GCE

Chemistry A

Unit F325: Equilibria, Energetics and Elements

Advanced GCE

Mark Scheme for June 2014
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All examiners are instructed that alternative correct answers and unexpected approaches in candidates’ scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

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## Annotations available in Scoris

<table>
<thead>
<tr>
<th>Annotation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>Blank Page – this annotation must be used on all blank pages within an answer booklet (structured or unstructured) and on each page of an additional object where there is no candidate response.</td>
</tr>
<tr>
<td>BOD</td>
<td>Benefit of doubt given</td>
</tr>
<tr>
<td>CON</td>
<td>Contradiction</td>
</tr>
<tr>
<td></td>
<td>Incorrect response</td>
</tr>
<tr>
<td>ECF</td>
<td>Error carried forward</td>
</tr>
<tr>
<td>I</td>
<td>Ignore</td>
</tr>
<tr>
<td>NAQ</td>
<td>Not answered question</td>
</tr>
<tr>
<td>NDOD</td>
<td>Benefit of doubt not given</td>
</tr>
<tr>
<td>POT</td>
<td>Power of 10 error</td>
</tr>
<tr>
<td></td>
<td>Omission mark</td>
</tr>
<tr>
<td>RE</td>
<td>Rounding error</td>
</tr>
<tr>
<td>SF</td>
<td>Error in number of significant figures</td>
</tr>
<tr>
<td>✓</td>
<td>Correct response</td>
</tr>
</tbody>
</table>
Abbreviations, annotations and conventions used in the detailed Mark Scheme (to include abbreviations and subject-specific conventions).

<table>
<thead>
<tr>
<th>Annotation</th>
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</tr>
</thead>
<tbody>
<tr>
<td>DO NOT ALLOW</td>
<td>Answers which are not worthy of credit</td>
</tr>
<tr>
<td>IGNORE</td>
<td>Statements which are irrelevant</td>
</tr>
<tr>
<td>ALLOW</td>
<td>Answers that can be accepted</td>
</tr>
<tr>
<td>( )</td>
<td>Words which are not essential to gain credit</td>
</tr>
<tr>
<td>__</td>
<td>Underlined words must be present in answer to score a mark</td>
</tr>
<tr>
<td>ECF</td>
<td>Error carried forward</td>
</tr>
<tr>
<td>AW</td>
<td>Alternative wording</td>
</tr>
<tr>
<td>ORA</td>
<td>Or reverse argument</td>
</tr>
</tbody>
</table>

The following questions should be marked using **ALL** appropriate annotations to show where marks have been awarded in the body of the text:

1(b), 2(b), 3(b)(ii), 4(c)(iii), 5(a), 5(b)(iv), 6c(iii), 6(d), 7(b)(ii), 8(d)
<table>
<thead>
<tr>
<th>Question</th>
<th>Answer</th>
<th>Marks</th>
<th>Guidance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (a) (i)</td>
<td>$2K^+(g) + S^{2-}(g)$</td>
<td>✓</td>
<td>Mark each marking point independently. Correct species AND state symbols required for each mark. For $S^{2-}$, DO NOT ALLOW $S^{-2}$. For $e^-$, ALLOW $e$. For $e^-$ only, IGNORE any state symbols added. ALLOW $k$ and $s$. It can be very difficult distinguishing $K$ from $k$; $S$ from $s$.</td>
</tr>
<tr>
<td></td>
<td>$2K^+(g) + S^-(g) + e^-$</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2K(g) + S(g)$</td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>
1 (a) (ii) (The enthalpy change that accompanies) the formation of one mole of a(n ionic) compound from its gaseous ions (under standard conditions) ✓ ✓

Award marks as follows.
1st mark: formation of compound from gaseous ions
2nd mark: one mole for compound only

DO NOT ALLOW 2nd mark without 1st mark

Note: A definition for enthalpy change of formation will receive no marks

2 IGNORE 'Energy needed' OR 'energy required'
ALLOW one mole of compound is formed/made from its gaseous ions
ALLOW as alternative for compound: lattice, crystal, substance, solid

IGNORE: \(2\text{K}^+(g) + \text{S}^{2-}(g) \rightarrow \text{K}_2\text{S}(s)\)
(question asks for words)

ALLOW 1 mark (special case) for absence of 'gaseous' only, i.e.
the formation of one mole of a(n ionic) compound from its ions (under standard conditions) ✓
### 1 (a) (iii)

**FIRST, CHECK THE ANSWER ON ANSWER LINE**

IF answer $=-2116$ (kJ mol$^{-1}$) award 2 marks

\[
\begin{align*}
-381 - (2 \times 89 + 279 + 2 \times 419 - 200 + 640) &< 0 \\
-381 - 1735 &< 0 \\
\Rightarrow -2116 &< 0 \\
\end{align*}
\]

**ALLOW for 1 mark ONE** mistake with sign OR use of 2:

- $2027$ ($2 \times 89$ not used for $K$)
- $1697$ ($2 \times 419$ not used for $K$)
- $2516$ ($+200$ rather than $-200$ for $S$ 1st electron affinity)
- $+2116$ (wrong sign)
- $-1354$ ($+381$ instead of $-381$)
- $+1354$ ($+1735$ instead of $-1735$)
- $-836$ ($-640$ instead of $+640$)
- $-1558$ ($-279$ instead of $+279$)
- $-1760$ ($-2 \times 89$ instead of $+2 \times 89$)
- $-439$ ($-2 \times 419$ instead of $+2 \times 419$)
- $-2120$ (rounded to 3SF)

**For other answers,** check for a single transcription error or calculator error which could merit 1 mark

**DO NOT ALLOW** any other answers, e.g.

- $-1608$ (2 errors: $2 \times 89$ and $2 \times 419$ not used for $K$)
- $-846$ (3 errors:)
**Mark Scheme**

