Answer **all** the questions in the spaces provided.

For Examiner's Use

1 The elements carbon and silicon are both in Group IV of the Periodic Table.
Carbon is the second most abundant element by mass in the human body and silicon is the second most common element in the Earth's crust.

Carbon and silicon each form an oxide of general formula XO_2.
At room temperature, CO_2 is a gas while SiO_2 is a solid with a high melting point.

(a) Briefly explain, in terms of the chemical bonds and intermolecular forces present in **each** compound, why CO_2 is a gas and SiO_2 is a solid at room temperature.

....

....

....

.... [3]

(b) Draw a simple diagram to show the structure of SiO_2. Your diagram should contain at least **two** silicon atoms **and** show clearly how many bonds each atom forms.

[2]

CO_2 does not behave as an ideal gas.

For Examiner's Use

(c) **(i)** State the basic assumptions of the kinetic theory as applied to an ideal gas.

....

....

....

....

....

....

(ii) Suggest **one** reason why CO_2 does not behave as an ideal gas.

....

[5]

Carbon exists in a number of forms, one of which is a conductor of electricity and one of which is a non-conductor of electricity. Silicon is the main component of most semi-conductors.

(d) Graphite is the form of carbon that is a conductor of electricity. Give a simple explanation for this property.

....

.... [1]

When carbon and silicon(IV) oxide are heated together at about 2000 °C, silicon carbide, SiC, is formed. Silicon carbide is a hard material which is widely used as an abrasive and in ceramics.

(e) **(i)** Construct an equation for the reaction of carbon and silicon(IV) oxide.

....

(ii) SiC has a similar structure to one of the common forms of carbon.
Which form is this? Give a reason for your answer.

form ....

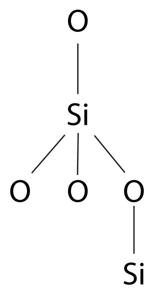
reason ....

[2]

[Total: 13]

1 **(a)** CO_2 is simple molecular/simple covalent/has discrete molecules (1)
CO_2 has induced dipole – induced dipole interactions/
van der Waals' forces/weak intermolecular forces (1)
SiO_2 is giant molecular/giant covalent/macromolecular (1)
SiO_2 has strong covalent bonds (1)
[any 3]

(b) minimum is 4-valent Si-O (1)
and at least one Si-O-Si (1)
i.e.



[2]

(c) **(i)** for an ideal gas, **any four** from the following
the molecules behave as rigid spheres (1)
there are no/negligible intermolecular forces
between the molecules (1)
collisions between the molecules are perfectly elastic (1)
the molecules have no/negligible volume (1)
the molecules move in random motion (1)
the molecules move in straight lines (1)
the kinetic energy of the molecules is
directly proportional to the temperature (1)
the pressure exerted by the gas is due to the collisions
between the gas molecules and the walls of the container (1)
not an ideal gas obeys $pV = nRT$
(max 4)

(ii) there are intermolecular forces between CO_2 molecules/
CO_2 molecules have volume (1) [5]

(d) graphite has delocalised electrons (1) [1]

(e) **(i)** $SiO_2 + 2C \rightarrow SiC + CO_2$ **or**
$SiO_2 + 3C \rightarrow SiC + 2CO$ (1)

(ii) diamond **because** SiC is hard (1) [2]

[Total: 13]

For Examiner's Use

(c) All the oxides of the elements in Group IV in their +4 oxidation state are high melting point solids except CO_2.

(i) Explain this observation by describing the bonding in CO_2, SiO_2 and SnO_2.

....

....

....

(ii) State the difference in the thermal stabilities of SnO_2 and PbO_2. Illustrate your answer with an equation.

....

....

CO_2 dissolves in water to form a weakly acidic solution containing the hydrogencarbonate ion.

(iii) Write an equation for the reaction of CO_2 with water, and write an expression for the equilibrium constant, K_c.

....

....

(iv) Explain the role of the hydrogencarbonate ion in controlling the pH of blood, illustrating your answer with relevant equations.

....

....

....

[7]

[Total: 15]

For Examiner's Use

3 The elements of Group IV all form tetrachlorides with the general formula MCl_4.

(a) Draw a diagram of a molecule of $SiCl_4$ stating bond angles.

[2]

(b) Describe and explain how the volatilities of the Group IV chlorides vary down the group.

