



**Part 1 – Criteria 4 and 7**

**Question 1**

- (a) (i) This question part was done very well by most candidates.  
(ii) A number of candidates gave the (ox)Br = +6 then correctly used  $\text{BrO}_3^-$  in (b). A small number of candidates wrote  $\text{Br}^{5+}$  instead of (ox)Br = +5.
- (b)  $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$  was correctly given with few errors arising. However, the reduction of  $\text{BrO}_3^-$  ion presented major problems with the usual mistake being  $\text{BrO}_3^- \rightarrow \text{Br}$ , rather than  $\text{Br}^-$  or  $\text{Br}_2$ . A minority of candidates used  $\text{BrO}_3^- \rightarrow \text{Br}^-$  and then cancelled out the bromides before and after arrows (reactants/products) in the overall net ionic equation.

Confusing bromine and bromide also featured in question 5 (b).

**Question 2**

- (a) Most candidates did very well although a minority used  $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$  as the oxidation half-equation. The shorthand notation for the cell was done very poorly with many writing either  $\text{C}/\text{Cr}_2\text{O}_7^{2-}/\text{Fe}^{3+}/\text{C}$  or the reverse of this.
- (b) Most did well, although a common error was  $E^\circ = \{1.36 - (-0.77)\} \text{V} = +2.13 \text{ V}$ .
- (c) This was very poorly answered. Many candidates wrote either:  $\text{Fe}^{2+}$  losing  $\text{e}^-$  and hence 'running out' of electrons or choosing the highest redox potential and saying that this was 'dropping' the fastest.
- (d) Practically all candidates recognised this would now entail the oxidation of the Fe electrode but few stated that the cathode half-reaction remained unchanged although many candidates calculated a new cell's EMF thus showing that the cathode was unchanged. Many candidates stated that the reaction would go on for longer and that the Fe anode would decrease in size.

**Question 3**

The high concentration of chloride ions ( $\text{Cl}^-$ ) was the clue to the oxidation half-equation and chlorine gas ( $\text{Cl}_2$ ) was the expected product. Many candidates ignored  $\text{Br}^-$  as a species possibly undergoing oxidation. Reduction of water at the cathode was the other half-equation and this was answered well.

**Question 4**

- (a) Most candidates wrote general, 'wet' corrosion explanations although a significant number wrote that 'water is the cathode'. A minority recognised that Cu was the inert cathode.
- (b) Nearly all candidates discussed either dissimilar metals or the effects of dissolved salts but gave vague reasons for the increased rate. The large surface area of the cathode was a key factor in the increased rate of corrosion.
- (c) This presented no problems for the overwhelming majority; multiple strategies were usually given. Many answers were given that involved modern day technology such as plastics, applied EMF, sacrificial Al/Zn anodes. This were accepted despite the question being about an eighteenth century ship!

**Question 5**

- (a) Very few candidates answered this part adequately. Most candidates wrote to: '...check for impurities' and wrote nothing more than that. A minority recognised the need to crosscheck  $\text{Fe}^{3+}$  with ferricyanide and  $\text{Fe}^{2+}$  with thiocyanate. Candidates choosing electrochemistry generally got lost. Alternate positive tests for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were not commonly considered.
- (b) This was done disastrously!! We looked desperately for marks to give away.

Frequent mistakes included reacting  $\text{Fe}^{3+}$  with halogens or reacting  $\text{Fe}^{2+}$  with the halides. A number of candidates suggested either precipitation after the reduction of  $\text{Fe}^{3+}$  or the use of electrochemical cells, but the setting up proper half cells was too difficult.

- (c) Candidates who answered (b) using  $\text{Fe}^{3+}$  and halides then used  $\text{Fe}^{2+}$  and halogens in (c). Electrolysis variations were also used but descriptions mostly incomplete. Some candidates utilised EMF with a 5<sup>th</sup> 'reference', usually Mg or Zn.

The vast majority of candidates showed they understood the aim, but could not figure out how to achieve it.

The average mark for the Criterion 4 question in this section was very disappointing.

**Part 2 – Criteria 4 and 8****Question 6**

This question was well done by a significant number of candidates. To gain the full 2 marks, candidates were required to mention that as time progressed not only that the reactants were used up but the number of collisions and hence the number of effective collisions decreased over time.

A reasonably high number of candidates however tried to base their answer on equilibrium conditions and mentioned a reverse reaction occurring, hence the products reacting as a reason for the amount of carbon dioxide gas decrease.

**Question 7**

Well answered by many candidates who again mentioned that the energy released by the exothermic reaction increased the average kinetic energy of the particles which increased the number of effective collisions. This sped up the reaction rates to a dangerous level.

Although a number of candidates mentioned that more energy was released when bonds were formed compared to the energy needed to break the bonds, this point alone did not get them full marks.

**Question 8**

Most candidates made a very good attempt at this question. Even though the single bonds were missing from the information, the candidates had a clear grasp of what was being asked.

The most common errors were the number of C–C bond needed to be broken in propane and the number of C=O and H–O bonds formed. Calculation errors were frequently encountered.

**Question 9**

- (a) This question was reasonably well done although some candidates had addition symbols as part of the equilibrium expression.
- (b) The position of equilibrium was well answered by most candidates indicating the position would tend to the products side. Most gave a reasonable explanation for this. However the affect on the equilibrium constant was very poorly done since the value of the constant would not change. Very few candidates explained this properly.

