Centre Number						Candidate Number				
Surname										
Other Names	Model Answers.									
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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8	
9	
TOTAL	

General Certificate of Education
Advanced Level Examination
January 2010

Chemistry CHEM5

Unit 5 Energetics, Redox and Inorganic Chemistry

Monday 1 February 2010 9.00 am to 10.45 am

For this paper you must have:
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. **Answers written in margins or on blank pages will not be marked.**
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

Areas outside the box will not be scanned for marking

SECTION A

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

1 This question is about the use of transition metals as catalysts.

1 (a) State how a catalyst speeds up a chemical reaction.

A catalyst provides an alternative pathway by lowering the activation energy.

(2 marks)

1 (b) State the characteristic property of transition metals that enables them to act as catalysts in redox reactions.

Variable oxidation states they can form compounds with different ions.

(1 mark)

1 (c) In the Contact Process for the conversion of sulfur dioxide into sulfur trioxide, vanadium(V) oxide acts as a heterogeneous catalyst.

1 (c) (i) Write **two** equations to show how the catalyst is involved in this reaction.

Equation 1 $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$ this comes up almost every year - know this!!

Equation 2 $O_2 + 2V_2O_4 \rightarrow 2V_2O_5$

(2 marks)

1 (c) (ii) Suggest **one** reason why poisoning reduces the effectiveness of a heterogeneous catalyst.

Poison can block the sites (active) - decreasing surface area. If more marks offered may have needed to explain adsorption + desorption.

(1 mark)

1 (c) (iii) Suggest how poisoning of a catalyst, used in an industrial process, can be minimised.

Use pure reactants.

(1 mark)

7

2 Nickel–cadmium cells are used to power electrical equipment such as drills and shavers. The electrode reactions are shown below.

×2 to balance e⁻.

$$2NiO(OH) + 2H_2O + 2e^- \longrightarrow 2Ni(OH)_2 + 2OH^- \qquad E^\ominus = +0.52\ V$$

$$\overset{+2}{Cd}(OH)_2 + 2e^- \longrightarrow Cd + 2OH^- \qquad E^\ominus = -0.88\ V$$

2 (a) Calculate the e.m.f. of a nickel–cadmium cell.

$E = R - L$ $\quad E = 0.52 - (-0.88)$ $\quad E = 1.4V$

most negative on the left.

(1 mark)

2 (b) Deduce an overall equation for the reaction that occurs in the cell when it is used.

must cancel + simplify

$Cd + 2OH^- + 2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2 + 2OH^-$

$\therefore$ $Cd + 2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$

(2 marks)

2 (c) Identify the oxidising agent in the overall cell reaction and give the oxidation state of the metal in this oxidising agent.

Oxidising agent $\overset{+3}{Ni}\overset{-2}{O}\overset{-1}{(OH)}$

Oxidation state $+3$

(2 marks)

5

Turn over for the next question

3 Hydrogen–oxygen fuel cells can operate in acidic or in alkaline conditions but commercial cells use porous platinum electrodes in contact with concentrated aqueous potassium hydroxide. The table below shows some standard electrode potentials measured in acidic and in alkaline conditions.

Half-equation	$E^{\ominus}$ / V
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.23
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$2H_2O(l) + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$	−0.83

3b

3b

3 (a) State why the electrode potential for the standard hydrogen electrode is equal to 0.00 V.

By definition.

(1 mark)

3 (b) Use data from the table to calculate the e.m.f. of a hydrogen–oxygen fuel cell operating in alkaline conditions.

$E = R - L$ $E = +0.40 - (-0.83)$ $E = +1.23\,V$

(1 mark)

3 (c) Write the conventional representation for an alkaline hydrogen–oxygen fuel cell.

$Pt \,|\, H_2(g), H_2O(l) \,||\, O_2(g), OH^-(aq) \,|\, Pt$

Even though answer is NOT in mark scheme - this is the correct answer!