....

....

.... [2]

(c) The relative stabilities of the M^{2+}(aq) and M^{4+}(aq) ions also vary down Group IV.

(i) Use the *Data Booklet* to illustrate this observation when *M* = Sn and *M* = Pb.

....

....

....

(ii) Use the *Data Booklet* to predict the products formed, and write equations for the reactions occurring, when

- an equimolar mixture of Sn^{2+}(aq) and Sn^{4+}(aq) is added to I_2(aq),

....

....

- an equimolar mixture of Pb^{2+}(aq) and Pb^{4+}(aq) is added to SO_2(aq).

....

....

[4]

(c) **(i)** CO_2: simple + molecular/covalent *or* weak intermolecular forces
SiO_2: giant/macro + molecular/covalent
SnO_2: ionic/electrovalent (ignore "giant") (all 3 correct) [2]
(2 correct = [1], 1 correct = [0])

(ii) SnO_2 is stable, PbO_2 is not *or* SnO_2 is the more stable [1]
$PbO_2 \longrightarrow PbO + ½ O_2$ [1]

(iii) $H_2O + CO_2$ (⇌) $H^+ + HCO_3$ [1]
$K_c = [H^+][HCO_3\ ]/[H_2O][CO_2]$ *or* = $[H^+][HCO_3\ ]/[CO_2]$ ecf [1]

(iv) $HCO_3\ + H^+ \longrightarrow H_2CO_3$ *or* $H_2O + CO_2$ (or equation with H_3O^+) [1]
$HCO_3\ + OH\ \longrightarrow CO_3^{2}\ + H_2O$ (NB **NOT** $H_2CO_3 + OH\ \rightarrow$) [1]

(words can substitute for one of the equations but not both. If two correct word descriptions are given, in the absence of at least one correct equation, award [1] mark only) **[8]**

[Total: 16 max 15]

3 **(a)** tetrahedral diagram (either dashed+wedge, or similar representation) [1]
angles (all) 109° – 110° [1]
(award [0] for part **(a)** if an angle of 90° or 180° is mentioned) **[2]**

(b) volatility decreases *or* boiling points increase
(allow b.pt. $CCl_4 > SiCl_4$ but b.pt. increases thereafter) [1]
due to greater van der Waals'/intermolecular forces *or* due to more electrons [1]
(mention of "ions" negates this mark) **[2]**

(c) **(i)** Pb^{4+}/Pb^{2+}: $E^{\ominus}$ = +1.69V, Sn^{4+}/Sn^{2+}: $E^{\ominus}$ = +0.15V, [both] [1]
a valid comment about relative redox power *or* stability, e.g.:
(hence) Sn^{2+} easily oxidised *or* Sn^{4+} is more stable than Sn^{2+} *or*
Pb^{4+} is easily reduced *or* Pb^{2+} is more stable than Pb^{4+} *or*
+2 oxidation state more stable down the group [1]

(ii) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I$ [1]
$Pb^{4+} + SO_2 + 2H_2O \longrightarrow 4H^+ + SO_4^{2}\ + Pb^{2+}$ [1]
(N.B. no marks in **(ii)** for $E^{\ominus}$ values) **[4]**

(d) **(i)** for Si: ΔH = 244 – 2(359) = **–474** (kJ mol ^{1}) [1]
for Sn: ΔH = 244 – 2(315) = **–386** (kJ mol ^{1}) [1]
(allow [1] out of [2] salvage mark for 474 & 386; 962 & 874; *or* –962 & –874)

(ii) Yes: the +4 state becomes decreasingly stable – the Δ*H* is less exothermic [1]
(mark is for relating Δ*H*s to stability: allow ecf from **d(i)** and also from **c(i)**) **[3]**

[Total: 11]

Section A

For Examiner's Use

Answer **all** questions in the spaces provided.

1 **(a)** The Group IV oxides CO_2 and SiO_2 differ widely in their physical properties. Describe these differences and explain them in terms of their structure and bonding.

....

....

....

.... [3]

(b) What are the properties of a *ceramic* material? Why is silicon(IV) oxide very suitable as a component of ceramics?

....

....

....

.... [2]

(c) Lead(II) oxide reacts with both acids and bases.

(i) What is the name given to oxides that have this property?

....