- (c) Many candidates were able to understand that the reaction was exothermic, but those candidates who could not interpret the missing delta symbol were not penalised if they mentioned that they were unsure. A lot of candidates mentioned both the changes in the position of equilibrium and also the change in the equilibrium constant but had contradicting answers. Most answers were well explained.
- (d) To gain full marks, candidates were required to mention that there would be no change to either the partial pressures or the concentration or the amount of the reacting particles due to the inclusion of the inert gas.

There were quite a few completely irrelevant answers.

### Question 10

- (a) Very few candidates successfully gained full marks for this question. Although many candidates realised that an I.C.E table or equivalent was required. Many errors were abundant in finding the concentrations of each species at equilibrium, the most common being a concentration subtracted from the amount of moles of carbonyl chloride.
- (b) This question was very poorly attempted by most candidates. Very few candidates had realised that the equilibrium constant found in question 10 (a) was to be used in the equilibrium expression to find the carbonyl chloride concentration. Candidates were given part marks if they again applied the equilibrium expression or created another I.C.E table incorrectly.

### Question 11

This question was very well attempted by the majority of candidates even though the reaction equations had significant symbol errors and formatting errors. Most candidates had figured the question to be a Hess' Law question and performed the necessary steps to get a correct answer.

There were a few errors where candidates had shown that they needed to use multiples of equations 2 and 3 but then actually forgot to multiply the enthalpy values.

Some candidates had the change in enthalpy equation around the wrong way and were slightly penalised. A significant number of candidates lost half a mark because they did not provide units in kJ along with their numerical answer.

Some candidates had left this entire question completely blank which obviously could have been for various reasons making the marking of this question impossible for those.

**Question 12**

The criterion 4 question was very poorly done by a significant number of candidates, however considering that an error in the equation left the question slightly ambiguous as to whether it was an equilibrium question or rate of reaction question this seemed quite understandable.

The correct answers that were sought for this question was either the  $\text{Mn}^{2+}$  acted as an autocatalyst as it was produced or that the reaction must have been exothermic for the rate of reaction to have sped up.

A large number of candidates believed that adding more permanganate to the mixture had increased the concentration of the permanganate but since a clear colour change had occurred after five minutes the permanganate had been completely reduced to manganese(II) ions.

- a) (i) marks were awarded if the candidate's hypothesis was sufficient to explain the observations.  
(ii) marks were awarded if candidates explained why their hypothesis was able to fit the observations.
- b) Candidates gained full marks if the test that had been written had sufficient information showing the steps they would take to confirm or reject the hypothesis. Many candidates wrote insufficient information to be a reasonable test or wrote nothing at all.

Candidates were given credit if they used a test where the concentration was changed and the change in the reaction rates found.

Some candidates chose to test by performing a titration of the oxalate against acidified permanganate as the question stated with no changes to testing conditions.

Some candidates chose to make comparisons by using other irrelevant reactants as part of their testing procedure.

**Part 3 – Criteria 4 and 9****Question 13**

- (a) Generally answered well.

Some candidates used far too simplistic e.g. boron  $\text{B} = 2)3$  shell designations rather than full electron configurations.

- (b) (i) This question actually required an explanation of why the inner shell electrons are so difficult to remove. Some candidates incorrectly stated that they were the most difficult to remove because they were furthest out.

One approach (taken by more than one candidate), which highlighted a possible ambiguity in the question, was a comparison of the energy required between the boron and fluorine atoms relating the number of protons to the attraction for the 1s electrons.

- (ii) This question required a **link** between the evidence given in the graph and the location of the atoms in the periodic table. The number of points on the graphs, was correctly noted by almost all candidates, as being the number of electrons. However it was not acceptable to simply note the number of electrons, equate this to the atomic number and thus place the atom on the periodic table. To attain full marks candidates needed to observe the ‘jump’ or discontinuity in the energies of the groups, showing discrete shells and hence period of the atom on the periodic table. The group was noted by few candidates as being the number of valence electrons (points) in the group on the graph with least energy.
- (c) The correct formula for the compound was awarded 1 mark, whereas a consistent diagram was awarded 1 mark.
- (d) This question was stated in a fashion that some candidates found difficult to interpret, however the information was available. To obtain full marks candidates needed to recognise that the weak intermolecular bonds (indicated by the low boiling point) are indicative of a covalent molecular substance. Few candidates explained that the covalent bonding **WITHIN** the molecule can be confirmed by looking at the size of the boron atom. Boron atoms being quite small mean that the outer electrons don’t experience the electron shielding of other group 3 elements and hence are unlikely to lose electrons. A number of candidates looked at boron’s position on the Periodic Table and assumed ionic bonding.

#### Question 14

A statement of electronegative/electropositive behaviour was given by most candidates and related to the valence electron shells (particularly of the noble gases).

To gain full marks, both a description of the increasing nuclear charge across the row and a comparison of noble gases to the halogens were required.

#### Question 15

Most candidates correctly identified the structures.

Candidates should however avoid using representations of benzene with fixed double bonds; delocalisation with a ring is preferred.

The main errors occurring were due to candidates confusing the 'pent' and 'prop' prefixes. Some very brief skeleton structures were presented by some candidates.

### Question 16

- (a) A part mark was deducted when water was not shown as a product. Condensed or Full structural formulae were accepted.
- (b) A significant proportion of candidates failed to realise there were both primary and tertiary alcohol functional groups present in 2-methylpropan-1,2-diol.