(2 marks)

3 (d) Use the appropriate half-equations to construct an overall equation for the reaction that occurs when an alkaline hydrogen–oxygen fuel cell operates. Show your working.

×2 $2H_2 + 4OH^- \rightarrow 2H_2O + 4e^-$ and $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Cancel + Simplify $2H_2 + 4\cancel{OH^-} + O_2 + 2\cancel{H_2O} + \cancel{4e^-} \rightarrow 4\cancel{H_2O} + \cancel{4e^-} + 4\cancel{OH^-}$

Cancel 2!

$\therefore\ 2H_2 + O_2 \longrightarrow 2H_2O$

(2 marks)

3 (e) Give **one** reason, other than cost, why the platinum electrodes are made by coating a porous ceramic material with platinum rather than by using platinum rods.

Increases the surface area.

(1 mark)

3 (f) Suggest why the e.m.f. of a hydrogen–oxygen fuel cell, operating in acidic conditions, is exactly the same as that of an alkaline fuel cell.

Overall reaction is the same. $2H_2 + O_2 \rightarrow 2H_2O$

(1 mark)

3 (g) Other than its lack of pollution, state briefly the main advantage of a fuel cell over a re-chargeable cell such as the nickel–cadmium cell when used to provide power for an electric motor that propels a vehicle.

Hydrogen and Oxygen supplied continuously so no need to recharge a battery.

(1 mark)

3 (h) Hydrogen–oxygen fuel cells are sometimes regarded as a source of energy that is carbon neutral. Give **one** reason why this may **not** be true.

Hydrogen is produced from electrolysis which requires energy - and this is likely <u>not</u> from a carbon neutral source.

(1 mark)

10

Turn over for the next question

4 The table below gives some values of standard enthalpy changes. Use these values to answer the questions.

Name of enthalpy change	$\Delta H^{\ominus}$/kJ mol^{-1}
Enthalpy of atomisation of chlorine	+121
Electron affinity of chlorine	−364
Enthalpy of atomisation of silver	+289
First ionisation enthalpy of silver	+732
Enthalpy of formation of silver chloride	−127

4 (a) Calculate the bond enthalpy of a Cl−Cl bond.

Bond enthalpy is ×2 the atomisation - know your definitions!

121 × 2 = 242 kJmol^{-1}

(1 mark)

4 (b) Explain why the bond enthalpy of a Cl−Cl bond is greater than that of a Br−Br bond.

Cl-Cl bond is shorter as bonding pair of electrons are closer to the nucleus. Attraction between nucleus and bonding pair is stronger. * Stronger bonds are shorter.

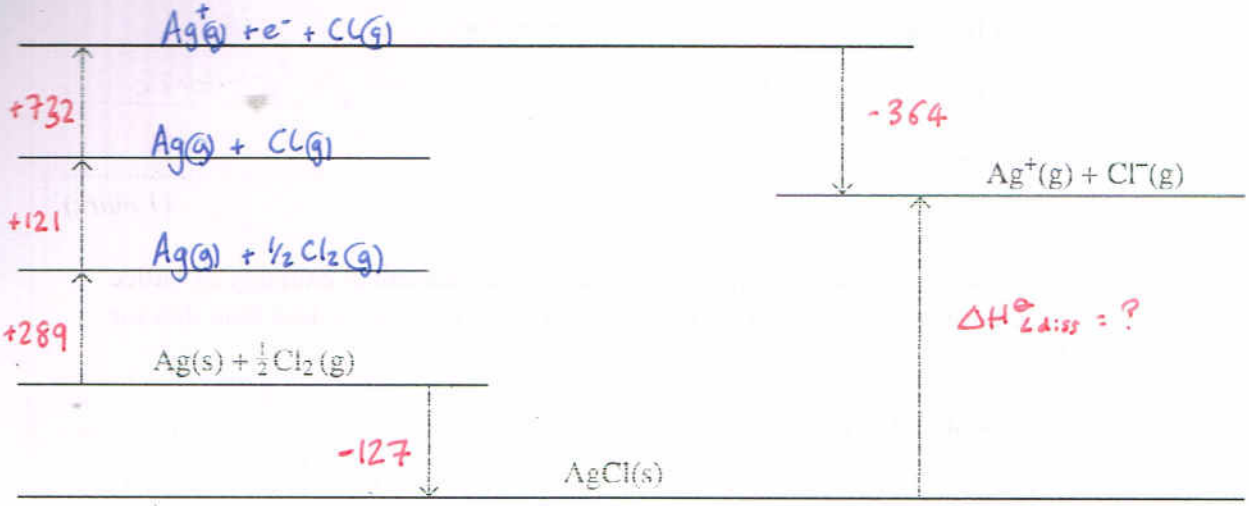
(2 marks)