<table>
<thead>
<tr>
<th>1</th>
<th>(b)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Lowest melting point</td>
<td>KI</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Highest melting point</td>
<td>NaBr</td>
<td>Correct order ✓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Mark 2nd and 3rd marking points independently**

**Attraction and ionic size linked:**
Greater attraction from smaller ions/closer ions/larger charge density ✓
*Comparison needed*

**Energy AND attraction/breaking bonds linked:**
More energy/heat to overcome attraction (between ions)
OR
More energy/heat to break (ionic) bonds ✓

<p>| | | | | | |</p>
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</tbody>
</table>

**TOTAL** 10

**FULL ANNOTATIONS MUST BE USED**

ORA throughout
Response must clearly refer to ions for explanation marks

2nd and 3rd marking point must be comparative

DO NOT ALLOW incorrect named particles, e.g.
‘atoms’, ‘molecules’, Na, Cl, Cl₂, ‘atomic’, etc
DO NOT ALLOW responses using nuclear size or attraction
DO NOT ALLOW responses linked with loss of electrons

ALLOW larger electron density

ALLOW smaller sum of radii gives a greater ionic attraction
IGNORE NaBr has greater ionic attraction
IGNORE NaBr has smallest ionic radius
*(not focussing on size of each ion)*

ASSUME bonds broken are ionic unless otherwise stated
DO NOT ALLOW incorrect named particles, e.g.
‘atoms’, ‘molecules’, Na, Cl, Cl₂, ‘atomic’, etc

Note: Comparison for energy only *(i.e. link between more energy and breaking bonds/overcoming attraction)*
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<tr>
<td>2 (a) (i)</td>
<td>(entropy) decreases AND (solid/ice has) less disorder/ more order/ fewer ways of arranging energy/ less freedom/ less random molecules ✓</td>
<td>1</td>
<td>ORA decreases and reason required for mark ASSUME change is for freezing of water unless otherwise stated DO NOT ALLOW atoms are more ordered</td>
</tr>
<tr>
<td>2 (a) (ii)</td>
<td>(entropy) increases AND (CO₂) gas is formed ✓ Could be from equation with CO₂(g)</td>
<td>1</td>
<td>increases and reason required for mark ASSUME gas is CO₂ unless otherwise stated BUT DO NOT ALLOW an incorrect gas (e.g. H₂) ALLOW more gas</td>
</tr>
<tr>
<td>2 (a) (iii)</td>
<td>entropy decreases AND 3 mol O₂ form 2 mol O₃ OR 3O₂ → 2O₃ OR 3 mol gas form 2 mol gas ✓</td>
<td>1</td>
<td>decreases and reason required for mark For mol, ALLOW molecules ALLOW multiples, e.g. 1½O₂ → O₃; O₂ + ½O₂ → O₃ ALLOW O₂ + O → O₃ Note: DO NOT ALLOW 2 mol gas forms 1 mol gas unless linked to O₂ + O → O₃ IGNORE reaction forms fewer moles/molecules</td>
</tr>
</tbody>
</table>
**2 (b) CARE: responses involve changes of negative values**

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**Feasibility AND $\Delta G$**
- Reaction becomes/is less feasible/not feasible
- $\Delta G$ increases
  - OR $\Delta G$ becomes/is less negative/more positive
  - OR $\Delta G > 0$ OR $\Delta H - T\Delta S > 0$
  - OR $\Delta H - T\Delta S$ becomes/is less negative/more positive
  - OR $\Delta H > T\Delta S$
  - OR $T\Delta S$ becomes/is more negative than $\Delta H$

---

**Effect on $T\Delta S$**
- $T\Delta S$ becomes more negative OR $T\Delta S$ decreases
  - OR $-T\Delta S$ becomes more positive OR $-T\Delta S$ increases
  - OR magnitude of $T\Delta S$ increases
  - OR $|T\Delta S|$ increases

---

**FULL ANNOTATIONS MUST BE USED**

- As alternative for ‘less feasible’
  - ALLOW ‘less spontaneous’
  - OR a comment that implies ‘reaction no longer take place’

- ALLOW for $\Delta G$ increases
  - $\Delta G < 0$ only at low $T$

- **DO NOT ALLOW** $T\Delta S > \Delta H$ (comparison wrong way round)

**NOTE:** Last statement automatically scores 2nd mark ALSO

- IGNORE significance
- IGNORE magnitude for 1st marking point

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**APPROACH BASED ON TOTAL ENTROPY:**

**Feasibility with increasing temperature**
- Reaction becomes less feasible/not feasible
  - AND
  - $\Delta S - \Delta H/T$ OR $\Delta S_{total}$ decreases/ less positive

**Effect on $\Delta H/T$**
- $\Delta H/T$ is less negative OR $\Delta H/T$ increases
  - OR $-\Delta H/T$ decreases
  - OR magnitude of $\Delta H/T$ decreases
| 2 | (c) | (i) | FIRST, CHECK THE ANSWER ON ANSWER LINE  
IF answer = 75.962 OR 75.96 OR 76.0 OR 76, award 2 marks  
------------------------------------------------------------  
\[ \Delta S = (33 + 3 \times 189) - (76 + 3 \times 131) \]  
\[ = (+)131 \text{ (J K}^{-1} \text{ mol}^{-1}) \] ✓  
\[ \Delta G = 115 - (298 \times 0.131) \]  
\[ = (+)75.962 \text{ OR 75.96 OR 76.0 OR 76 (kJ K}^{-1} \text{ mol}^{-1}) \] ✓  
| | | 2 | DO NOT ALLOW \(-131\)  
| | | | ALLOW ECF from incorrect calculated value of \(\Delta S\)  

| 2 | (c) | (ii) | FIRST, CHECK THE ANSWER ON ANSWER LINE  
IF answer = 878 OR 877.9 OR 877.86, award 2 marks  
--------------------------------------------------------------------  
(Minimum temperature when) \(\Delta G = 0\) OR \(\Delta H - T\Delta S = 0\) OR  
(For feasibility) \(\Delta G = 0\) OR \(\Delta G < 0\) OR \(\Delta H - T\Delta S < 0\) OR  
\[ T = \frac{\Delta H}{\Delta S} \] ✓  
\[ T = \frac{115}{0.131} = 878 \text{ K} \] ✓  
| | | 2 | ALLOW total entropy statement:  
\(\Delta S(\text{total}) = 0\) OR \(\Delta S(\text{total}) > 0\)  
ALLOW ECF from incorrect calculated value of \(\Delta S\) from 2(c)(i)  
ALLOW 878 up to calculator value of 877.862595 correctly rounded  

