

Mark Scheme - PI1.2 Redox Reactions

- 1 (a) 1 dm^3 at 20°C contains 52.9 g and at 0°C it contains 17.5 g (1)
 \therefore amount crystallised = $52.9 - 17.5 = 35.4 \text{ g}$ (1) [2]
- (b) (i) 2 mol of $\text{K}_2\text{S}_2\text{O}_8$ give 1 mol of O_2
 2 mol of $\text{K}_2\text{S}_2\text{O}_8$ give 29.0 dm^3 of O_2 (1)
 $\therefore 0.1 \text{ mol}$ of $\text{K}_2\text{S}_2\text{O}_8$ gives $29.0/20 = 1.45 \text{ dm}^3$ of oxygen (1) [2]
- (ii) Measure the volume of oxygen produced at specified time intervals /
Measure the pH of the solution at specified time intervals [1]
- (c) (i) An (inert) electrode that is used to carry the charge / current / electron flow [1]
- (ii) A comment on the relative values (e.g. the persulfate system is the more positive of the two systems) (1)
The more positive 'reagent' / persulfate ions acts as the oxidising agent, accepting electrons via the external circuit (1)
- must have the first mark to get second [2]
- (d) (i) The experiments show that both the concentrations of iodide and persulfate have doubled (1) therefore the initial rate should increase four times
 $4 \times 8.64 \times 10^{-6} = 3.46 \times 10^{-5}$ (1) [2]
- (ii) Rate = $k [\text{S}_2\text{O}_8^{2-}] [\text{I}]$ (1)
 $\therefore k = \frac{8.64 \times 10^{-6}}{0.0400 \times 0.0100}$
 $= 0.0216$ (1) $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (1) [3]
- (iii) In the rate equation one $\text{S}_2\text{O}_8^{2-}$ ion reacts with one I^- ion.
The rate-determining step therefore has to have 1 mole of each reacting, as (only) seen in step 1 [1]

Total [14]

- 2 (a) Filtration [1]
- (b) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ [1]
- (c) (i) Carbon O.S. at start = +3; Carbon O. S. at end = +4 [1]
- (ii) $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$ [1]
- (d) Colour change of manganate(VII) is used to indicate the change [1]
- (e) Volume of manganate(VII) = 27.92 cm³ (1)
- Moles manganate = $27.92 \times 0.020 / 1000 = 5.584 \times 10^{-4}$ mol (1)
- Moles oxalate = $5.584 \times 10^{-4} \times 5/2 = 1.396 \times 10^{-3}$ mol (1)
- Concentration = $1.396 \times 10^{-3} / 25 \times 10^{-3} = 0.0558$ mol dm⁻³ (1) [4]
- (f) (i) $K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$ [1]
- (ii) $[\text{H}^+]^2 = K_a \times [\text{HCOOH}] = 1.8 \times 10^{-4} \times 0.2 = 0.36 \times 10^{-4}$ (1)
- $[\text{H}^+] = 6.0 \times 10^{-3}$ mol dm⁻³ (1)
- pH = $-\log [\text{H}^+] = 2.22$ (1) [3]
- (iii) A buffer keeps the pH almost constant when **small amounts** of acid or base are added (1)
- $\text{HCOOH} \rightleftharpoons \text{HCOO}^- + \text{H}^+$ (1)
- Adding acid shifts the equilibrium to the left which removes H⁺ /
 Adding base removes H⁺ shifts equilibrium to right which replaces H⁺ (1)
 OR answer in terms of H⁺ reacting with methanoate from
 sodium methanoate when acid added (1) and methanoic acid replacing H⁺
 when base removes H⁺ (1)
- MAX 3 [3]
- QWC *Selection of a form and style of writing appropriate to purpose and to complexity of subject matter* [1]
- (g) (i) Orange to green [1]
- (ii) CrO₄²⁻ (1) Yellow (1) [2]
- Total [20]**

- 3 (a) diagram with labels to show
- H₂/H⁺ shown in electrode (1)
 - platinum (in both electrodes) (1)
 - Fe²⁺(aq) and Fe³⁺(aq) (1)
 - high resistance voltmeter (1)
 - salt bridge (1)
 - gas at 1atm pressure, solutions of concentration 1 mol dm⁻³, temperature 298K (1)
- [any 5] [5]
- (b) (i) successive ionisation energies increase gradually/ the energies of the d orbitals are similar [1]
- (ii) 1s²2s²2p⁶3s²3p⁶4s²3d¹⁰ / 3d¹⁰4s² [1]
- (iii) after 4s electrons lost 3d is full/ stable/ d electrons ionisation energy very high [1]
- (c) (i) violet solution contains V²⁺ (1)
- SEP Zn²⁺/ Zn is more negative than VO₃⁻/ VO²⁺ and VO²⁺/ V³⁺ and therefore releases electrons/ VO₃⁻/ VO²⁺ and VO²⁺/ V³⁺ are more positive than Zn²⁺/ Zn and are stronger oxidising agents (1)
- V²⁺ cannot be reduced (to V) since SEP is more negative than Zn²⁺/ Zn (1) [3]
- (ii) 1.1V (ignore sign) [1]
- (iii) Zn(s) → Zn²⁺(aq) + 2e / Zn(s) ⇌ Zn²⁺(aq) + 2e with some indication of direction [1]
- (iv) if Zn²⁺(aq) concentration increased equilibrium moves to LHS (1)
- so electrode potential becomes less negative (1) [2]