The primary alcohol group will be oxidised to a carboxylic acid with **excess** oxidising agent, rather than an aldehyde. The tertiary alcohol will not be oxidised.

- (c) Most candidates recognised the presence of the 3 hydroxyl groups, fewer mentioned the resulting hydrogen bonding and even fewer referred to the significant extent of hydrogen bonding being the cause of the relatively high boiling point. A number of candidates stated that the OH group was a strong bond requiring a lot of energy to break.
- (d) Few candidates successfully represented the correct addition polymer. Most candidates drew the monomer, but many failed to recognise the double bond is broken in formation of the polymer. Common also was the representation of the polymer with repeating units comprised of 3 carbons linearly joined as being part of the polymer chain.

### Question 17

The majority of candidates answered this question very poorly.

Few candidates recognised that the compound had two functional groups present. It was in fact an **enol**.

The question seemed to cause some confusion regarding the 'clue' about the initial structure reacting with bromine. The 'reaction' of aldehydes with bromine was used by a number of candidates in question 18.

The fact that the initial structure could be oxidised to form an acidic product would indicate either an alcohol or aldehyde.

Compound C did not follow Markovnikov's Rule, but the fact that the clue regarding the magnesium indicated that D was a **dioic** acid. This was confirmed by the last clue but was not realised by the vast majority of candidates.

### Question 18

This question was answered reasonably well by many candidates and was the best attempted out of the Criterion 4 questions in this exam. Many candidates could demonstrate some understanding of the chemistry of organic functional groups.

A key to this question was the statement that all of the organic unknowns were soluble in water, indicating short carbon chain lengths.

To obtain full marks in this question it was essential that the candidate not only described a correct experimental procedure, but that they **stated the expected observations**.

A relatively commonly suggested test to identify the unknowns was the determination of melting/boiling points. However it should be realised that this is generally only really valid for molecules with the same number of carbons, and may be ambiguous at best.

A number of quite complex experimental tests were proposed including, silver mirrors, 2,4-dinitrophenylhydrazines, and Benedict's.

Other procedures indicated knowledge of the organic chemistry but a poor understanding of the experiments, e.g. noting an decrease in pH on reaction with excess acidified permanganate solution.

### Part 4 – Criteria 4 and 10

It was noted that the majority of candidates solved equations by substituting values into equations before rearranging the equation. This led to many arithmetic errors through miscopying numbers from one line to the next. Overall, a high proportion of candidates made errors in transcribing numbers and used inappropriate numbers of significant figures. A penalty for such an error was only applied once in a question so that it was possible to score 9 out of 10 for a question even in the final answer was wrong.

### Question 19

This question was successfully answered by most candidates using:

$$V_2 = \frac{p_1 V_1 T_2}{p_2 T_1} = 6.99 \times 10^3 \text{ L}$$

Some candidates mixed up initial and final values or forgot to convert temperatures to absolute temperatures.



**Question 20**

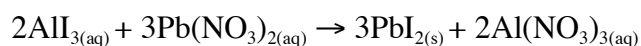
$$M = \frac{m}{n} = \frac{mRT}{pV} = \frac{3.91 \text{ g} \times 8.315 \text{ J mol}^{-1}\text{K}^{-1} \times 296 \text{ K}}{125 \text{ kPa} \times 1.75 \text{ L}} = 44.0 \text{ g mol}^{-1}$$

$$M_r = 44.0$$

Few candidates answered to an appropriate number of significant figures.

**Question 21**

The majority of candidates were able to obtain the correct answer; however, the equation was often wrongly balanced or ignored. To obtain full marks it was necessary to identify the limiting reagent.



$$n(\text{AlI}_3) = 0.250 \text{ mol L}^{-1} \times 0.125 \text{ L} = 0.0312_5 \text{ mol}$$

$$n(\text{Pb}(\text{NO}_3)_2) = 0.200 \text{ mol L}^{-1} \times 0.150 \text{ L} = 0.0300 \text{ mol}$$

Thus,  $\text{Pb}(\text{NO}_3)_2$  is the limiting reagent and so the  $n(\text{PbI}_2) = n(\text{Pb}(\text{NO}_3)_2)$

$$m \text{ PbI}_2 = 0.0300 \text{ mol} \times 461.0 \text{ g mol}^{-1} = 13.8 \text{ g}$$

It was disappointing to see the number of mistakes in finding the molar mass of  $\text{PbI}_2$ .

**Question 22**

This question was done very poorly.

- (a) Most failed to find the molar mass of  $\text{K}_2\text{Cr}_2\text{O}_7 = 294.0 \text{ g mol}^{-1}$

$$n \text{ K}_2\text{Cr}_2\text{O}_7 = \frac{11.32 \text{ g}}{294.0 \text{ g mol}^{-1}} = 3.848 \times 10^{-2} \text{ mol}$$

$$c \text{ K}_2\text{Cr}_2\text{O}_7 = \frac{3.848 \times 10^{-2} \text{ mol}}{0.2000 \text{ L}} = 0.1924 \text{ mol L}^{-1}$$

- (b) Many confused the volumes of samples and standard solutions and failed to use the ratio of the  $\text{Fe}^{2+}$  to  $\text{Cr}_2\text{O}_7^{2-}$ .

