation 3.1**

ClO_2 is used for water purification and for bleaching the pulp used to make paper.

Table 3.1 shows some electrode potential data.

Half-reaction	$E^\ominus$/V
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$ClO_3^-(aq) + 2H^+(aq) + e^- \rightleftharpoons ClO_2(aq) + H_2O(l)$	+1.15
$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36

Table 3.1

(i) The forward reaction in **equation 3.1** does **not** occur under standard conditions.

Use data from **Table 3.1** to explain why.

....

....

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.... **[2]**

(ii) Suggest why the forward reaction in **equation 3.1 does** occur in the presence of concentrated hydrochloric acid.

....

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.... **[2]**

(c) A student investigates the reactions of some halogen compounds using the data in **Table 3.1**.

Half-reaction	***E*⊖/V**
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$ClO_3^-(aq) + 2H^+(aq) + e^- \rightleftharpoons ClO_2(aq) + H_2O(l)$	+1.15
$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36

Table 3.1

(i) The student uses a $Cu^{2+}(aq)/Cu(s)$ half-cell to confirm the $E^\ominus$ of a $Cl_2(aq)/Cl^-(aq)$ half-cell.

Complete and label the diagram of the apparatus the student would set up.

Show state symbols.

Indicate how standard conditions are achieved.

[4]

(ii) Give the value of $E^\ominus_{cell}$ for the cell in **(c)(i)**.

$E^\ominus_{cell}$ = ... V **[1]**

(iii) State where the electrons move and which way they are moving when the cell delivers a current.

....

.... **[1]**

(iv) A standard hydrogen electrode is used to measure $E^{\ominus}$ values, such as those in **Table 3.1**.

Give the half-cell reaction that occurs at a hydrogen electrode.

Show state symbols.

[1]

(v) The E value for the copper electrode at 298 K varies with the concentration of copper ions. The equation for this is shown below.

$E = E^{\ominus} + 0.0128\ ln\ [Cu^{2+}]$

Calculate the E value for a copper electrode where $[Cu^{2+}] = 0.010\ mol\ dm^{-3}$.

E = ... V **[2]**

(d) From data in **Table 3.1**, the student knows that chlorine reacts with iodide ions in aqueous solution.

(i) Write an equation for the reaction that occurs.

[1]

(ii) **Name** the reducing agent in your reaction in **(d)(i)**.

.... **[1]**

(iii) What will be **seen** when the reaction in **(d)(i)** occurs?

.... **[1]**

(iv) Explain, in terms of electrons, why chlorine is more reactive than iodine.

....

....

.... **[1]**

(e) The student uses a simple apparatus to prepare a test-tube full of hydrogen chloride gas in the laboratory.

Draw a diagram of an apparatus the student could use, labelling the reactants.

[2]

4 Dinitrogen pentoxide, N_2O_5 is an oxide of nitrogen that is formed in the stratosphere by reactions such as those shown below.

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \rightleftharpoons N_2O_5$$

The dinitrogen pentoxide acts as a 'sink' for NO_2, stopping it breaking down ozone.

(a) A student says that oxides of nitrogen catalyse the breakdown of ozone in the stratosphere by the reactions shown below.

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$O_3 + NO_3 \rightarrow NO_2 + 2O_2$$

Discuss the student's choice of reactions, giving the correct chemistry if necessary.

....

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.... **[2]**

(b) In the troposphere, dinitrogen pentoxide decomposes as shown below.

$2N_2O_5 \rightarrow 4NO_2 + O_2$ **Equation 4.1**

The table shows how the concentration of $2N_2O_5$ varies with time at 315 K.

Time / s	**$[N_2O_5]$ / mol dm^{-3}**
0	0.330
1000	0.210
2000	0.124
3000	0.078
4000	0.048

(i) Use the data in the table to plot a graph to determine the half-life for the reaction. Label the axes.

half-life = ... s **[4]**

(ii) How does the graph show that the reaction in **equation 4.1** is first order with respect to N_2O_5?

