Q1 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.

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

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(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.

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(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 $I_2(aq)$,

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

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(d) (i) The Sn–Cl bond energy is +315 kJ mol^{-1}. Use this and other values from the *Data Booklet* to calculate $\Delta H^{\ominus}$ for the reaction

$$MCl_2(g) + Cl_2(g) \rightarrow MCl_4(g)$$

for the following cases.

for the following cases.

• *M* = Si

• *M* = Sn

(ii) Do your results agree with the trend in relative stabilities of the +2 and +4 oxidation states in **(c)**? Explain your answer.

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(June 2008)

Q2 **(a)** Describe how the behaviour of the oxides of tin and lead in their +4 oxidation states differ on heating.

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(b) Explain the following by using data from the *Data Booklet* where appropriate, and writing equations for all reactions.

(i) A sample of liquid $PbCl_4$ is placed in a flask and the flask is gently warmed. A gas is evolved and a white solid is produced. When the gas is bubbled through KI(aq), purple fumes are produced.

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(ii) Repeating the same experiment using liquid $SnCl_4$ instead of $PbCl_4$ results in no evolution of gas, and no reaction with KI(aq).

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(c) The molecule dichlorocarbene, CCl_2, can be produced under certain conditions. It is highly unstable, reacting with water to produce carbon monoxide and a strongly acidic solution.

(i) Suggest the electron arrangement in CCl_2 and draw a dot-and-cross diagram showing this. Predict the shape of the molecule.

(ii) Construct an equation for the reaction of CCl_2 with water.

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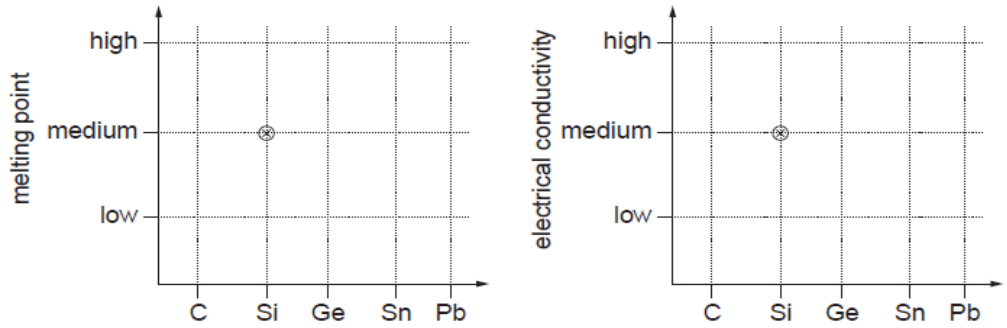
(June 2010 P41)

Q3 **(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

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electrical conductivity

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(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.

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(ii) CO is easily oxidised to CO_2.

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

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(June 2011 P42)

Q4 **(a) (i)** Describe and explain the trend in the volatilities of the Group IV chlorides CCl_4, $GeCl_4$ and $PbCl_4$.

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

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(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.

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(June 2012 P41)

Q5 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 HCl(aq)

formula of oxide .....

equation .....

(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.

(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 $PbCl_2$.

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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.

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

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(Nov 2010 P41)