(ii) Write a balanced equation for the reaction between PbO and NaOH.

....

[2]

For Examiner's Use

(d) Tin forms an oxide, **A**, that contains the metal in both oxidation states II and IV. The formula of **A** can be found by the following method.

- A sample of **A** was dissolved in $H_2SO_4(aq)$, producing solution **B**, which was a mixture of tin(II) sulfate and tin(IV) sulfate.
- A 25.0 cm^3 sample of solution **B** was titrated with 0.0200 mol dm^{-3} $KMnO_4$. 13.5 cm^3 of $KMnO_4$ was required to reach the end-point.
- Another 25.0 cm^3 sample of solution **B** was stirred with an excess of powdered zinc. This converted all the tin into tin(II). The excess of zinc powder was filtered off and the filtrate was titrated with 0.0200 mol dm^{-3} $KMnO_4$, as before. This time 20.3 cm^3 of $KMnO_4$ was required to reach the end-point.

The equation for the reaction occurring during the titration is as follows.

$$2MnO_4^- + 16H^+ + 5Sn^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 5Sn^{4+}$$

(i) Write a balanced equation for the reaction between Zn and Sn^{4+}.

....

(ii) Use the *Data Booklet* to calculate the $E^\ominus$ values for the reactions between

- Zn and Sn^{4+}, ...
- MnO_4^- and Sn^{2+}.. ....

(iii) Use the results of the two titrations to calculate

- the number of moles of Sn^{2+} in the first titration sample,

....

....

- the number of moles of Sn^{2+} in the second titration sample.

....

....

(iv) Use the results of your calculation in **(iii)** to deduce the Sn^{2+}/ Sn^{4+} ratio in the oxide **A**, and hence suggest the formula of **A**.

....

....

....

[8]

(e) A major use of tin is to make 'tin plate', which is composed of thin sheets of mild steel electroplated with tin, for use in the manufacture of food and drinks cans. A tin coating of 1.0×10^{-5} m thickness is often used.

(i) Calculate the volume of tin needed to coat a sheet of steel 1.0 m × 1.0 m to this thickness, on one side only.

....

....

(ii) Calculate the number of moles of tin that this volume represents.
[The density of tin is 7.3 g cm^{-3}.]

....

....

....

(iii) The solution used for electroplating contains Sn^{2+} ions. Calculate the quantity of electricity in coulombs needed to deposit the amount of tin you calculated in **(ii)**.

....

....

....
[4]

[Total: 19]

1 **(a)** CO_2 is a gas (at room temperature); SiO_2 is a high melting solid [1]
CO_2: simple / discrete molecular / covalent [1]
SiO_2: giant covalent *or* macromolecular / giant molecular [1]
[3]

(b) (a substance that is..) hard, high melting, electrical insulator any two [1]
SiO_2 has **strong covalent** bonds (can be in **(a)**) [1]
[2]

(c) **(i)** amphoteric [1]

(ii) $2NaOH + PbO \longrightarrow Na_2PbO_2 + H_2O$ [1]
(*or* $NaOH + PbO + H_2O \longrightarrow NaPb(OH)_3$ etc.)
[2]

(d) **(i)** $Zn + Sn^{4+} \longrightarrow Zn^{2+} + Sn^{2+}$ [1]

(ii) $E^{\theta} = 0.15 - (-0.76) =$ **0.91** V [1]
$E^{\theta} = 1.52 - 0.15 =$ **1.37** V [1]

(iii) $n(Sn^{2+}) = 0.02 \times 13.5/1000 \times 5/2 =$ **6.75×10^{-4}** mol use of the 5/2 ratio [1]
correct rest of working [1]
$n(Sn^{2+}) = 0.02 \times 20.3/1000 \times 5/2 =$ **1.02×10^{-3}** mol [1]

(iv) $n(Sn^{4+}) = 1.02 \times 10^{3} - 6.75 \times 10^{4} = 3.45 \times 10^{4}$ mol [1]
$\therefore$ ratio = 6.75/3.45 = 1.96:1 $\approx$ **2:1**
$\therefore$ formula is $2SnO + SnO_2 \Rightarrow$ **Sn_3O_4** *(cond^l on calculation, but allow ecf)* [1]
[8]

(e) **(i)** volume = $1 \times 1 \times 1 \times 10^{5} = 1 \times 10^{5}$ m^3 *or* **10** cm^3 [1]

(ii) mass = vol × density = 10 × 7.3 = **73** g ecf [1]
moles = mass/A_r = 73/119 = **0.61** mol ecf [1]

(iii) Q = nFz = $0.61 \times 9.65 \times 10^4 \times 2 =$ **1.18 (1.2) × 10^5** coulombs ecf [1]
[4]

[Total: 19]

For Examiner's Use

4 The most typical oxides of tin and lead are SnO, SnO_2, PbO and PbO_2.

The following two generalisations can be made about the oxides of the elements in Group IV.

