Paper 3 Section A Data Response (4) with worked answers

At 25 °C iron pentacarbonyl, $Fe(CO)_5$, is a, straw-coloured liquid with a pungent odour. It can react with chlorine to give $Fe(CO)_4Cl_2$.

One of the uses of iron pentacarbonyl is to make nanotubes. When $Fe(CO)_5$ is heated at 1400 K in the presence of carbon monoxide at high pressure it reacts to form nanoparticles of iron.

$Fe(CO)_5(g) \longrightarrow Fe(s) + 5CO(g)$

These iron nanoparticles provide a nucleation surface for the transformation of carbon monoxide into carbon during the growth of the nanotubes (CNT).

$xCO(g) \longrightarrow CNT(s) + \frac{1}{2}xCO_2(g)$

where *x* is typically 6000 giving a carbon nanotube containing 3000 carbon atoms.

(a) Comment on the fact that iron pentacarbonyl is a liquid under standard conditions (its melting point is - 21 °C and its boiling point is 103 °C). ***[1]***

Even though the M_r for $Fe(CO)_5$ is quite high (195.9), the fact that the melting point is quite low suggests that the molecule is non-polar. ***[1]***

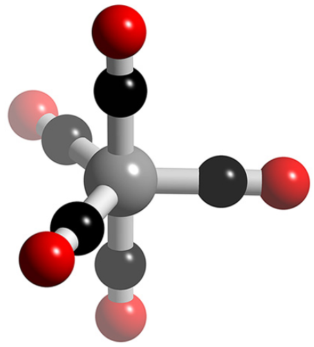
(The attractive forces between the non-polar $Fe(CO)_5$ molecules are therefore weak London (dispersion forces) so little energy is required to overcome these attractive forces resulting in a low melting point. The boiling point is above room temperature as the molecules do have considerable mass/electrons which does increase the London (dispersion) forces.

Underlying chemistry concepts can be found in 4.4 Intermolecular forces.)

(b) Deduce the geometric shape of a molecule of iron pentacarbonyl. ***[1]***

There are five bonding pairs and no non-bonding pairs so the shape is the regular shape for five electron domains - trigonal bipyramid. ***[1]***

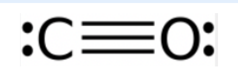
(Since $Fe(CO)_5$ is non-polar it must have a symmetrical shape with no non-bonding pairs of electrons around the central iron atom (if there were it would be octahedral and polar). Although each CO ligand is polar, when the five ligands are arranged in a trigonal bipyramid shape the resultant dipole is zero.



Fe(CO)$_5$ - trigonal bipyramid

(Underlying chemistry concepts can be found in 14.1 Further aspects of covalent bonding.)

(c) (i) Draw the Lewis structure of carbon monoxide. ***[1]***



[1]

(Carbon monoxide contains a coordinate bond as the two electrons in one of the triple bond pairs originate from the oxygen atom.)

(Underlying chemistry concepts can be found in 4.2 Covalent bonding.)

(ii) Use the concept of formal charge to explain why iron bonds to the carbon atom of the carbon monoxide molecules rather than the oxygen atom. ***[2]***

The formal charge on the C atom = 4 - 2 - (½ x 6) = – 1
and the formal charge on the O atom = 6 -2 - (½ x 6) = + 1 ***[1]***

Since the negative formal charge is on the carbon atom it is this non-bonding pair that forms a coordinate bond to the iron atom. ***[1]***

(Underlying chemistry concepts can be found in 14.1 Further aspects of covalent bonding.)

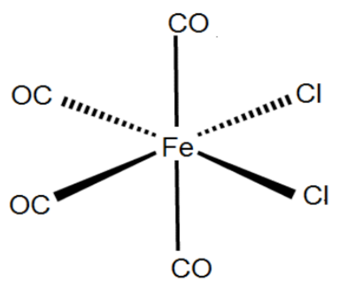
(d) (i) Use oxidation states to show whether iron pentacarbonyl is oxidized or reduced when it reacts with chlorine. ***[1]***

The oxidation state of Fe goes from 0 in $Fe(CO)_5$ to +2 in $Fe(CO)_4Cl_2$
The oxidation state of Cl goes from 0 in Cl_2 to – 1 in $Fe(CO)_4Cl_2$
Therefore this is a redox reaction in which the iron is oxidized from 0 to +2 and the chlorine is reduced from 0 to – 1. ***[1]***

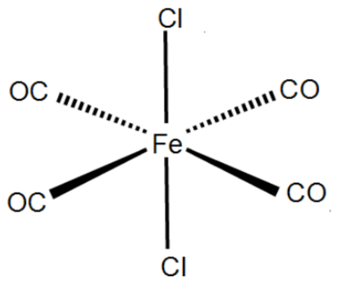
(Underlying chemistry concepts can be found in 9.1 Oxidation & reduction.)

(ii) Deduce all the possible structures for $Fe(CO)_4Cl_2$. ***[2]***

There are six ligands and no non-bonding pairs of electrons around the central iron ion so the geometric shape of the complex will be octahedral. ***[1]***
However there are two possibilities as it could exist as a cis- or trans- isomer. ***[1]***



cis-isomer



trans-isomer

(Underlying chemistry concepts can be found in 14.1 Further aspects of covalent bonding and 20.3 Stereoisomerism.)

(e) Assuming the carbon dioxide in the above process is lost to the atmosphere and the iron produced is discarded, calculate the atom economy of the reaction assuming it gives 100% yield of carbon nanotubes. ***[2]***

From the two equations $Fe(CO)_5(g) \rightarrow Fe(s) + 5CO(g)$ and $xCO(g) \rightarrow CNT(s) + \frac{1}{2}xCO_2(g)$, 1 mol of $Fe(CO)_5(g)$ produces 2.5 mol of CNT. ***[1]***

Assuming molar quantities
Mass of reactants = 55.85 + 5 x (12.01 + 16.00) = 195.90 g
Mass of desired product = 2.5 x 12.01 = 30.025 g
Atom economy = (30.025/195.90) x 100 = 15.3% ***[1]***

(Obviously if the iron and/or the carbon dioxide can be recycled then the atom economy would be much higher.

(Underlying chemistry concepts can be found in 1.3 Reacting masses and volumes.)
Strictly speaking this sub-topic talks about the importance of percentage yield in industrial processes but atom economy does appear in Option A : Materials (A.5 Polymers) and Option B : Biochemistry (B.6 Biochemistry & the environment) and Green chemistry is mentioned in Option D : Medicinal chemistry (D6 - Environmental impact of some medications).