<p>| | | | Total 9 |</p>
<table>
<thead>
<tr>
<th>Question</th>
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</tr>
</thead>
</table>
| 3 (a)    | \((K_c = ) \frac{[C_2H_2] [H_2]^3}{[CH_4]^2} \checkmark\) | 1 | Square brackets are **essential**
|          |        |       | State symbols not required. |
|          |        |       | **IGNORE** incorrect state symbols |
| 3 (b)    | (i) amount of \(H_2 = 3 \times 0.168\) \(= 0.504 \text{ (mol)} \checkmark\) | 1 |
FIRST, CHECK THE ANSWER ON ANSWER LINE
IF answer = 0.153 mol dm$^{-6}$, award 3 marks
IF answer = 0.153 with incorrect units, award 2 marks

IF answer from 3(b)(i) for $n(H_2)$ ≠ 0.504, mark by ECF.

Equilibrium concentrations (from $n(H_2)$ = 0.504 mol dm$^{-3}$)

\[ [\text{CH}_4] = 2.34 \times 10^{-2} \text{ (mol dm}^{-3} \text{)} \]

AND \[ [\text{C}_2\text{H}_2] = 4.20 \times 10^{-2} \text{ (mol dm}^{-3} \text{)} \]

AND \[ [\text{H}_2] = 0.126 \text{ (mol dm}^{-3} \text{)} \]

Calculation of $K_c$ and units

\[ K_c = \frac{4.20 \times 10^{-2} \times (0.126)^3}{(2.34 \times 10^{-2})^2} = 0.153 \text{ } \text{mol}^2 \text{ dm}^{-6} \]

3 significant figures are required

3

FULL ANNOTATIONS MUST BE USED

IF there is an alternative answer, check to see if there is any ECF credit possible using working below

ALLOW ÷ by 4 of equilibrium amounts in all expressions, i.e.

ALLOW $[\text{CH}_4] = \frac{9.36 \times 10^{-2}}{4} \text{ mol dm}^{-3}$

AND $[\text{C}_2\text{H}_2] = \frac{0.168}{4} \text{ mol dm}^{-3}$

AND $[\text{H}_2] = \frac{0.504}{4} \text{ mol dm}^{-3}$

ALLOW ECF from incorrect concentrations or from moles

From moles: 9.36 $\times$ 10$^{-2}$, 0.168 and 0.504, $K_c$ = 2.45 by ECF

ALLOW dm$^{-6}$ mol$^2$

DO NOT ALLOW mol$^2$/dm$^6$

ALLOW ECF from incorrect $K_c$ expression for both calculation and units

COMMON ECF

From 3(b)(i) answer of 0.1404,

$K_c = 3.32 \times 10^{-3}$ 2 marks + units

$K_c = 0.0531$ No ÷ 4 throughout 1 mark + units

NO ECF possible (all data given in question)
### 3 (c)

<table>
<thead>
<tr>
<th>Change</th>
<th>$K_c$</th>
<th>Equilibrium amount of $\text{C}_2\text{H}_2$ / mol</th>
<th>Initial rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature increased</td>
<td>greater</td>
<td>greater</td>
<td>greater</td>
</tr>
<tr>
<td>smaller container</td>
<td>same</td>
<td>smaller</td>
<td>greater</td>
</tr>
<tr>
<td>catalyst added</td>
<td>same</td>
<td>same</td>
<td>greater</td>
</tr>
</tbody>
</table>

Mark by COLUMN

ALLOW obvious alternatives for greater/smaller/same, e.g. increases/decreases; more/less

- ✓
- ✓
- ✓

### 3 (d)

**ONE** mark only
USE ONE TICK ONLY ✓
from TWO uses:

1. fuel cells
2. manufacture of margarine
3. making of ammonia OR Haber process
4. making of HCl/hydrochloric acid
5. making of methanol

Mark by COLUMN

- ✓
- ✓
- ✓

**ONE** mark only
USE ONE TICK ONLY ✓
from TWO uses:

1. fuel cells
2. manufacture of margarine
3. making of ammonia OR Haber process
4. making of HCl/hydrochloric acid
5. making of methanol

Mark by COLUMN

- ✓
- ✓
- ✓

IGNORE just 'fuel'
IGNORE hydrogenation of margarine
ALLOW hydrogenation of fats/oils