- As the metallic character of the elements increases down the Group, the oxides become more basic.
- The oxides of the elements in their higher oxidation states are more acidic than the oxides of the elements in their lower oxidation states.

(a) Use these generalisations to suggest which of the above oxides of tin or lead is **most likely** to react with each of the following reagents. In each case write a balanced equation for the reaction.

(i) with NaOH(aq)

formula of oxide ....

equation ....

(ii) with HC*l*(aq)

formula of oxide ....

equation ....

[4]

(b) 'Red lead' is used as a pigment, and as a metal primer paint to prevent the corrosion of steel. It is an oxide of lead that contains 9.30% oxygen by mass.

Calculate to **3 significant figures** the number of moles of oxygen and lead contained in a 100.0 g sample of red lead. Hence calculate its empirical formula.

empirical formula: .... [2]

For Examiner's Use

(c) Lead(II) chloride is slightly soluble in water.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = 2.0 \times 10^{-5}$$

(i) Write an expression for the solubility product, K_{sp} for lead(II) chloride and state its units.

K_{sp} = ... units ....

(ii) Calculate $[Pb^{2+}(aq)]$ in a saturated solution of $PbCl_2$.

....

....

An excess of $PbCl_2(s)$ is stirred with 0.50 mol dm^{-3} NaCl until equilibrium has been established. The excess $PbCl_2(s)$ is then filtered off.

(iii) Assuming $[Cl^-]$ remains at 0.50 mol dm^{-3} throughout, calculate the $[Pb^{2+}(aq)]$ in the remaining solution.

....

....

(iv) Suggest an explanation for the difference between this value and the value that you calculated in **(ii)**.

....

[4]

[Total: 10]

3 **(a)** **(i)** $Cu(s) – 2e \rightarrow Cu^{2+}(aq)$ allow electrons on RHS (1)

(ii) $E^{\ominus}$ for Ag^{+}/Ag is +0.80V which is more positive than +0.34V for Cu^{2+}/Cu, (1)
so it's less easily oxidised (owtte) (1)

(iii) $E^{\ominus}$ for Ni^{2+} is –0.25V, (1)
Ni is readily oxidised and goes into solution as $Ni^{2+}(aq)$ (1) [Mark **(ii)** and **(iii)** to max 3]

(iv) $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ (1)

(v) $E^{\ominus}$ for Zn^{2+}/Zn is negative / = –0.76V, so Zn^{2+} is not easily reduced. (1)

(vi) The blue colour fades because $Cu^{2+}(aq)$ is being replaced by $Zn^{2+}(aq)$ *or* $Ni^{2+}(aq)$ *or* $[Cu^{2+}]$ decreases (1) **[7]**

(b) amount of copper = 225/63.5 = **3.54**(3) mol (1)
amount of electrons needed = 2 × 3.54 = **7.08/9** (7.087) mol (1)

no. of coulombs = 20 × 10 × 60 × 60 = 7.2×10^5 C
no. of moles of electrons = $7.2 \times 10^5/9.65 \times 10^4$ = **7.46** mol (1)

percentage "wasted" = 100 × (7.461 – 7.087)/7.461 = 5.01 (**5.0**)% (accept 4.98–5.10) (1)
[4]

(c) $E^{\ominus}$ data: Ni^{2+}/Ni = –0.25V
Fe^{2+}/Fe = –0.44V (1)

Because the Fe potential is more negative than the Ni potential, the iron will dissolve (1) **[2]**

[Total: 13]

4 **(a)** **(i)** SnO_2 Can be read into equation (1)
$2NaOH + SnO_2 \rightarrow Na_2SnO_3 + H_2O$ (1)

(ii) PbO Can be read into equation (1)
$PbO + 2HCl \rightarrow PbCl_2 + H_2O$ (1)