4 (c) Suggest why the electron affinity of chlorine is an exothermic change.

There is an overall attraction between chlorine nucleus and the extra electron.

(1 mark)

4 (d) The diagram below is an incomplete Born–Haber cycle for the formation of silver chloride. The diagram is not to scale.



4 (d) (i) Complete the diagram by writing the appropriate chemical symbols, with state symbols, on each of the three blank lines. *(3 marks)*

4 (d) (ii) Calculate a value for the enthalpy of lattice dissociation for silver chloride.

(127 + 289 + 121 + 732) − 364 = +905

Must be a +ve value as arrow points up.

(2 marks)

Question 4 continues on the next page

Areas outside the box will not be scanned for marking

4 (e) The enthalpy of lattice dissociation for silver chloride can also be calculated theoretically assuming a perfect ionic model.

4 (e) (i) Explain the meaning of the term *perfect ionic model*.

Ions are regarded as point charges or perfect ionic spheres. the perfect ionic model assumes no covalent character.

(1 mark)

4 (e) (ii) State whether you would expect the value of the theoretical enthalpy of lattice dissociation for silver chloride to be greater than, equal to or less than that for silver bromide. Explain your answer.

Theoretical lattice enthalpy for silver chloride Greater than

Explanation Chloride ions are smaller than Bromide ions which means they are more strongly attracted to the Silver ions

(3 marks)

(Extra space)

4 (e) (iii) Suggest why your answer to part (d) (ii) is greater than the theoretical value for the enthalpy of lattice dissociation for silver chloride.

Silver ion is large and Cl^- ion is small - hence more overlap.

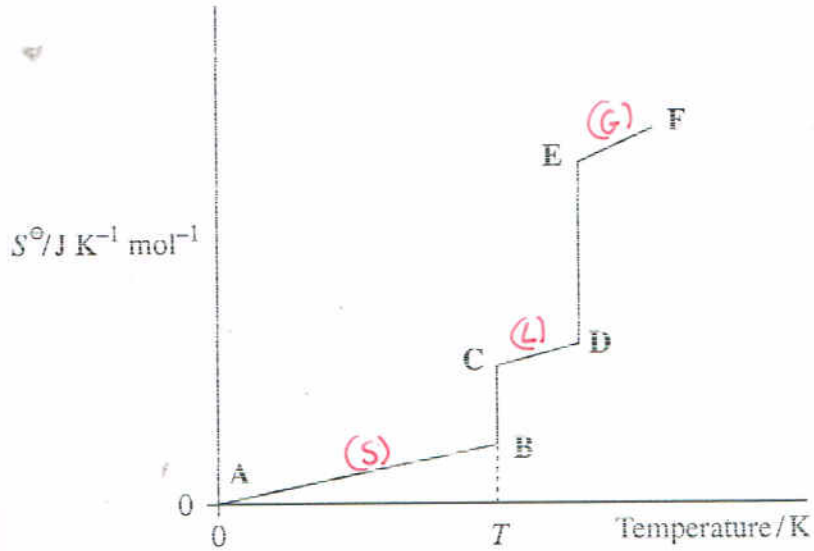
AgCl has covalent character and therefore bonding is stronger than purely ionic.