Draw construction lines on the graph to explain your answer.

.... **[1]**

(c) The gradient of the graph at 1000 s is 9.8×10^{-5} mol dm^{-3} s^{-1}.

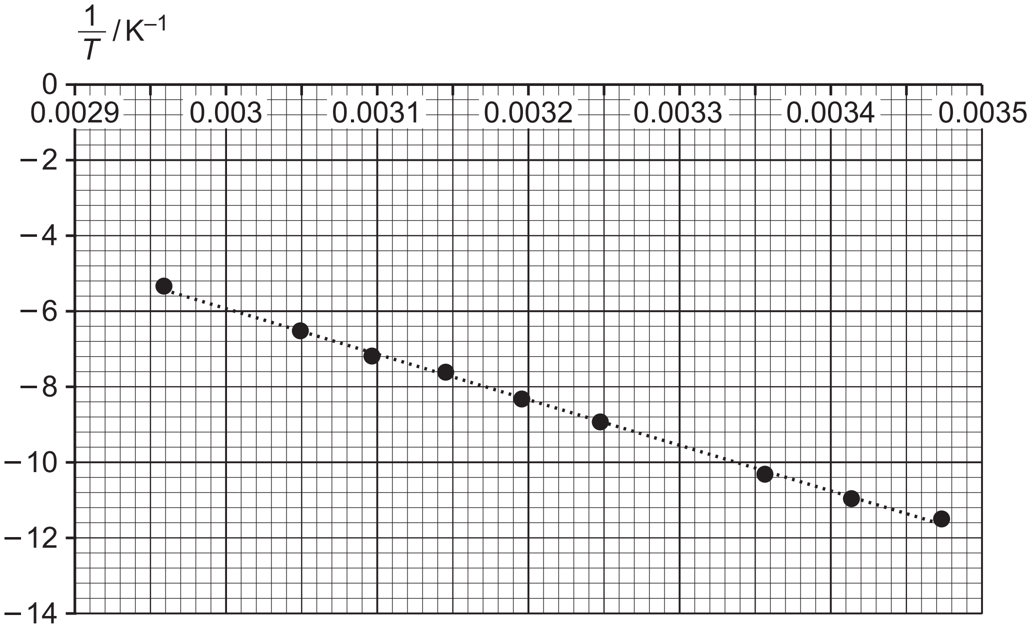
Work out the rate constant for the reaction in **equation 4.1** at 315 K.

Give the units in your answer.

rate constant = ... units .... **[2]**

(d) The reaction in **equation 4.1** was repeated with a fixed concentration of N_2O_5 at different temperatures.

A graph of *l*n k against $\frac{1}{T}$ for the reaction in **equation 4.1** is given below.



Use the graph to work out a value for the activation enthalpy (in kJ mol^{-1}) for the reaction.

E_a = ... kJ mol^{-1} **[3]**

$2N_2O_5 \rightarrow 4NO_2 + O_2$ **Equation 4.1**

(e) A student suggests the following mechanism for the reaction in **equation 4.1**.
The reaction is first order with respect to N_2O_5.

$N_2O_5 \rightarrow NO_2 + NO_3$ **step 1**
$NO_3 \rightarrow O_2 + NO$ **step 2**
$NO + N_2O_5 \rightarrow 3NO_2$ **step 3**

Show that this is a possible mechanism.

Consider which step(s) could be rate-determining.

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.... **[3]**

5 This question refers to the Advance Notice Article ‘Clearing the air around smoke formation’ that is included as an insert in this paper.

(a) The enthalpy change of combustion of acetylene, C_2H_2, can be calculated using enthalpy changes of formation.

Draw the Hess cycle that shows this, giving formulae and state symbols.

Label the enthalpy changes of formation and show how they can be combined to give the enthalpy change of combustion.