DO NOT ALLOW explosives OR fertilisers

Total 10
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>4 (a) (i)</td>
<td>5 OR 5th (order) ✓</td>
<td>1</td>
<td>ALLOW moles/ions/species/particles/molecules/atoms throughout (i.e. emphasis on particles)</td>
</tr>
<tr>
<td>4 (a) (ii)</td>
<td>(stoichiometry in) rate equation does not match (stoichiometry) in overall equation ✓</td>
<td>2</td>
<td>IF number of species is stated, ALLOW 3–5 only (rate equation contains 5 ions) DO NOT ALLOW negative ions would repel (there is a mixture of positive and negative ions) IGNORE more than two reactants collide (not related to rate equation)</td>
</tr>
<tr>
<td>4 (b)</td>
<td><img src="image" alt="Graph" /> Straight upward line AND starting at 0,0 ✓</td>
<td>2</td>
<td>ALLOW lines starting close to 0,0 ALLOW 2nd order line with 'straight' section early or late as long as an upward curve is seen between.</td>
</tr>
<tr>
<td>4 (c) (i)</td>
<td>5.4(0) ✓ 614.4(0) ✓</td>
<td>2</td>
<td>IGNORE sign ALLOW 614 OR 610</td>
</tr>
</tbody>
</table>
| 4 | (c) | (ii) | FIRST, CHECK THE ANSWER ON ANSWER LINE IF answer = $6.7 \times 10^8$ OR $670000000$ dm$^{12}$ mol$^{-4}$ s$^{-1}$, award 3 marks IF answer = $6.7 \times 10^8$ OR $670000000$ with incorrect units, award 2 marks $k$ to >2 SF: 666666666.7 ✓ OR $k$ to 2 SF: $6.7 \times 10^8$ OR $670000000$ ✓✓
units: dm$^{12}$ mol$^{-4}$ s$^{-1}$ ✓

| 4 | (c) | (iii) | $(K_a) = 10^{-3.75}$ OR $1.78 \times 10^{-4}$ (mol dm$^{-3}$) ✓
$[H^+] = \sqrt{1.78 \times 10^{-4} \times 0.0200}$
$= 1.89 \times 10^{-3}$ (mol dm$^{-3}$) ✓

initial rate = $6.7 \times 10^9 \times 0.01 \times 0.015^2 \times (1.89 \times 10^{-3})^2$
$= 5.33 \times 10^{-3}$ to $5.38 \times 10^{-3}$ (mol dm$^{-3}$ s$^{-1}$) OR $5.3 \times 10^{-3}$ to $5.4 \times 10^{-3}$ (mol dm$^{-3}$ s$^{-1}$) ✓

Actual value will depend on amount of acceptable rounding in steps and whether figures kept in calculator even if rounding is written down. ALLOW any value in range given above.

ALLOW ECF from incorrect initial rates if 1st experimental results have not been used. (Look to 4(c)(i) to check) i.e. IF other rows have been used, then calculate the rate constant from data chosen.

For $k$, ALLOW 1 mark for the following:
$6.6 \times 10^8$ recurring
$6.6 \times 10^8$
2 SF answer for $k$ BUT one power of 10 out i.e. $6.7 \times 10^9$ OR $6.7 \times 10^7$

ALLOW units in any order, e.g. mol$^{-3}$ dm$^{12}$ s$^{-1}$

FULL ANNOTATIONS MUST BE USED

For ALL marks, ALLOW 2 SF up to calculator value correctly rounded $1.77827941 \times 10^{-4}$
ALLOW $\sqrt{10^{-3.75} \times 0.0200}$ for first marking point ALLOW $1.88 \times 10^{-3}$ (mol dm$^{-3}$)

ALLOW ECF from calculated $[H^+(aq)]$ and calculated answer for $k$ from 4(c)(ii)
e.g. If no square root taken, $[H^+] = 3.56 \times 10^{-6}$ mol dm$^{-3}$ and rate = $1.91 \times 10^{-8}$ OR $1.9 \times 10^{-8}$ by ECF

Total 13
<table>
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</table>
| 5 (a)    | (Transition element) has **an ion** with an incomplete/partially-filled d **sub-shell/d-orbital** ✓ | 5 | **FULL ANNOTATIONS MUST BE USED**
<p>|          |                                                   |     | ALLOW capital ‘D’ within definition |
|          |                                                   |     | <strong>DO NOT ALLOW</strong> d shell |
|          | Scandium/Sc and zinc/Zn are not transition elements ✓ | 1 | ALLOW if <strong>ONLY</strong> Sc and Zn are used to illustrate d block elements <strong>that are NOT</strong> transition elements |
|          |                                                   |     | This can be from anywhere in the overall response in terms of Sc, Sc$^{3+}$, Zn, Zn$^{2+}$ <strong>OR</strong> incorrect charges, i.e. only Sc$^+$, Sc$^{2+}$, Zn$^+$ |
|          | <strong>Electron configurations of ions</strong>               |     | In electron configurations, <strong>IF</strong> subscripts <strong>OR</strong> caps used, <strong>DO NOT ALLOW</strong> when first seen but credit subsequently |
|          | Sc$^{3+}$ <strong>AND</strong> 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$ ✓ | 1 | ALLOW 4s$^0$ in electron configurations |
|          | Zn$^{2+}$ <strong>AND</strong> 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$3d$^{10}$ ✓ | 1 | <strong>IGNORE</strong> [Ar] |
|          | <strong>Sc$^{3+}$ AND d sub-shell empty / d orbital(s) empty</strong> ✓ | 1 | <strong>IGNORE</strong> electron configurations for other Sc and Zn ions |
|          | <strong>Note</strong>: Sc$^{3+}$ must be the <strong>ONLY</strong> scandium ion shown for this mark | 1 | ALLOW for Sc$^{3+}$: Sc forms a 3+ ion; ALLOW Sc$^{3+}$ |
|          | Zn$^{2+}$ <strong>AND</strong> d sub-shell full /ALL d-orbitals full ✓ | 1 | ALLOW for Zn$^{2+}$: Zn forms a 2+ ion; ALLOW Zn$^{2+}$ |
|          | <strong>Note</strong>: Zn$^{2+}$ must be the <strong>ONLY</strong> zinc ion shown for this mark | 1 | ALLOW Sc$^{3+}$ has no d sub-shell |
|          | <strong>DO NOT ALLOW</strong> ‘d sub-shell is incomplete’ <strong>(in definition)</strong> | 1 | <strong>DO NOT ALLOW</strong> ‘d sub-shell is incomplete’ <strong>(in definition)</strong> |</p>
<table>
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<tbody>
<tr>
<td>5</td>
<td>(b)</td>
<td>(i)</td>
</tr>
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</table>
|   | Donates **two** electron/lone pairs to a metal ion **OR** Co^{3+} **✓** | ALLOW ‘forms two coordinate bonds/dative covalent/dative bonds’ as an alternative for ‘donates two electron/lone pairs’  
**Two is required for 1st marking point**  
**Two can be implied using words such as ‘both’ or ‘each’**  
For metal ion, ALLOW transition (metal) ion |