(2 marks)

15

Areas outside the box will not be scanned for marking

5 The simplified diagram below shows how the entropy of ammonia varies with temperature at a pressure of 100 kPa. In this diagram, ammonia is a solid at point **A** and a gas at point **F**.



5 (a) State why the entropy value for ammonia is equal to zero at 0 K.

There is no disorder.

(1 mark)

5 (b) Explain, in terms of the movement of particles, why the entropy value increases between points **A** and **B** on the diagram.

Molecules are vibrating more - so more disorder.

(1 mark)

5 (c) Temperature T is marked on the diagram. What does the value of this temperature represent?

The melting point of ammonia.

(1 mark)

5 (d) Explain why there is a large entropy change between points **D** and **E** on the diagram.

The liquid ammonia is becoming a gas and there is a big increase in disorder.

(2 marks)

Areas outside the box will not be scanned for marking

5 (e) An equation for the reaction in the Haber Process is shown below, together with some entropy data.

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g) \qquad \Delta H^{\ominus} = -46.2\,kJ\,mol^{-1}$$

	$N_2(g)$	$H_2(g)$	$NH_3(g)$
$S^{\ominus}$/ J K^{-1} mol^{-1}	192	131	193

5 (e) (i) Calculate a value for the entropy change, $\Delta S^{\ominus}$, for the formation of one mole of ammonia.

$(\frac{1}{2} \times 192) + (\frac{3}{2} \times 131) = 292.5$

$193 - 292.5 = -99.5\ J K^{-1} mol^{-1}$

(breaking - making)

(2 marks)

5 (e) (ii) Give the equation that relates free-energy change, $\Delta G^{\ominus}$, to enthalpy change, $\Delta H^{\ominus}$, and entropy change, $\Delta S^{\ominus}$.

Use this equation to calculate the temperature at which the value of $\Delta G^{\ominus} = 0$ for the formation of ammonia in the Haber Process.
(If you have been unable to calculate an answer to part (e) (i), you may assume that $\Delta S^{\ominus} = -81.4$ J K mol^{-1} but this is not the correct value.)

Equation $\Delta G = \Delta H - T\Delta S$

Calculation If $\Delta G = 0$ then $T = \frac{\Delta H}{\Delta S}$

need to ensure units are same

$T = \frac{-46.2 \times 1000}{-99.5} = 464$

(4 marks)

(Extra space)

5 (e) (iii) What can you deduce about the formation of ammonia if the reaction mixture is heated to a temperature above the value that you have calculated in part (e) (ii)?

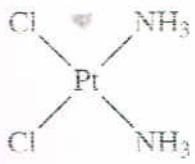
It would no longer be feasible (ΔG = +ve)

(1 mark)

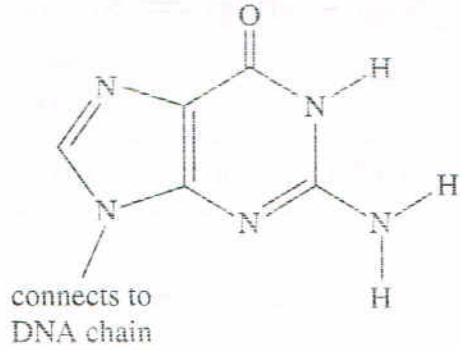
12

Turn over ▶

6 The complex cisplatin acts as an anticancer drug by changing the properties of DNA when it reacts with guanine, a component of DNA.



cisplatin



guanine

When cisplatin is absorbed into the human body, it undergoes a ligand substitution reaction and one chloride ligand is replaced by a water molecule forming a complex ion **Q**.

6 (a) Write an equation for this substitution reaction to form the complex ion **Q**.

order doesnt matter but should be alphabetical on name...