You do not need to give ΔH values.

[3]

(b) The Article refers to a ‘back-of-the-envelope’ calculation. This shows that the number of acetylene molecules combusting is approximately 1.4 times greater than the number of ethane molecules in the same volume of air/fuel mixture.

Use a similar calculation for **propane**.

Calculate how many more acetylene molecules combust in air in a given volume of air/fuel mixture compared with propane.

(Assume air contains 20% oxygen by volume.)

Number of acetylene molecules combusting is approximately .... times greater than the number of propane molecules in the same volume. **[4]**

(c) In an sp^2 hybrid carbon atom, one s orbital joins with two p orbitals to form three 'hybrid' sp^2 orbitals of the same energy. This leaves one other p orbital of a similar energy containing one electron.

(i) Explain why the remaining p orbital contains one electron.

....

....

....

.... **[2]**

(ii) State what happens to these single p electrons in the structures of ethene and naphthalene.

ethene ....

naphthalene ....
[2]

(d) **Fig. 2** in the Article shows the formation of naphthalene from benzene.

Suggest the first step in the formation of a larger PAH from naphthalene.

....

.... **[1]**

(e) The equation $C_4H_{10} + M \rightarrow C_3H_7 + CH_3 + M$, is given in the Article. M is a molecule.

(i) Classify this reaction as *initiation*, *propagation* or *termination* with a reason.

....

.... **[1]**

(ii) Suggest a reason for the involvement of the molecule M.

....

.... **[1]**

(f)* Oxygen is involved in the formation of soot in the flame of a burning hydrocarbon.

Discuss the role of oxygen in controlling the flame temperature, causing small molecule reactions and providing competing routes.

Illustrate your answer with equations where appropriate. **[6]**

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Additional answer space if required

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END OF QUESTION PAPER

ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

OCR
Oxford Cambridge and RSA

Tuesday 11 June 2019 – Afternoon

A Level Chemistry B (Salters)

H433/02 Scientific literacy in chemistry

Insert

Time allowed: 2 hours 15 minutes

INSTRUCTIONS
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- Please contact OCR Copyright should you wish to re-use this document.

INFORMATION
- This Insert contains the Advance Notice.
- This document consists of **4** pages.

Turn over

Clearing the air around smoke formation

Adapted from an article in Education in Chemistry March 2017 by Declan Fleming

Why do unsaturated hydrocarbons burn in such a distinctive way compared to their saturated counterparts? It's a simple enough question, and with the smoky flame test sitting alongside the bromine water test for unsaturation on many chemistry courses, you'd think there would be a simple answer. Unsaturated hydrocarbons can prove more complicated.

Getting to the heat of the matter

Take the flame temperatures for example. In terms of hydrocarbon fuels, the oxygen acetylene flame can't be beaten, with a flame temperature of around 3500 °C. Using air (rather than pure oxygen) as the oxidiser, acetylene can burn around 2500 °C, while its saturated cousin ethane can't even reach 2000 °C. A teacher might suggest a student investigates the relevant Hess cycles. However, using enthalpy of formation values, a predicted enthalpy of combustion (without condensing the water in the flame) for acetylene would be $-1257\,\text{kJ}\,\text{mol}^{-1}$ but ethane's would be $-1428\,\text{kJ}\,\text{mol}^{-1}$.

Clearly then, calorimetry alone doesn't explain the differences in flame temperatures. To answer this conundrum the other molecules present need to be considered (see equations 1 and 2). It's a great example of Avogadro's law in action – the same volumes of gases at equal temperatures and pressures must contain the same numbers of particles – and this comes at a cost for ethane.