$$n \text{ Cr}_2\text{O}_7^{2-} = 0.1924 \text{ mol L}^{-1} \times 0.02080 \text{ L} = 4.002 \times 10^{-3} \text{ mol}$$

$$n \text{ Fe}^{2+} = 6 n \text{ Cr}_2\text{O}_7^{2-} = 2.401 \times 10^{-2} \text{ mol}$$

$$[\text{Fe}^{2+}] = \frac{2.401 \times 10^{-2} \text{ mol}}{2.000 \times 10^{-2} \text{ L}} = 1.200_5 \text{ mol L}^{-1}$$

- (c) A minority of candidates were able to use the original information to find the % Ni in the alloy.

$$n(\text{Fe}) = 1.200_5 \text{ mol L}^{-1} \times 0.1000 \text{ L} = 0.1200_5 \text{ mol}$$

$$\text{mass Fe} = 0.1200_5 \text{ mol} \times 55.85 \text{ g mol}^{-1} = 6.705 \text{ g}$$

$$\% \text{Fe} = \frac{6.705 \text{ g}}{11.60 \text{ g}} \times 100 \% = 57.80 \%$$

$$\% \text{Ni} = 100.00 \% - 57.80 \% = 42.20 \%$$

### Question 23

- (a) It was pleasing to note that many recognised that  $\text{pOH} = 14.0 - 12.4 = 1.6$

$$[\text{OH}^-] = 10^{-1.6} \text{ mol L}^{-1} = 0.025 \text{ mol L}^{-1}$$

Those who found the concentration of hydrogen ions were awarded one mark.

- (b) Less than 5 % of candidates recognised that  $[\text{Ca}^{2+}] = \frac{1}{2} [\text{OH}^-]$  or found the molar mass of calcium hydroxide.

$$[\text{Ca}^{2+}] = \frac{1}{2} [\text{OH}^-] = 0.012_5 \text{ mol L}^{-1}$$

$$\text{Solubility} = c(\text{Ca}(\text{OH})_2) \times M(\text{Ca}(\text{OH})_2) = 0.012_5 \text{ mol L}^{-1} \times 74.1 \text{ g mol}^{-1} = 0.93 \text{ g L}^{-1}.$$

### Question 24

It was pleasing that many candidates achieved full marks on this question.

- (a)  $\text{Cr}^{3+}_{(\text{aq})} + 3\text{e}^- \rightarrow \text{Cr}_{(\text{s})}$

$$n \text{Cr} = \frac{255 \text{ g}}{52.0 \text{ g mol}^{-1}} = 4.90_4 \text{ mol}$$

$$n \text{e}^- = 3 n \text{Cr} = 14.7_1 \text{ mol}$$

$$t = \frac{n \text{e}^- F}{I} = \frac{14.7_1 \text{ mol} \times 96485 \text{ C mol}^{-1}}{125 \text{ C s}^{-1}} = \frac{1.13_5 \times 10^4 \text{ s}}{3600 \text{ s h}^{-1}} = 3.15 \text{ h} = 3 \text{ h } 9 \text{ min}$$

- (b) Some candidates correctly reasoned that if the time was shorter by a factor of 3.15, the current would increase by the same factor.

$$I = 3.15 \times 125 \text{ A} = 394 \text{ A}$$

**Question 25**

Very few candidates were able to achieve full marks. Answers tended to be vague and generally scored poorly. Few saw the point of (b).

- (a) The first point gave sufficient information to find the charge on M.

$$n \text{ M} = 0.50 \text{ mol L}^{-1} \times 0.025 \text{ L} = 0.012_5 \text{ mol}$$

$$n \text{ SO}_4^{2-} = 0.25 \text{ mol L}^{-1} \times 0.050 \text{ L} = 0.012_5 \text{ mol}$$

It follows that M must have a charge of 2+.

About 6 candidates recognised that by weighing the dried precipitate of  $\text{MSO}_4$  its molar mass could be calculated by dividing the mass by  $0.012_5 \text{ mol}$ . The relative atomic mass of M could be found by subtracting  $96.1 \text{ g mol}^{-1}$  from the molar mass.

Many candidates realised that it was important to weigh the electrodes before and after electrolysis and that this would provide useful information, unfortunately few recognised that this would yield  $A_r/z$  rather than  $A_r$ .

- (b) Few candidates realised that because the cells were in series that the mass of Ag deposited could be used to find the amount of electrons so that it was not necessary to know the current and time. Nevertheless sensible answers received some credit.

**Comments from the TQA's Chief Executive Officer about the 2006 Examination Paper:**

The role of the Assessment Panel, led by the Chief Marking Examiner, is to take into account in the marking and determination of cut-offs any problems, ambiguities or faults in questions.

The paper was created by a setting examiner, scrutinised by critics and, to give us an additional check on the demands made by the paper, worked through by a person who had previously successfully completed senior secondary chemistry. We do not have comparative information about previous chemistry examinations. An analysis of the marks on each item, however, shows that:

- the items have an average facility (difficulty) of 52% (the average mark on each question is 52% of the available marks). This is a common value for the average facility for a test that is designed to distinguish student achievement.
- there are two very easy items (facilities > 80%) and no correspondingly difficult items (facility < 20%). Half the items have facilities close to the average facility (42% to 62%)
- the highest score is 153 out of 160 possible marks.