$Pt(NH_3)_2Cl_2 + H_2O \longrightarrow [Pt(NH_3)_2(H_2O)Cl]^+ + Cl^-$

(2 marks)

6 (b) The complex ion **Q** can bond to guanine in two different ways.

6 (b) (i) The first way involves a hydrogen atom, from one of the ammonia ligands on **Q**, bonding to an atom in a guanine molecule. State the type of bond formed to guanine and identify an atom in guanine that could form a bond to this hydrogen atom.

Type of bond Hydrogen bonding

Atom in guanine Oxygen (or Nitrogen).

(2 marks)

6 (b) (ii) The second way involves a ligand substitution reaction in which an atom in a guanine molecule bonds to platinum by displacing the water molecule from **Q**. State the type of bond formed between guanine and platinum when a water molecule is displaced and identify an atom in guanine that could bond to platinum in this way.

Type of bond Coordinate bond

Atom in guanine Nitrogen (or oxygen) would need a lone pair. *(2 marks)*

Areas outside the box will not be scanned for marking

6 (c) State and explain **one** risk associated with the use of cisplatin as an anticancer drug.

Risk it can be fatal or cause damage

Explanation Can attach to DNA in non-cancerous cells.

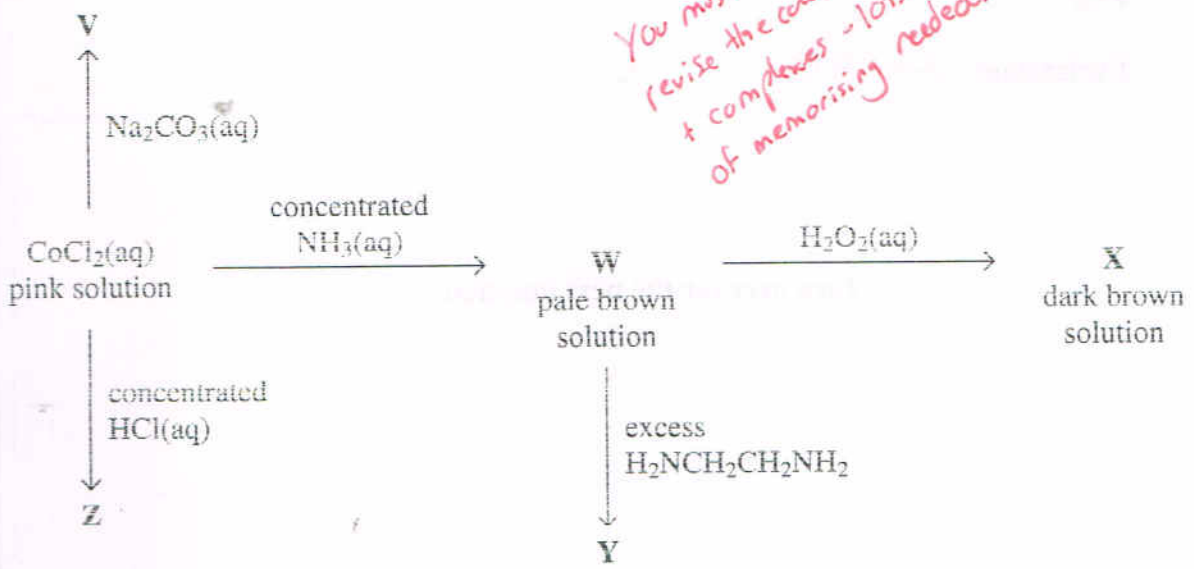
(2 marks)

8

Turn over for the next question

7 This question is about some reactions of cobalt compounds.

You must revise the colours + complexes - lots of memorising needed.



7 (a) Give the formula of the complex responsible for the pink colour in aqueous $CoCl_2$ and name its shape.

Formula $[Co(H_2O)_6]^{2+}$

Name of shape octahedral

(2 marks)

7 (b) Give the formula of the cobalt-containing compound **V** and describe its appearance.