$C_2H_2 + 2.5O_2 \rightarrow 2CO_2 + H_2O$
(equation 1)

$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$
(equation 2)

Imagine these reactions taking place in two equally-sized boxes containing stoichiometric mixtures. Because extra oxygen molecules are needed to combust the ethane, and it is necessary to keep the pressures the same, there is less space in the 'box' for molecules of ethane themselves. The mole fraction of fuel in the box is therefore higher for acetylene – a back-of-the-envelope calculation for a stoichiometric mix in air shows the number of acetylene molecules combusting is approximately 1.4 times greater than the number of ethane molecules in the same volume.

So, the combustion reaction equations don't explain the flame temperature differences, but might they help us explain why the acetylene flame is sootier? Again, the answer is no. The equations show that ethane requires more, not less oxygen than acetylene to completely combust and therefore incomplete combustion (that typically produces a sooty flame) should be more likely in ethane if it was just a matter of getting the oxygen to where it's needed.

Working backwards

Naturally at the high temperatures inside a flame, activation energy barriers become less of a hindrance than they are closer to room temperature, and many alternative reaction pathways open up. To explain why unsaturated hydrocarbons burn with a sootier flame than their saturated cousins, we need to start at soot and work backwards to determine which reaction pathways are important here.

Although the composition of soot varies significantly depending on its source, it typically consists of approximately 50 nm particles. When produced in high enough quantities, in a small enough space, these aggregate together to make particulates of varying sizes – some large enough to be visible to the naked eye. These particles are mostly graphitic in nature, made up of sheet-like carbon structures that vary widely in architecture from highly crystalline to highly amorphous.

To make one of these soot particles, the first step is to construct a planar, graphene-like layer of carbon. The similarities between this sp^2-hybridised carbon sheet and a smaller polyaromatic structure such as that of naphthalene are clear (Fig. 1).

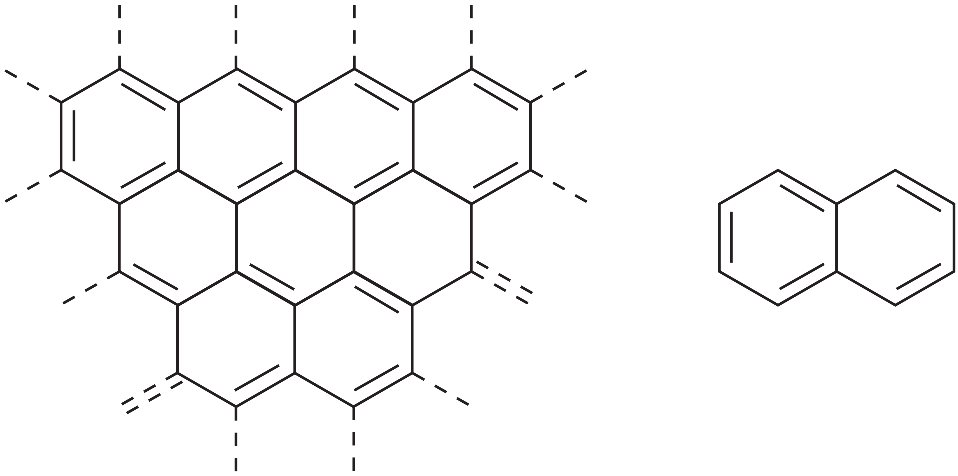

Fig. 1: Structures of graphene (left) and naphthalene (right)

Structures of this type are so important to the study of soot that they have been given their own name: polycyclic aromatic hydrocarbons (PAHs). To make soot it is necessary to rapidly create and grow PAHs.

There are two key ingredients needed to grow a PAH: hydrogen atoms and plenty of acetylene. The mechanism of the conversion of a small molecule like naphthalene to an extensive graphite-like structure is known as hydrogen-abstraction-C_2H_2-addition, or HACA for short.

The first step to forming a new PAH ring is the abstraction of a hydrogen atom from a benzene ring. An acetylene molecule then adds at this site, to make a two-carbon long side chain. A further HACA reaction onto the end of this chain grows the unsaturated side group to four carbons long. This chain then wraps around to form another aromatic ring and build up the PAH (see Fig. 2).