[4]

(b) moles of oxygen = 9.3/16 = 0.581 mol
moles of lead = 90.7/207 = 0.438 mol <u>(both 3 s.f.)</u> (1)

so formula is Pb_3O_4 (1) **[2]**

(c) **(i)** $K_{sp} = [Pb^{2+}][Cl^{\ }]^2$ (1) units = $mol^3\ dm^{\ 9}$ (1)

(ii) if $[Pb^{2+}] = x$, $K_{sp} = 4x^3$, so $x = \sqrt[3]{K_{sp}/4}$
$[Pb^{2+}] = \sqrt[3]{2 \times 10^{\ 5}/4}$ = $\mathbf{1.71 \times 10^{-2}}$ mol dm ^{3} (1)

(iii) $[Pb^{2+}] = 2 \times 10^{\ 5}/(0.5)^2$ = $\mathbf{8.0 \times 10^{-5}}$ mol dm ^{3} (1)

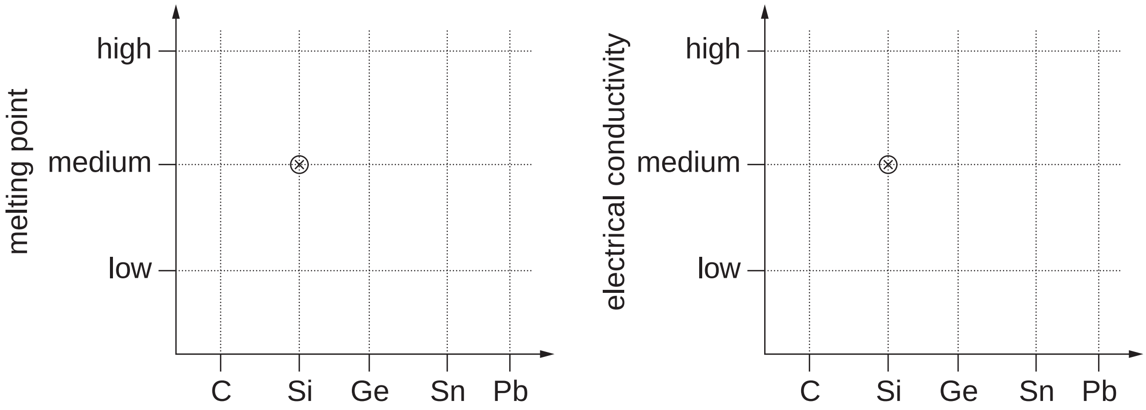
(iv) common ion effect, or increased $[Cl^{\ }]$ forces solubility equilibrium over to the left (1)

[Max 4]

[Total: 10]

For Examiner's Use

2 **(a)** **(i)** On the following grids, plot points showing the variation in the named property of the Group IV elements. Your points should show for each element, whether the melting point/electrical conductivity is 'high', 'medium' or 'low'. The point for silicon has already been plotted in each case.



(ii) Suggest explanations of these trends in terms of the structure and bonding of the Group IV elements.

melting point

....

....

electrical conductivity

....

.... [6]

(b) Choose **one** reaction to illustrate **each** of the following statements. Write an equation for each of your chosen reactions, and describe what you would see as the reaction is carried out.

(i) PbO is more stable than PbO_2.

....

....

(ii) CO is easily oxidised to CO_2.

....

....

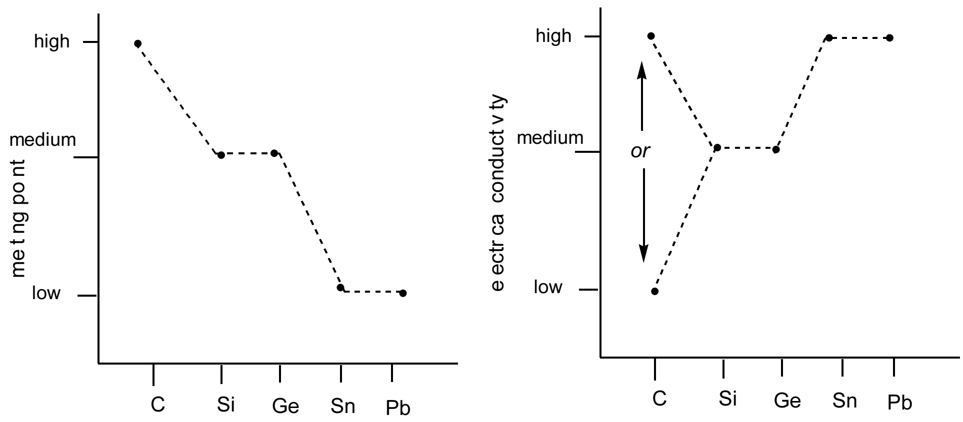
(iii) Aqueous $SnCl_2$ is a useful reducing agent.