Electron/lone pair on N **OR** NH$_2$ (groups) **✓**  

Second mark is for the atom that donates the electron/lone pairs  
ALLOW both marks for a response that communicates the same using N as the focus:  
e.g. The two N atoms each donate an electron pair to metal ion |

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<td>5</td>
<td>(b)</td>
<td>(ii)</td>
</tr>
</tbody>
</table>
|   | [Co(H$_2$NCH$_2$CH$_2$NH$_2$)$_2$Cl$_2$]$^+$ **✓** | Square brackets **AND** + charge required  
DO NOT ALLOW any charges included within square brackets  
ALLOW [Co(C$_2$H$_6$N$_2$)$_2$Cl$_2$]$^+$ **OR** [CoC$_4$H$_8$N$_2$Cl$_2$]$^+$  
ALLOW structural **OR** displayed **OR** skeletal formula  
**OR** mixture of the above (as long as unambiguous)  
**IGNORE** [Co(en)$_2$Cl$_2$]$^+$ *simplifies question*  
Within formula, ALLOW ….Cl$_2$, (Cl$_2$)  
ALLOW CO  
Within the context of the question, CO is Co |

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<tr>
<td>5</td>
<td>(b)</td>
<td>(iii)</td>
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<td></td>
<td>6 <strong>✓</strong></td>
<td>1</td>
</tr>
</tbody>
</table>
Note: For each structure, **ALL** NH$_2$ groups must be shown **AND** bonding between Co **AND** N of NH$_2$.

For H$_2$NCH$_2$CH$_2$NH$_2$, **ALLOW** C–C without Hs and NH$_2$ NH$_2$.

**IF NH$_2$ shown without Hs, e.g.** N N, **penalise first time ONLY**

**IF ALL 3 isomers are 'correct', but 2 x Cl AND no Ns, e.g.**

**AWARD 1 mark**

**FULL ANNOTATIONS MUST BE USED**

________________________________________________________________________________________

**IGNORE** charges (**anywhere**) and labels (even if wrong)

Square brackets **NOT** required

Must contain 2 'out wedges', 2 'in wedges' and 2 lines in plane of paper **OR** 4 lines, 1 'out wedge' and 1 'in wedge':

**ALLOW** for bond into paper:

**ALLOW** following geometry throughout:

**TAKE CARE**: structures may be in different orientations.

**FOR H$_2$NCH$_2$CH$_2$NH$_2$, ALLOW** NH$_2$ H$_2$N

(-connectivity within 'loop' only)