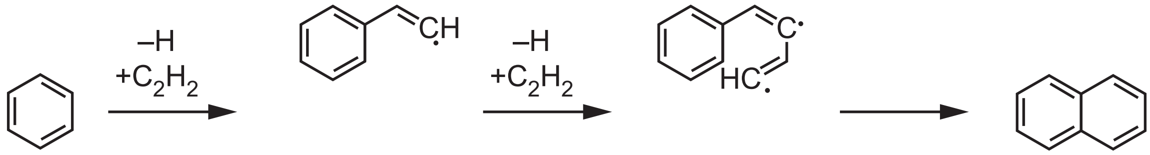

Fig. 2: The mechanism of PAH growth

Two key components explain the success of this growth pathway: thermodynamically stable intermediates and a kinetic lever which pushes the reaction forward from each of these stable intermediates.

The stable intermediates are themselves PAHs, each populated with relatively strong carbon-carbon sp^2-hybridised covalent bonds with the extra stability afforded by aromatic numbers of p electrons. Numerous intermediates have been identified and studied so far. The reactions proceed like ratchet mechanisms – ensuring that once formed, each intermediate is difficult to break down, preventing the reverse reaction taking place.

This stability is however somewhat balanced by the entropic disfavourability of producing one large molecule from many small ones. A swell of hydrogen atoms is necessary to overcome the thermodynamic brake applied to the growth of the PAH. These hydrogens abstract other hydrogen atoms from the thermodynamically stable growing structure and push the reaction onwards.

Thankfully they are in plentiful supply with numerous ‘small molecule’ reactions, such as $CH + O \rightarrow CO + H$ and $CH_2 + O_2 \rightarrow CO_2 + 2H$, providing a pool of hydrogen atoms. Many of these small molecule reactions require oxygen. Because soot is typically attributed to a lack of oxygen, it’s surprising to realise that oxygen is so important to the reactions that form it.

You can think of complete combustion versus incomplete combustion as the outcome of a race between soot formation and the formation of CO_2, rather than being due to an overall deficiency of oxygen. Looking at the mechanism of how PAHs grow it is clear how the presence of acetylene in a flame dramatically favours the formation of soot, by providing a competing reaction pathway to the traditional oxidation route to CO_2. If you burn acetylene itself, the fates of the carbon atoms within it are all but sealed.

What about other fuels?

But what about fuels other than acetylene, how do they produce smoke? It turns out acetylene must be produced in any flame for the PAH growth process that produces soot to start. And the closer the starting ingredient’s structure is to that of acetylene (for example if it contains double or triple bonds) the more dominant that reaction will be, and therefore the more soot will be produced. In the case of saturated fuels the oxidation route to CO_2 will dominate instead, but some soot may still be produced under the right conditions.

Let’s look, for example, at how soot forms when burning the saturated molecule butane. A typical first step in hydrocarbon combustion involves the formation of a radical by homolytic fission of a C−C bond, as it is weaker than a C−H bond. An example reaction is $C_4H_{10} + M \rightarrow C_3H_7 + CH_3 + M$, where M is another colliding molecule involved in the reaction (usually nitrogen).

In the second step the C_3H_7 radical decays to form an alkene. Ethene can react on to form acetylene itself, e.g. $C_2H_4 + H \rightarrow C_2H_3 + H_2$ followed by H-abstraction: $C_2H_3 \rightarrow C_2H_2 + H$.

It’s easy to see that all these additional steps make the production of soot much less favourable for butane than acetylene.

So we’ve finished at the start. Why do unsaturated molecules have a predisposition to produce smoky flames? Because the soot itself is unsaturated and is formed from small molecules that are unsaturated too. Molecules that will be produced in any flame, but if already present in large quantities to begin with, can give the competing soot-formation reaction a head start over the combustion reaction to give us our familiar yellow sooty flame.