Formula $CoCO_3$

Appearance Pink precipitate

(2 marks)

7 (c) Write an equation for the reaction that occurs when the pink solution is converted into **W**.

$[Co(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Co(NH_3)_6]^{2+} + 6H_2O$

(2 marks)

Areas outside the box will not be scanned for marking

7 (d) Give the formula of the cobalt-containing complex in **X** and state the role of the H_2O_2 in this reaction.

Formula $[Co(NH_3)_6]^{3+}$

Role of H_2O_2 oxidising agent

(2 marks)

7 (e) Give the formula of the cobalt-containing complex in **Y** and explain why this complex is more stable than the cobalt-containing complex in **W**.

common question!! know this one.

Formula $[Co(H_2NCH_2CH_2NH_2)_3]^{2+}$

Explanation The entropy change for this reaction is positive as 4 moles of reactants become 7 mol of products.

(3 marks)

7 (f) Identify the cobalt-containing complex in solution **Z** and explain why its co-ordination number is different from that in the pink solution of $CoCl_2$

another common question!

Complex $[CoCl_4]^{2-}$

Explanation Cl^- ligand is too big, so only 4 are possible.

(2 marks)

13

Turn over for the next question

Areas outside the box will not be scanned for marking

SECTION B

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

ability to withdraw a pair of electrons in a covalent bond.

8 (a) State and explain the trend in electronegativities across Period 3 from sodium to sulfur.

The electronegativities increase as the proton number increases (nuclear charge). However they each have the same number of orbitals, hence similar shielding. So the overall attraction of the bond pair to the nucleus increases.

4 marks so look for 4 separate statements.

(4 marks)

(Extra space)

DoNT forget shielding!

Areas outside the box will not be scanned for marking

8 (b) Explain why the oxides of the Period 3 elements sodium and phosphorus have different melting points. In your answer you should discuss the structure of and bonding in these oxides, and the link between electronegativity and the type of bonding.

Sodium Oxide has ionic bonding whereas phosphorus oxide is covalent.

Na_2O has a giant ionic lattice with strong electrostatic attractions between positive and negative ions.

P_4O_{10} is a simple molecular structure with weak intermolecular forces (vdw) between molecules. These are easy to separate hence P_4O_{10} having a lower melting point than Na_2O.

(6 marks)

(Extra space)

The big differences in electronegativity between the atoms give rise to ionic

Lots of separate points
Don't forget structure and bonding definitions.

Question 8 continues on the next page

8 (c) A chemical company has a waste tank of volume 25 000 dm^3. The tank is full of phosphoric acid (H_3PO_4) solution formed by adding some unwanted phosphorus(V) oxide to water in the tank.

A 25.0 cm^3 sample of this solution required 21.2 cm^3 of 0.500 mol dm^{-3} sodium hydroxide solution for complete reaction.

Calculate the mass, in kg, of phosphorus(V) oxide that must have been added to the water in the waste tank.

conc × vol = mole $0.500 \times \left(\frac{21.2}{1000}\right) = 0.01055$ moles of NaOH.

Tank reaction → $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

titration → $H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$

mole ratio

0.01055 moles $\div 3 = 3.52 \times 10^{-3}$ moles of H_3PO_4

$25cm^3 \rightarrow 25000dm^3$!

$3.52 \times 10^{-3} \times 1{,}000{,}000 = 3520$ moles in $25000dm^3$

3520 moles $\div 4 = 882.5$ moles of P_4O_{10}

Mr of P_4O_{10}

882.5 moles $\times 284 = 250630$ g or 250.63 kg of P_4O_{10}

(5 marks)

(Extra space)

251 kg 3s.f

15

Areas outside the box will not be scanned for marking

9 (a) State the electron configuration of a Ti(III) ion and that of a Ti(IV) ion. Explain, in terms of electron configurations and electron transitions, why Ti(III) compounds are usually coloured but Ti(IV) compounds are colourless.