**IF Cl$_2$s are shown instead of Cl, penalise 1st time only**
| 5  | (c) (i) | O$_2$/oxygen **bonds** to Fe$^{2+}$/Fe(II) ✓  
Fe$^{2+}$/Fe(II) essential for 1st marking point  
(When required,) O$_2$ substituted OR O$_2$ released ✓  
Fe$^{2+}$ not required for 2nd marking point (e.g. **IGNORE** Fe) | 2  | **ASSUME** that ‘it’ refers to oxygen  
ALLOW O$_2$ binds to Fe$^{2+}$ OR O$_2$ donates electron pair to Fe$^{2+}$  
OR O$_2$ is a ligand with Fe$^{2+}$  
**IGNORE** O$_2$ reacts with Fe$^{2+}$ OR O$_2$ is around Fe$^{2+}$  
ALLOW bond to O$_2$ breaks when O$_2$ required  
OR H$_2$O replaces O$_2$ OR vice versa  
ALLOW CO$_2$ replaces O$_2$ OR vice versa  
ALLOW O$_2$ bonds/binds reversibly |
| 5  | (c) (ii) | $K_{stab} =$  
$\frac{[\text{HbO}_2(\text{aq})]}{[\text{Hb}(\text{aq})][\text{O}_2(\text{aq})]}$ ✓  
ALL Square brackets essential | 1  | ALLOW expression without state symbols (given in question) |
| 5  | (c) (iii) | Both marks require a comparison  
Stability constant/$K_{stab}$ value with CO is **greater** (than with complex in O$_2$) ✓  
(Coordinate) bond with CO is **stronger** (than O$_2$)  
OR CO binds more strongly ✓ | 2  | **IGNORE** (complex with) CO is more stable  
ALLOW bond with CO is less likely to break (than O$_2$)  
OR CO is a stronger ligand (than O$_2$)  
OR CO has greater affinity for ion/metal/haemoglobin (than O$_2$)  
ALLOW CO bond formation is irreversible  
OR CO is not able to break away  
**IGNORE** CO bonds more easily  
OR CO complex forms more easily |
<p>| 5  |  | <strong>Total</strong> | 18 |</p>
<table>
<thead>
<tr>
<th>Question</th>
<th>Answer</th>
<th>Marks</th>
<th>Guidance</th>
</tr>
</thead>
</table>
| **6 (a)** | CH₂COOH + H₂O ⇌ H₃O⁺ + CH₃COO⁻  
Acid 1    Base 2    Acid 2    Base 1 √ | 2 | IGNORE state symbols (even if incorrect)  
ALLOW 1 AND 2 labels the other way around.  
ALLOW ‘just acid’ and ‘base’ labels if linked by lines so that it is clear what the acid–base pairs are  
ALLOW A and B for ‘acid’ and ‘base’  
IF proton transfer is wrong way around  
ALLOW 2nd mark for idea of acid–base pairs, i.e.  
CH₂COOH + H₂O ⇌ CH₃COOH⁺ + OH⁻ ×  
Base 2    Acid 1    Acid 2    Base 1 √ | |
| **6 (b) (i)** | Water dissociates/ionises  
OR  
H₂O ⇌ H⁺ + OH⁻  
OR  
2H₂O ⇌ 2H₃O⁺ + 2OH⁻ √ | 1 | ALLOW K_w = [H⁺][OH⁻]  
OR [H⁺][OH⁻] = 10⁻¹⁴ (mol² dm⁻⁶)  
IGNORE breaking for dissociation  
IGNORE water contains H⁺ and OH⁻  
IGNORE H₂O → H⁺ + OH⁻ i.e. no equilibrium sign  
IGNORE 2H₂O → H₃O⁺ + OH⁻ i.e. no equilibrium sign |
<table>
<thead>
<tr>
<th>6</th>
<th>(b)</th>
<th>(ii)</th>
<th>FIRST, CHECK THE ANSWER ON ANSWER LINE</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td>IF answer = $1.15 \times 10^{-11}$, award 2 marks</td>
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<td>-----------------------------------------</td>
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<td></td>
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<td></td>
<td>$[H^+] = 10^{-3.06} = 8.71 \times 10^{-4}$ (mol dm$^{-3}$) ✓</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[OH^-] = \frac{1.00 \times 10^{-14}}{8.71 \times 10^{-4}} = 1.15 \times 10^{-11}$ (mol dm$^{-3}$) ✓</td>
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<td>ALLOW answer to two or more significant figures</td>
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<td></td>
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<td></td>
<td>2SF: $1.1 \times 10^{-11}$; 4SF: $1.148 \times 10^{-11}$;</td>
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<td></td>
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<td></td>
<td>calculator $1.148153621 \times 10^{-11}$</td>
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<td>2</td>
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<td></td>
<td>IF there is an alternative answer, check to see if there is any ECF credit possible using working below.</td>
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<td>ALLOW 2 SF: $8.7 \times 10^{-4}$ up to calculator value of $8.7096359 \times 10^{-4}$ correctly rounded</td>
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<td>ALLOW alternative approach using pOH:</td>
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<td></td>
<td>pOH = $14 - 3.06 = 10.94$ ✓</td>
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<tr>
<td></td>
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<td></td>
<td>$[OH^-] = 10^{-10.94} = 1.15 \times 10^{-11}$ (mol dm$^{-3}$) ✓</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th>6</th>
<th>(c)</th>
<th>(i)</th>
<th>$2\text{CH}_3\text{COOH} + \text{CaCO}_3 \rightarrow (\text{CH}_3\text{COO})_2\text{Ca} + \text{CO}_2 + \text{H}_2\text{O}$ ✓</th>
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<tbody>
<tr>
<td>1</td>
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<td>IF there is an alternative answer, check to see if there is any ECF credit possible using working below.</td>
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<td>-----------------------------------------</td>
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<td></td>
<td>ALLOW state symbols</td>
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<td></td>
<td>ALLOW provided that reactants on LHS</td>
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<td></td>
<td>For $\text{CO}_2 + \text{H}_2\text{O}$, ALLOW $\text{H}_2\text{CO}_3$</td>
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<td></td>
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<td></td>
<td>ALLOW $\text{Ca(\text{CH}_3\text{COO})}_2$</td>
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<td></td>
<td></td>
<td>ALLOW $(\text{CH}_3\text{COO})_2\text{Ca}^{2+}$</td>
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<td></td>
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<td></td>
<td>BUT DO NOT ALLOW if either charge is missing or incorrect</td>
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<table>
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<tr>
<th></th>
<th>(c)</th>
<th>(ii)</th>
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<td>6</td>
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<td>1</td>
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<tr>
<td></td>
<td>solution contains CH$_3$COOH <strong>AND</strong> CH$_3$COO$^-$ ✓</td>
<td><strong>ALLOW</strong> names: ethanoic acid for CH$_3$COOH ethanoate for CH$_3$COO$^-$</td>
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<td></td>
<td>ALLOW calcium ethanoate <strong>OR</strong> (CH$_3$COO)$_2$Ca for CH$_3$COO$^-$</td>
<td><strong>IGNORE</strong> ‘acid, salt, conjugate base; responses must identify the acid and conjugate base as ethanoic acid and ethanoate</td>
<td></td>
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<td></td>
<td><strong>IGNORE</strong> ethanoic acid is in excess <em>(in question)</em> <strong>BUT DO ALLOW</strong> some ethanoic acid is left over/present/some ethanoic acid has reacted</td>
<td></td>
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<td></td>
<td><strong>IGNORE</strong> equilibrium: CH$_3$COOH $\rightleftharpoons$ H$^+$ + CH$_3$COO$^-$</td>
<td><em>Dissociation of ethanoic acid only</em></td>
<td></td>
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<tr>
<td></td>
<td>(c)</td>
<td>(iii)</td>
<td>Quality of written communication, QWC</td>
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<td>6</td>
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<td>2 marks are available for explaining how the equilibrium system allows the buffer solution to control the pH on addition of H⁺ and OH⁻ (see below)</td>
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<td></td>
<td>CH₃COOH ⇌ H⁺ + CH₃COO⁻ ✓</td>
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<td>CH₃COOH reacts with added alkali OR CH₃COOH + OH⁻ → OR added alkali reacts with H⁺ OR H⁺ + OH⁻ → ✓</td>
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<td>Equilibrium → right OR Equilibrium → CH₃COO⁻ ✓ (QWC)</td>
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<td>CH₃COO⁻ reacts with added acid ✓</td>
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<td>Equilibrium → left OR Equilibrium → CH₃COOH ✓ (QWC)</td>
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**FULL ANNOTATIONS MUST BE USED**