- (d) (i) 2.74×10^{-3} (mol) [1]
- (ii) 1.37×10^{-3} (mol) [1]
- (iii) $M_r \text{KIO}_3 = 214.1$
moles $\text{KIO}_3 = 0.978 / 214.1 = 4.57 \times 10^{-3}$ in 250 cm^3
 4.57×10^{-4} in 25 cm^3 [1]
- (iv) $1.37 \times 10^{-3} / 4.57 \times 10^{-4} = 3$ (1)
equation 1 is correct since 3 moles of iodine formed (mark awarded for reason) (1) [2]
- Total [20]**

- 4 (a)
$$\begin{array}{c} \cdot\cdot \quad \cdot\cdot \\ \text{H} : \text{O} : \text{O} : \text{H} \\ \cdot\cdot \quad \cdot\cdot \end{array}$$
 [1]
- (b) 20 dm³ oxygen = 0.83 mol (1)
 Moles H₂O₂ = 1.67 and [H₂O₂] = 1.67 mol dm⁻³ (1) [2]
- (c) (i) Variable oxidation states / partially filled 3d energy levels /ability to adsorb 'molecules' / form complexes (or temporary bonds) with reacting molecules (Accept any two answers) Do not accept 'empty / unfilled d-orbitals' [2]
- (ii) 3d orbitals split by ligands (1)
 Three d-orbitals have lower energy, two have higher energy (1)
 Electrons absorb (visible light) energy to jump from lower level to higher level (1)
 The colour is that due to the remaining / non-absorbed frequencies (1)
 (Appropriate diagrams are acceptable alternatives) [4]
- QWC Legibility of text; accuracy of spelling, punctuation and grammar, clarity of meaning* [1]
- (d) (i) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ [1]
- (ii) $5\text{H}_2\text{O}_2 + 6\text{H}^+ + 2\text{MnO}_4^- \longrightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$ [2]
- (Mark consequentially from (i) – 1 mark if formulae correct but equation not balanced properly)
- (iii) Moles MnO₄⁻ = $\frac{0.02 \times 14.8}{1000} = 2.96 \times 10^{-4}$ (1)
 Moles H₂O₂ = 7.40×10^{-4} (1)
 Concentration H₂O₂ = $\frac{7.40 \times 10^{-4}}{0.020} = 0.037 \text{ mol dm}^{-3}$ (1) [3]
- (e) Oxidation state of oxygen starts at -1 (in peroxide) (1)
 Oxidation state in water is -2 (reduced)
 oxidation state in oxygen is 0 (oxidised) (1) [2]

Total [18]

- 5 (a) $1\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ [1]
- (b) Oxidation state of carbon at start = +2 and at end = +4 so it has been oxidised (1)
 Oxidation state of iron at start = +3 and at end = 0 so it has been reduced (1)
 Credit 1 mark if all oxidation states are given correctly with incorrect or no
 reference to what has been oxidised/reduced [2]

- (c) (i) 6:6 [1]
- (ii)

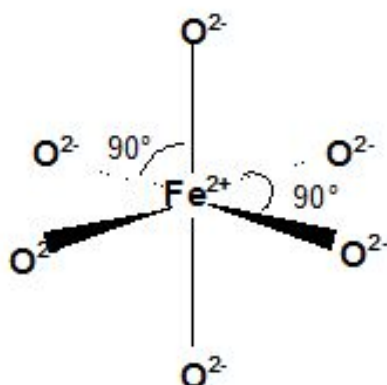


Diagram must be unambiguous,
 either by showing 3 dimensions,
 bond angles or through labelling,
 must identify iron and oxide as
 ions

[1]

- (d) Moles FeO = $20,000 \div (55.8 + 16) = 278.6$ mol (1)
 Moles Fe = moles FeO = 278.6 mol (1)
 Mass Fe = $278.6 \times 55.8/1000 = 15.5$ kg (1) [3]
- (e) Pair of shared electrons in both (1)
 Covalent – 1 electron from each atom **and**
 Co-ordinate – 2 electrons from same atom (1) [2]
- (f) Lattice / regular arrangement of positive ions (1)
 Sea of delocalised electrons (1)
 Electrons can move to form an electrical current (1)
 Strong forces / bonds between the delocalised electrons and the metal ions
 require a lot of energy to break / high temperature to overcome (1) [4]
*QWC: selection of a form and style of writing appropriate to purpose and to
 complexity of subject matter* [1]

Total [15]