The total test has a reliability coefficient (Cronbach's alpha – a lower bound estimate) of 0.896, which is a satisfactory value for a test of this nature.

The standard procedure when there are problems, faults or errors on external examination papers. Is:

- the Assessment Panel, led by the Chief Marking Examiner, works with markers to make sure that student responses are assessed taking into account any problems with questions on the paper.
- borderline consideration, which involves a review by the Assessment Panel of a student's responses to all questions, has been applied.
- a qualitative review by the Assessment panel of a student's script is made whenever there have been quantitative or qualitative indications of any possible anomaly, including where there is a significant difference between their internal ratings and corresponding external ratings.

We asked the Assessment panel to look very carefully for any evidence in student scripts of impact of the printing faults on their performance and to take this into account in reaching their decisions.

Quantitative analyses of the marks have shown the following:

- a. The damaged items (the ones affected by the printing faults) have a higher facility (are easier) than the undamaged ones.
- b. A principal components analysis of the data does **not** show that the damaged items form an obviously identifiable group.
- c. We used a sub-score based on the undamaged items to test for differences in student performance on the undamaged and the damaged items. The correlations of scores on individual items with scores on this sub-score (omitting the individual item from the sub-score as required) does **not** show that there is any systematic difference in student performance on the damaged and undamaged items.
- d. A linear regression modelling student performance on the damaged items from student performance on the undamaged items was used to identify potential outliers – students with a much lower performance on the damaged items than would be expected from their performance on the undamaged items. The one significant outlier and some near outliers were referred to the assessment panel for review of their scripts along with other potentially anomalous or borderline cases.

Inconsistency in response to the printing issue in different examination centres:

We have checked with every examination centre. At three centres supervisors went outside the boundary set by our rules covering the advice they can give students. At the other centres, either students did not ask any questions (11 centres) or they were told to work with the paper as it was. We take the departure from our rules, however small, very seriously.

We have looked for any evidence of systematic impact of the different advice at these three centres. There is none apparent. The search for evidence of systematic impact included an analysis of the average differences between performance on the damaged and undamaged items at different examination centres as follows:

- a. Calculate the residuals (difference between observed and modelled scores) for student performance on the damaged and undamaged items.
- b. Compare the mean residual at the three centres with the other centres. There is no significant difference.
- c. Perform a linear regression, modelling the residuals from gender and from examination centre. There are significant differences in some centres, but these differences are **not** associated with the advice given to students. While overall there is a difference in residuals between girls and boys, the girls at some examination centres performed (significantly) relatively higher on the damaged items than on the undamaged items.

We have sought to identify and use any evidence of the impact of the faults with this Chemistry examination to give students fair results, to give them credit for the achievement they have demonstrated taking into consideration the possible impact of the faults in the paper. The Assessment Panel, led by the Chief Marking Examiner, have worked with skill and dedication and I want to record my appreciation of this.

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Q1. (a) (i)  $Br_2$  OK ( $Br^+$ ) = 0

(ii)  $BrO_3^-$  Ox ( $Br^+$ ) = +5

(b)  $2Br^- \rightarrow Br_2 + 2e^-$  (x 5)

$2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$

Sum the 2 equations:

$10Br^- + 2BrO_3^- + 12H^+ \rightarrow 6Br_2 + 6H_2O$

or  $5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$

Q2.  $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$   $E^{\circ} = +1.36$

(REDUCTION @ CATHODE)

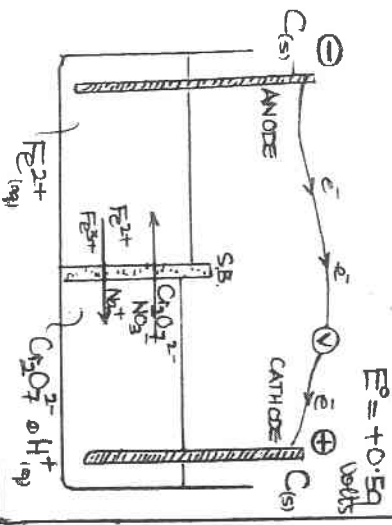
$Fe^{2+} \rightarrow Fe^{3+} + e^-$   $E^{\circ} = -0.77$

(OXIDATION @ ANODE)

NET CELL EQN:

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

$E^{\circ} = +0.59$  volts



Shortcut for the cell is  $C(s) / Fe^{2+} / Fe^{3+} // Cr_2O_7^{2-} / Cr^{3+} / C(s)$

(b) Max. voltage =  $(+1.36 - 0.77)$   
 $E_{NET}^{\circ} = 0.59$  volts

(c) The anode  $\frac{1}{2}$  cell will be the main cause because the  $Fe^{2+}$  ions will move away from the anode towards the cathode. Similarly the  $Cr_2O_7^{2-}$  ions move away from the cathode towards the anode. But the net cell reaction shows  $Fe^{2+}$  ions are used at ox the mole amount of  $Cr_2O_7^{2-}$

$\therefore$  the migration of  $Fe^{2+}$  ions results in the greater effect on  $E^{\circ}$  than the migration of dichromate ions ( $Cr_2O_7^{2-}$ ).