Note: If there is no equilibrium equation then the two subsequent equilibrium marks are not available: max 2

**DO NOT ALLOW** HA ⇌ H⁺ + A⁻

**DO NOT ALLOW** more than one equilibrium equation.

**ALLOW** response in terms of H⁺, A⁻ and HA

**IF** more than one equilibrium shown, it **must** be clear which one is being referred to by labeling the equilibria.

**ALLOW** weak acid reacts with added alkali

**DO NOT ALLOW** acid reacts with added alkali

**ALLOW** conjugate base reacts with added acid

**DO NOT ALLOW** salt/base reacts with added acid
FIRST, CHECK THE ANSWER ON ANSWER LINE
IF answer = 11.48 OR 11.5 (g), award 5 marks

\[ [H^+] = 10^{-5} \text{ (mol dm}^{-3} \text{)} \]

\[ [\text{CH}_3\text{COO}^-] = \frac{1.75 \times 10^{-5}}{10^{-5}} \times 0.200 = 0.350 \text{ mol dm}^{-3} \]

\[ n(\text{CH}_3\text{COONa}/\text{CH}_3\text{COO}^-) \text{ in 400 cm}^3 = 0.350 \times \frac{400}{1000} = 0.14(0) \text{ (mol)} \]

mass $\text{CH}_3\text{COONa} = 0.140 \times 82.0 = 11.48 \text{ OR 11.5 (g)}$

For ECF, $n(\text{CH}_3\text{COONa}/\text{CH}_3\text{COO}^-)$ must have been calculated in step before

---

**FULL ANNOTATIONS MUST BE USED**

IF there is an alternative answer, check to see if there is any ECF credit possible.

Incorrect use of $[H^+] = \sqrt{[\text{CH}_3\text{COOH}] \times K_a}$ scores zero
BUT IGNORE if an alternative successful method is present

Incorrect use of $K_w$, 1 max for $[H^+] = 10^{-5} \text{ (mol dm}^{-3} \text{)}$
BUT IGNORE if an alternative successful method is present

ALLOW \[ n(\text{CH}_3\text{COONa}/\text{CH}_3\text{COO}^-) \]
\[ = \frac{1.75 \times 10^{-5}}{10^{-5}} \times 0.08 = 0.14(0) \text{ (mol)} \]

Note: There is no mark just for $n(\text{CH}_3\text{COOH}) \text{ in 400 cm}^3 = 0.200 \times \frac{400}{1000} = 0.08 \text{ (mol)}$

As alternative for the 4th and 5th marks, ALLOW:
mass of $\text{CH}_3\text{COONa} \text{ in 1 dm}^3 = 0.350 \times 82.0 = 28.7 \text{ g}$
mass of $\text{CH}_3\text{COONa} \text{ in 400 cm}^3 = 28.7 \times \frac{400}{1000} = 11.48 \text{ g}$

---

COMMON ECF
4.592 OR 4.6 g AWARD 4 marks
use of 400/1000 twice
ALLOW variants of Henderson–Hasselbalch equation.

\[ pK_a = -\log(1.75 \times 10^{-5}) = 4.757 \quad \text{Calc: 4.75696.....} \]

\[ \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \text{pH} - pK_a = 5 - 4.757 = 0.243 \]

\[ \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 10^{0.243} = 1.75 \]

\[ [\text{CH}_3\text{COO}^-] = 1.75 \times 0.200 = 0.350 \text{ mol dm}^{-3} \]

\[ n(\text{CH}_3\text{COONa/CH}_3\text{COO}^-) \text{ in 400 cm}^3 \]
\[ = 0.350 \times \frac{400}{1000} = 0.14(0) \text{ (mol)} \]

\[ \text{mass } \text{CH}_3\text{COONa} = 0.140 \times 82.0 = 11.48 \text{ OR 11.5 (g)} \]

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**Total 17**
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<thead>
<tr>
<th>Question</th>
<th>Answer</th>
<th>Marks</th>
<th>Guidance</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 (a)</td>
<td>Definition&lt;br&gt;The e.m.f. (of a half-cell) compared with/connected to a (standard) hydrogen half-cell/(standard) hydrogen electrode ✓</td>
<td>2</td>
<td>As alternative for e.m.f., ALLOW voltage OR potential difference OR p.d. OR electrode potential OR reduction potential OR redox potential ALLOW /(standard) hydrogen cell IGNORE S.H.E. (as abbreviation for standard hydrogen electrode) ALLOW 1M DO NOT ALLOW 1 mol ALLOW 1 atmosphere/1 atm OR 101 kPa OR 101325 Pa</td>
</tr>
<tr>
<td>7 (b)</td>
<td>(i) 2Ag⁺(aq) + Cu(s) → 2Ag(s) + Cu²⁺(aq) ✓</td>
<td>1</td>
<td>State symbols not required ALLOW = provided that reactants on LHS</td>
</tr>
<tr>
<td>7 (b)</td>
<td>(ii) Assume Cu²⁺</td>
<td>Cu OR Cu half cell unless otherwise stated. &lt;br&gt;([\text{Cu}^{2+}] ) decreases OR &lt; 1 mol dm⁻³ AND &lt;br&gt;Equilibrium (shown in table) shifts to left ✓ &lt;br&gt;more electrons are released by Cu ✓ &lt;br&gt;The cell has a bigger difference in ( E ) ✓</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>(c)</td>
<td>(i)</td>
<td>no/less CO₂ <strong>OR</strong> H₂O is <strong>only</strong> product <strong>OR</strong> greater efficiency ✓</td>
</tr>
<tr>
<td>---</td>
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<td>---</td>
</tr>
<tr>
<td>7</td>
<td>(c)</td>
<td>(ii)</td>
<td>liquefied/as a liquid <strong>AND</strong> under pressure/pressurised ✓</td>
</tr>
<tr>
<td>7</td>
<td>(d)</td>
<td>(i)</td>
<td>(E = -2.31 \text{ (V)} \checkmark)</td>
</tr>
<tr>
<td>7</td>
<td>(d)</td>
<td>(ii)</td>
<td>(4\text{Al}(s) + 4\text{OH}^−(aq) + 3\text{O}_2(g) + 6\text{H}_2\text{O}(l) \rightarrow 4\text{Al(OH)}_4^−(aq)) (\text{species ✓ balance ✓})</td>
</tr>
</tbody>
</table>