....

.... [4]

[Total: 10]

2 (a) (i)



[2] + [2]

(ii) m. pt. trend: (from) giant/macro molecular/covalent to metallic bonding (or implied from at least two specific examples, e.g. diamond and tin) [1]
(mention of *simple* covalent anywhere negates this mark)

conductivity trend: increasing delocalisation of electrons (down the group) [1]
or e are more free-moving
(or implied from at least two examples, e.g. Si is semiconductor, lead has delocalised e)

[6]

(b) (i) heat PbO_2, or T > 200°C *or* Δ on arrow: $PbO_2 \rightarrow PbO + ½O_2$ (N.B. $½O_2$ NOT [O]) [1]

(ii) (burning CO in air produces CO_2):$CO + ½O_2 \rightarrow CO_2$ [1]
blue flame (ignore ref to limewater test) [1]

(iii) e.g. $SnCl_2$(aq) will turn $KMnO_4$ from purple to colourless [1]
$5Sn^{2+} + 2MnO_4 + 16H^+ \rightarrow 5Sn^{4+} + 2Mn^{2+} + 8H_2O$ [1]

or $SnCl_2$(aq) will turn $K_2Cr_2O_7$ from orange to green [1]
$3Sn^{2+} + Cr_2O_7^{2} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$ [1]

or $SnCl_2$(aq) will turn Fe^{3+} from orange/brown/yellow to green/colourless [1]
$Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+}$ [1]

or $SnCl_2$(aq) will turn Cu^{2+}(aq) from blue to colourless *or* give a pink/brown/copper-coloured ppt. [1]
$Sn^{2+} + Cu^{2+} \rightarrow Sn^{4+} + Cu$ [1]

Other possible oxidants ($E^{\ominus}$ must be > +0.2V) include: $S_2O_8^{2}$, H_2O_2, Cl_2, Br_2, I_2 and Ag^+. No observations with the first three of these, but this should be stated explicitly, e.g. "no colour change".

[5]

[Total: 11 max 10]

For Examiner's Use

4 (a) (i) Describe and explain the trend in the volatilities of the Group IV chlorides CCl_4, $GeCl_4$ and $PbCl_4$.

....

....

....

....

....

....

(ii) Describe and explain the reactions, if any, of these chlorides with water. Write equations for any reactions that occur.

....

....

....

....

....

....

....

[7]

For Examiner's Use

(b) SnO_2 and PbO_2 react with acids in different ways.

- SnO_2 reacts with concentrated sulfuric acid to form a colourless solution with no evolution of gas.
- PbO_2 reacts with concentrated sulfuric acid to give a white solid, **B**, and oxygen gas.
- PbO_2 reacts with cold concentrated hydrochloric acid to give a yellow solution containing the $[PbCl_6]^{2-}$ ion, with no evolution of gas.
- Warming this yellow solution causes the evolution of Cl_2 gas, leaving a colourless solution which on cooling in ice precipitates a white solid, **C**.

(i) Identify the two white solids, **B** and **C**, mentioned above.

B ....

C ....

(ii) Suggest an equation for **each** of the four reactions described above.

....

....

....

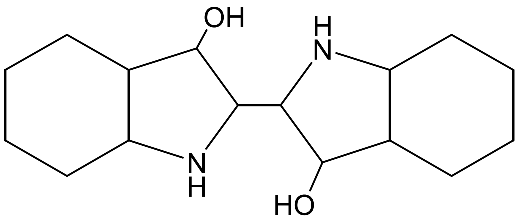
....

....