(d)  $Fe(s)$  is a stronger reducer than  $Fe^{2+}$   $\therefore$  if  $Fe(s)$  is used as the anode the  $\pm$  equation would be  $Fe(s) \rightarrow Fe^{2+} + 2e^-$   $E^{\circ} = +0.41$

as opposed to:  $Fe^{2+} \rightarrow Fe^{3+} + e^-$   $E^{\circ} = -0.77$   
 Thus, the net cell reaction would now be:  
 $Cr_2O_7^{2-} + 14H^+ + 3Fe(s) \rightarrow 2Cr^{3+} + 3Fe^{2+} + 7H_2O$   
 $E^{\circ} = +1.36 + 0.41$   
 $= +1.77$  V

$\therefore$  Initial cell's EMF would be 1.77V

Q3.

ANODE:  $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

CATHODE:  $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

If there is a high chloride ion concentration,  $Cl_2$  gas will form at the anode but if the concentration of  $Cl^-$  is lower than  $Br_2$  or possibly  $O_2$  will form at the anode  $2Br^-(aq) \rightarrow Br_2 + 2e^-$  or  $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$   
 In either case,  $H_2$  gas will be formed at the cathode by way of the reduction of water (see Q4)

Q4 (a) (i) When two different metals (Cu & Fe) are in electrical contact in an aqueous environment, the more reactive metal (Fe) will undergo oxidation ( $\therefore$  cathode) at the anode:  $Fe(s) \rightarrow Fe^{2+} + 2e^-$

The less reactive metal (Cu) becomes the site where reduction occurs  $\therefore$  the cathode:  $2H_2O(l) + O_2(g) + 4e^- \rightarrow 4OH^-(aq)$   
(the very large cathode area makes this corrosion rapid)

$\therefore$  the nails (Fe) corrode (rust) away and the Cu(s) is protected. The EMF generated by the  $Fe | Fe^{2+} || H_2O | O_2 | OH^- | Cu(s)$  cell increases the rate of corrosion.

(c) corrosion of the iron could be prevented by:  
 (i) preventing electrical contact between the  $Fe(s)$  &  $Cu(s)$  by

placing a non-electrically conducting material between the Cu sheet and the Fe nails.

(ii) using copper nails instead of iron nails.

$\therefore$  2 identical metals in contact  $\Rightarrow$  No EMF  $\Rightarrow$  no corrosion.

Q5. (CRITERION 4)

(a) one needs to be assured that no other metal ions give the same results as:

$Fe^{3+}$  with  $SCN^- \Rightarrow$  BLOOD RED!  
 $Fe^{2+}$  with  $Fe(CN)_6^{3-} \Rightarrow$  DEEP BLUE!  
 eg ensure  $Fe^{2+}$  doesn't give a blood red colour with  $KSCN(aq)$

(b) Test the reactivity of  $Fe^{2+}$  ions with each of  $Cl_2(aq)$ ,  $Br_2(aq)$  and  $I_2(aq)$ . If  $Fe^{2+}$  is oxidised to  $Fe^{3+}$  by  $Cl_2$ ,  $Br_2$  or  $I_2$  then  $Fe^{3+}$  will be detectable using the  $SCN^-$  and a deep red colour will be observed. Only oxidisers more powerful than  $Fe^{3+}$  should oxidise  $Fe^{2+}$ .

eg,  $I_2(aq)$  won't oxidise  $Fe^{2+}$  to  $Fe^{3+}$  but  $Cl_2$  and  $Br_2$  will  $\therefore Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$  fits in between  $I_2$  &  $Br_2$   $\pm$  eqns!

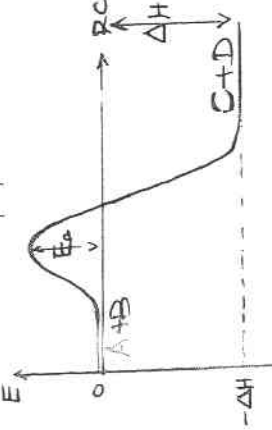
(c) React  $Fe^{3+}$  with  $I^-$ ,  $Cl^-$  &  $Fe^{2+}$  soln. Only with  $I^-$  will  $Fe^{3+}$  be reduced to  $Fe^{2+}$  and give a 'blue' colour with  $Fe(CN)_6^{3-}$ .

$\therefore Cl^- < Br^- < Fe^{2+} < I^-$   
 INCREASING REDUCERS!  
 STRENGTH AS REDUCERS!

CRITERION 5

Q6. Consider  $2\text{H}^+_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$   
 As the reaction proceeds, the concentrations of  $[\text{H}^+]$  and  $[\text{CO}_3^{2-}]$  decrease because these reactants are used up (consumed). This means there are fewer & fewer effective collisions between  $\text{H}^+_{(aq)}$  &  $\text{CO}_3^{2-}$  as their concentrations decrease.  $\therefore$  the reaction rate progressively decreases with time.