$Ti(III) = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$

$Ti(IV) = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Though markscheme allow [Ar] configs - you should show it fully.

Ti(III) has coloured compounds as it has a d electron that can be excited and move into a higher level. It can do this by absorption of a specific frequency of light.

(Extra space) Ti(IV) has no d electrons so does not have coloured compounds.

(5 marks)

Question 9 continues on the next page

9 (b) Transition metal ions and their complexes can often be identified from their colours. For each of the following, identify a complex ion responsible for the colour of the aqueous solution. Restrict your answers to complexes formed from the elements Cr, Fe, Co and Cu.

(1) A deep blue solution formed in an excess of concentrated aqueous ammonia.

(2) A green solution formed in an excess of aqueous sodium hydroxide.

(3) A yellow–green solution formed in an excess of concentrated hydrochloric acid.

(1) $[Cu(NH_3)_4(H_2O)_2]^{2+}$

(2) $[Cr(OH)_6]^{3-}$

(3) $[CuCl_4]^{2-}$

Must know your complex ions and their colours.

(3 marks)

9 (c) An experiment is carried out to investigate the rate of the autocatalysed reaction between aqueous potassium manganate(VII) and ethanedioate ions in an excess of dilute sulfuric acid. When these reagents are mixed together, the colour of the reaction mixture gradually fades. The concentration of the manganate(VII) ions is recorded at different times using a spectrometer. The temperature of the reaction mixture is constant.

9 (c) (i) Give **two** reasons why the use of a spectrometer is the most appropriate method for measuring the concentration of the coloured ions in this experiment.

It is both quick and precise, giving many readings. It also does not use up any of the reagents.

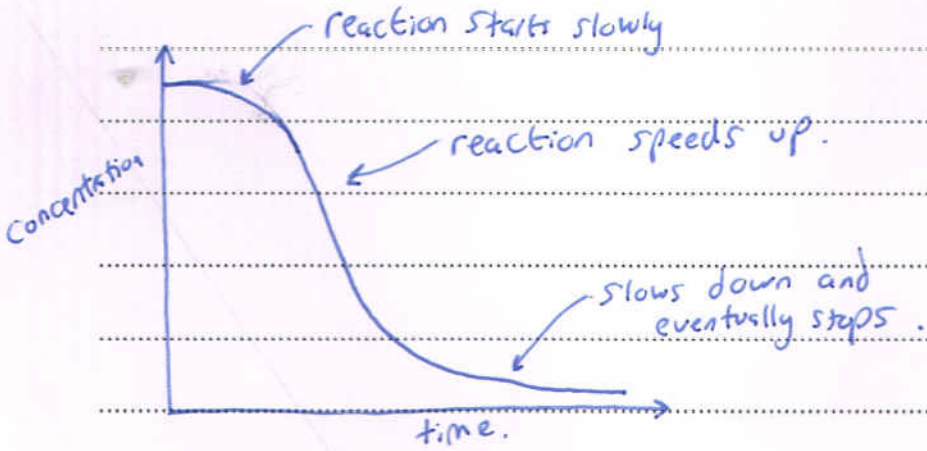
for current specifications they would usually refer to a colarimeter.

(2 marks)

(Extra space)

Areas outside the box will not be scanned for marking

9 (c) (ii) Sketch a curve to show how you would expect the concentration of manganate(VII) ions to change with time until the colour has faded because the concentration has reached a very low value. Explain the shape of the curve.



At start curve has a small gradient showing a slow rate. This is because at the start negative ions are colliding, which gives a very high Ea. However as reaction progresses Mn^{2+} ion form which autocatalyses the reaction speeding it up. Eventually reaction stops as MnO_4^- ions are used up. *(5 marks)*

(Extra space)

$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

two negative ions repel until is formed.

15

END OF QUESTIONS