....
[4]

[Total: 11]

(d) **(i)**

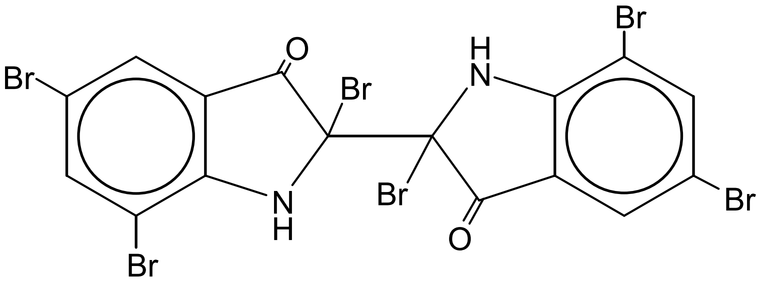


[1]

(ii) M_r = 262, so 2.5 g = 2.5/262 = $9.54 \times 10^{\ 3}$ mol [1]
(1 mol indigo absorbs 9 mol of H_2)
so volume of H_2 = 9 × 24 – $9.54 \times 10^{\ 3}$ = **2.06 dm³** (2060 cm^3)

[1]
[3]

(e)



2 x Br **on C=C** [1]
a Br on each ring [1]
TWO non-adjacent Br on **each ring** [1]
[3]

[Total: 16]

4 **(a)** **(i)** volatilities decrease down the group [1]

due to greater van der Waals (VDW) forces (*intermolecular is not sufficient*) [1]

due to larger no of electrons [1]

(ii) CCl_4 does not react with water [1]

CCl_4 unreactive due to no **d**-orbitals [1]

$GeCl_4$ **and** $PbCl_4$ hydrolyse/react [1]

$MCl_4 + 2H_2O \longrightarrow MO_2 + 4HCl$ (M = Ge *or* Pb) [1]
[7]

(b) (i) **B** is $PbSO_4$ **and** **C** is $PbCl_2$ [1]

(ii) $SnO_2 + 2H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2H_2O$ [1]

$PbO_2 + H_2SO_4 \longrightarrow PbSO_4 + H_2O + \frac{1}{2} O_2$ [1]

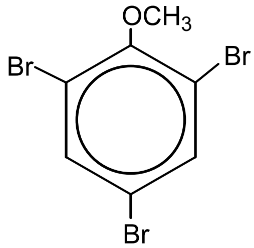
$PbO_2 + 6HCl \longrightarrow H_2PbCl_6 + 2H_2O$ [1]

$H_2PbCl_6 \longrightarrow PbCl_2 + 2HCl + Cl_2$ [1]

[5 max 4]

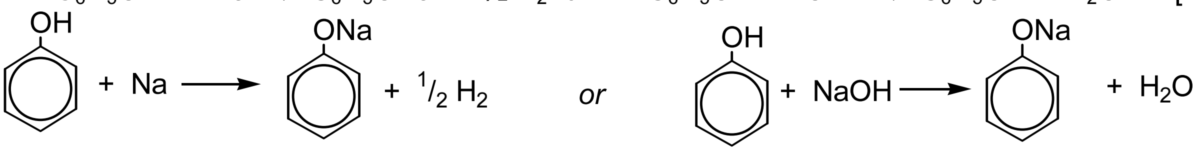
[Total: 11]

5 (a) (i)



[1]

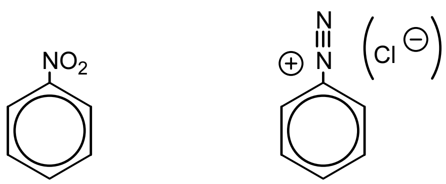
(ii) Na metal *or* NaOH [1]
Fizzes/gas given off with phenol *or* phenol dissolves (anisole doesn't) [1]
$C_6H_5OH + Na \rightarrow C_6H_5ONa + \frac{1}{2} H_2$ *or* $C_6H_5OH + OH \rightarrow C_6H_5O + H_2O$ [1]



(neutral) iron(III) chloride *[1]*
Solution goes purple/violet *[1]*
$3C_6H_5OH + FeCl_3 \rightarrow Fe(OC_6H_5)_3 + 3HCl$ *[1]*

[4]

(b) (i)



D **E**

[1] + [1]

(ii) step 2: Sn **+** HCl **NOT** $LiAlH_4$, $NaBH_4$ [1]
conc. **+** reflux *(warm is insufficient)* [1]

step 4 is conditional of structure E
step 4: warm + in H_2O [1]

[5 max 4]