Q7. Consider  $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$   $\Delta H = \text{EXO}$   
 As  $\text{A}$  &  $\text{B}$  react there is a release of energy  $\therefore$  the reaction temp. of mixture increases  $\rightarrow$  ave  $E_k$  of  $\text{A}$  and  $\text{B}$  increases  $\therefore$  more effective collisions occur  $\rightarrow$  faster rate  $\rightarrow$  more heat release  $\therefore$  rate of reaction accelerates due to continuing temp. increase  $\rightarrow E_k \uparrow \therefore$  faster rate. Thus reaction rate may become explosively fast! **DANGER!!**



Q8.  $-\overset{\cdot}{\text{C}}-\overset{\cdot}{\text{C}}-\overset{\cdot}{\text{C}}- + 5(\text{O}=\text{O}) \rightarrow 3(\text{O}=\text{C}=\text{O}) + 4(\text{H}-\text{O}-\text{H})$

<u>BONDS BROKEN</u>		<u>kJ (RELEAS)</u>	
$2 \times (\text{C}-\text{C})$	$2 \times 347$		$+ 694$ kJ
$8 \times (\text{C}-\text{H})$	$8 \times 435$		$+ 3480$ kJ
$5 \times (\text{O}=\text{O})$	$5 \times 498$		$+ 2490$ kJ
$\therefore$ Total			$+ 6664$ kJ

<u>BONDS FORMED</u>		<u>kJ (RELEASED)</u>	
$6 \times (\text{C}=\text{O})$	$6 \times 805$		$= -4830$ kJ
$8 \times (\text{O}-\text{H})$	$8 \times 464$		$= -3712$ kJ
$\therefore$ Total			$= -8542$ kJ

Comparing; there is a net release of  $-1878$  kJ  $\therefore$   
 $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$   
 $\Delta H = -1878$  kJ

Q9. (a)  $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$   
 (b) CHANGE: add  $\text{SO}_2$   
EFFECT system adjusts to remove  $\text{SO}_2$   
RESULT forward reaction is favoured and position of equilibrium shifts so as to produce more  $\text{SO}_3$ .  
 $K_c$  would not alter because the temperature is kept constant.

(c) CHANGE  $T \downarrow$   
EFFECT  $T \uparrow$   
RESULT position favours the exothermic direction  $\therefore$  more  $\text{SO}_3$  is present at equilibrium and less  $\text{O}_2$  &  $\text{SO}_2$   $\therefore K_c$  DECREASES!

Q9 (d) Adding  $\text{H}_2(g)$  at constant volume will cause an increase in total pressure, but the increase is due to the pHe.  $\therefore p_{\text{SO}_2}, p_{\text{O}_2}$  &  $p_{\text{SO}_3}$  DON'T alter  $\therefore$  there is no change to the equilibrium position.  $\therefore$  adding  $\text{H}_2(g)$  at const T & V has no effect on the position of equilibrium.

Q10. (a)

$\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$			
INITIAL	2.25	0	0
CHG	-0.15	+0.15	+0.15
EQUIL	2.10	0.15	0.15

$V = 2\text{L}$

$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{0.15 \times 0.15}{2.10} = 0.0107 \text{ (M)}$$

(b)  $[\text{Cl}_2] = [\text{CO}] = 0.200 \text{ mol L}^{-1}$   
 $\Rightarrow K_c = 0.11 = \frac{0.200 \times 0.200}{[\text{COCl}_2]}$   
 $\therefore [\text{COCl}_2] = \frac{0.200 \times 0.200}{0.11} = 3.6 \text{ (2 sf)}$

$\therefore$  New  $[\text{COCl}_2] = 3.6 \text{ mol L}^{-1}$

Q11.  
 Eq 1  $\times$  reverse  $\Delta H = +277$  kJ  
 Eq 2  $\times 2$   $\Delta H = -786$  kJ  
 Eq 3  $\times 3$   $\Delta H = -852$  kJ  
 Summing (Hess's Law) gives  
 $\text{CaH}_2\text{O} + 3\text{O}_2 \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(g)$   
 $\Delta H = -1361$  kJ

Q12 (CRITERION 4)

(a) A number of possible answers exist eg  
 •  $\text{Mn}^{2+}$  is a catalyst  
 • the reaction is exothermic  $\therefore$  becomes faster as temp. increases etc...

(ii) If  $\text{Mn}^{2+}$  is a catalyst for the reaction, then initially there is none present but as the reaction proceeds, the amount of  $\text{Mn}^{2+}$  catalyst formed is increasing  $\therefore$  rate continues to increase.

(1) Test the hypothesis by adding additional  $\text{Mn}^{2+}$  in the form of (say)  $\text{MnSO}_4(aq)$  to the reaction flask and see if the  $\text{CO}_2$  bubbles off more rapidly. This shows a faster rate but we need to check finally that the  $\text{Mn}^{2+}$  is still present at the end and NOT changed, otherwise  $\text{Mn}^{2+}$  could not be described as a CATALYST!





CRITERION 10.

Q19.

$$\left. \begin{aligned} P_1 &= 104 \text{ kPa} \\ V_1 &= 2250 \text{ L} \\ T_1 &= 298 \text{ K} \end{aligned} \right\} \begin{aligned} P_2 &= 245 \text{ kPa} \\ V_2 &= ? \text{ L} \\ T_2 &= 218 \text{ K} \end{aligned}$$

Thus  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\rightarrow \frac{104 \times 2250}{298} = \frac{245 \times V_2}{218}$$

$$\therefore V_2 = \left( \frac{2250 \times 104 \times 218}{245 \times 298} \right) \text{ L} = 6987 \text{ L}$$

$\therefore$  Final volume =  $699 \times 10^3 \text{ L}$

Q20.

$P = 125 \text{ kPa}$

$V = 1.75 \text{ L}$

$n = \left( \frac{3.91}{M_r} \right) \text{ mole}$

$R = 8.31$

$T = 296 \text{ K}$

Thus, using  $PV = nRT$

$$\rightarrow 125 \times 1.75 = \frac{3.91}{M_r} \times 8.31 \times 296$$

$$\therefore M_r = \left( \frac{3.91 \times 8.31 \times 296}{125 \times 1.75} \right) = 44.0$$

$= 44.0$

$\therefore$   $M_r$  of unknown gas = 44.0

$\therefore$  molar mass of gas = 44.0 g mol<sup>-1</sup>

Q21.