**Total** 11
<table>
<thead>
<tr>
<th>Question</th>
<th>Answer</th>
<th>Marks</th>
<th>Guidance</th>
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</thead>
</table>
| **8 (a)** | Fe₂O₃ + 3Cl₂ + 10OH⁻ → 2FeO₄²⁻ + 6Cl⁻ + 5H₂O ✓✓ | 2 | ALLOW multiples  
ALLOW oxidation half equation for two marks  
Fe₂O₃ + 10OH⁻ → 2FeO₄²⁻ + 5H₂O + 6e⁻  
Correct species would obtain 1 mark  
– question: equation for oxidation  
ALLOW variants forming H⁺ for 1 mark, e.g:  
Fe₂O₃ + 3Cl₂ + 5OH⁻ → 2FeO₄²⁻ + 6Cl⁻ + 5H⁺  
Fe₂O₃ + 3Cl₂ + 5OH⁻ → 2FeO₄²⁻ + 5HCl + Cl⁻ |
| **8 (b)** | Ba²⁺(aq) + FeO₄²⁻(aq) → BaFeO₄(s) ✓ | 1 | Balanced ionic equation AND state symbols required  
DO NOT ALLOW +2 or –2 for ionic charges |
| **8 (c)** | Reason can ONLY be correct from correct reducing agent  
**reducing agent**: I⁻ OR KI ✓  
I⁻ adds/donates/loses electrons  
AND  
to FeO₄²⁻ OR to BaFeO₄ OR to Fe(VI) or to Fe(+6) ✓  
ALLOW Fe(6⁺) OR Fe⁶⁺ | 2 | IGNORE H⁺ OR acidified  
ALLOW iodide/potassium iodide but DO NOT ALLOW iodine  
ALLOW I⁻ loses electrons AND to form I₂  
ALLOW Fe(6+) OR Fe⁶⁺ |
F325  Mark Scheme  June 2014

8 (d) 

FIRST, CHECK THE ANSWER ON ANSWER LINE
IF answer = 51.8%, award 4 marks.

___________________________________________________________________

\[ n(S_{2}O_{3}^{2-}) \text{ used} = 0.1000 \times \frac{26.4}{1000} = 2.64 \times 10^{-3} \text{ (mol)} \checkmark \]

\[ n(FeO_{4}^{2-}) = \frac{1}{2} \times 2 \times 3 \times 2.64 \times 10^{-3} = 8.8(0) \times 10^{-4} \text{ (mol)} \checkmark \]

Mass BaFeO₄ in sample
= \(8.8 \times 10^{-4} \times 257.1\) g = 0.226248 g \checkmark

% purity = \(\frac{0.226248}{0.437} \times 100 = 51.8\% \checkmark\)

MUST be to one decimal place (in the question)

As an alternative for the final two marks, ALLOW:

Theoretical amount of BaFeO₄ = \(\frac{0.437}{257.1}\) = 0.00170 (mol) \checkmark

% purity = \(\frac{8.8 \times 10^{-4}}{1.70 \times 10^{-3}} \times 100 = 51.8\% \checkmark\)

___________________________________________________________________

FULL ANNOTATIONS MUST BE USED

For alternative answers, look first at common ECFs below. Then check for ECF credit possible using working below
IF a step is omitted but subsequent step subsumes previous, then award mark for any missed step

Working must be to at least 3 SF throughout until final % mark
BUT ignore trailing zeroes, ie for 0.880 allow 0.88

ECF answer above \(\times \frac{1}{2} \times 2/3\)
This mark may be seen in 2 steps via I₂ but the mark is for both steps combined

ECF \(\frac{257.1 \times \text{answer above}}{0.437} \times 100\)

ALLOW 51.7% FROM 0.226 g BaFeO₄ (earlier rounding)

Common ECFs:
No \(\times 2/3\) for \(n(FeO_{4}^{2-})\):
% purity = 77.7%/77.6% 3 marks

No \(+\) 2 for \(n(FeO_{4}^{2-})\):
% purity = 25.9% 3 marks

24.6 used instead of 26.4:
% purity = 48.2% 3 marks

4
| 8 | (e) | **gas**: O₂ ✓  
**precipitate**: Fe(OH)₃ ✓  
**equation**:  
\[ 2\text{FeO}_4^{2-} + 5\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{Fe(OH)}_3 + 4\text{OH}^- \]  
**OR**  
\[ 2\text{FeO}_4^{2-} + \text{H}_2\text{O} + 4\text{H}^+ \rightarrow \frac{1}{2}\text{O}_2 + 2\text{Fe(OH)}_3 ✓ \] | 3 | **DO NOT ALLOW** names  
**IGNORE** a balancing number shown before a formula  
**ALLOW** Fe(OH)₃(H₂O)₃  
**ALLOW** multiples  
**ALLOW**  
\[ 2\text{FeO}_4^{2-} + 11\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{Fe(OH)}_3(\text{H}_2\text{O})_3 + 4\text{OH}^- \] | 12 | **Total** |
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