$n(\text{AlI}_3) = (0.250 \times 0.125) \text{ mole} = 0.0313 \text{ mole}$

$n(\text{Pb(NO}_3)_2) = (0.200 \times 0.150) \text{ mole} = 0.0300 \text{ mole}$  (limit)

$\therefore n(\text{PbI}_2) \text{ ppt} = 0.0300 \text{ mole}$

$\rightarrow$  mass of  $\text{PbI}_2 \text{ ppt} = (0.0300 \times 461) \text{ g} = 13.8 \text{ g}$

Q22.

(a)  $n(\text{K}_2\text{Cr}_2\text{O}_7) = \frac{\text{mass}}{M} = \frac{2.94}{294} = 0.01 \text{ mole}$

$\therefore [\text{K}_2\text{Cr}_2\text{O}_7] = \frac{\text{mole}}{V} = \frac{0.01}{0.200} = 0.05 \text{ mol L}^{-1}$

(b)  $n(\text{Cr}_2\text{O}_7^{2-}) = \text{molarity} \times V = 0.05 \times 0.200 = 0.01 \text{ mole}$

$\therefore n(\text{Fe}^{2+}) = 4.00 \times 10^{-3} \text{ mole} = 0.004 \text{ mole}$

$\rightarrow [\text{Fe}^{2+}] = \frac{\text{mole}}{V} = \frac{0.004}{0.020} = 0.20 \text{ mol L}^{-1}$

(c). Thus, in the original solution of volume 0.100 L

$n(\text{Fe}^{2+}) = 0.120 \text{ mole}$

$\therefore$  mass  $\text{Fe} = (0.120 \times 55.8) \text{ g} = 6.70 \text{ g}$

$\therefore$  Percentage  $\text{Fe}$  in alloy

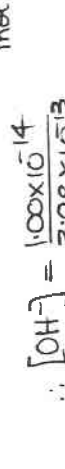
$\rightarrow \left( \frac{6.70}{11.60} \times 100 \right) \% = 57.7\%$

$\therefore$  percentage  $\text{Ni} = (100 - 57.7)\% = 42.3\%$  (by mass)

Q23.

(a)  $\text{pH} = 12.4 \therefore [\text{H}^+] = 10^{-12.4} = 3.98 \times 10^{-13} \text{ mol L}^{-1}$

$\therefore [\text{OH}^-] = \frac{1.00 \times 10^{-14}}{3.98 \times 10^{-13}} = 0.0251 \text{ mol L}^{-1}$



$\therefore$  solution with hydroxide ion conc<sup>n</sup> of  $0.0251 \text{ mol L}^{-1}$

$\rightarrow [\text{Ca(OH)}_2] = (0.0251 \times \frac{1}{2}) \text{ mol L}^{-1} = 0.0126 \text{ mol L}^{-1}$

$\rightarrow$  solubility =  $(0.0126 \times 74.0) = 0.929 \text{ g L}^{-1}$

Q25. (cont.)  $n(\text{Ag}) = n(e^-)$  because  $\text{Ag}^+$

Because  $M^{2+} \therefore n(M) = \frac{n(e^-)}{2} \rightarrow n(M) = \text{known and so } Ar(M) = \left( \frac{\text{mass of } M}{n(M)} \right)$

Q24. mass  $G = \left( \frac{A_r \times I \times t}{Z \times 96500} \right) \text{ g}$

$\therefore t = \left( \frac{\text{mass} \times Z \times 96500}{A_r \times I} \right) \text{ sec}$

$= \left( \frac{255 \times 3 \times 96500}{52.0 \times 12.5} \right) \text{ sec}$

$= 1.14 \times 10^4 \text{ sec}$

Time = 3.15 hours.

(b)  $I = \left( \frac{\text{mass} \times Z \times 96500}{A_r \times t} \right)$

$= \left( \frac{255 \times 3 \times 96500}{52.0 \times 60 \times 60} \right)$

$= 394 \text{ amp}$

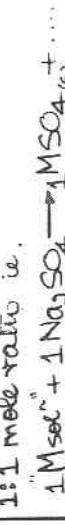
$\therefore$  Current needed = 394 A

Q25. (CRITERION 4)

$n(\text{Na}_2\text{SO}_4) \text{ reacted} = 0.25 \times 50.0 \times 10^{-3} = 0.0125 \text{ mole}$

$n(\text{M}^{2+}) \text{ reacted} = 0.500 \times 2.50 \times 10^{-3} = 0.0125 \text{ mole}$

These solutions thus reacted on a 1:1 mole ratio i.e.



$\therefore$  M must form 2+ ions!

The electrolysis data should thus enable us to determine the  $A_r(M)$

i.e.  $A_r(M) = \left( \frac{\text{mass} \times Z \times 96500}{I \times t} \right)$

where  $m =$  mass of M plated on cathode

$Z = 2$  (from above)

(b) No! Use the mass of the Ag plated out on the series cells

cathode:  $n(\text{Ag}) = \left( \frac{\text{mass}}{108} \right) \text{ mole}$  (CONT. OVER)