Mark Scheme - 3.1 Redox and Standard Electrode Potentials

1. (a) 1 dm^3 at 20°C contains 52.9 g and at 0°C it contains 17.5 g (1)
∴ amount crystallised = 52.9 – 17.5 = 35.4 g (1) [2]

(b) (i) 2 mol of $K_2S_2O_8$ give 1 mol of O_2
2 mol of $K_2S_2O_8$ give 29.0 dm^3 of O_2 (1)
∴ 0.1 mol of $K_2S_2O_8$ gives 29.0/20 = 1.45 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 = $k [S_2O_8^{2-}] [I^-]$ (1)

$$\therefore k = \frac{8.64 \times 10^{-6}}{0.0400 \times 0.0100}$$

= 0.0216 (1) $dm^3\ mol^{-1}\ s^{-1}$ (1) [3]

(iii) In the rate equation one $S_2O_8^{2-}$ 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.

Both O_2 and O_3 have oxidation states of zero (1) No change in oxidation state (1) [2]

3.

(a) diagram with labels to show

H_2/H^+ shown in electrode (1)

platinum (in both electrodes) (1)

$Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ (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) $1s^22s^22p^63s^23p^64s^23d^{10}$ / $3d^{10}4s^2$ **[1]**

(iii) after 4s electrons lost 3d is full/ stable/ d electrons ionisation energy very high **[1]**

(c) (i) violet solution contains V^{2+} (1)

SEP Zn^{2+}/ Zn is more negative than VO_3^-/ VO^{2+} and VO^{2+}/ V^{3+} and therefore

releases electrons/ VO_3^-/ VO^{2+} and VO^{2+}/ V^{3+} are more positive than

Zn^{2+}/ Zn and are stronger oxidising agents (1)

V^{2+} cannot be reduced (to V) since SEP is more negative than Zn^{2+}/ Zn (1) **[3]**

(ii) 1.1V (ignore sign) **[1]**

(iii) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e$ / $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e$ with some indication of direction **[1]**

(iv) if $Zn^{2+}(aq)$ 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) $M_r KIO_3 = 214.1$

moles $KIO_3 = 0.978/ 214.1 = 4.57 \times 10^{-3}$ 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) (i) Oxidising agent [1]

(ii) A = lead(II) chloride / $PbCl_2$ (1)

B = chlorine / Cl_2 (1) [2]

(iii) $[Pb(OH)_6]^{4-}$ / $[Pb(OH)_4]^{2-}$ / $Na_4[Pb(OH)_6]$ etc. [1]

(iv) Yellow [1]

(v) $PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$ [1]

(b) (i) Each C atom covalently bonded to three other C atoms forming layers (1)

Layers held together by weak intermolecular forces (1)

BN is isoelectronic with C so it forms similar structures (1)

Graphite conducts electricity since electrons are delocalised but in BN, each N has a full unbonded p-orbital and each B has an empty unbonded p-orbital so it does not conduct electricity (1) [4]

(Accept electrons are not delocalised in BN so it does not conduct electricity)

QWC The information is organised clearly and coherently, using specialist vocabulary where appropriate [1]

(ii) Wear-resistant coatings/catalyst support/for mounting high power electronic components / drills in industry / cutting instruments [1]

(c) (i) $\Delta G = \Delta H - T\,\Delta S$ ($\Delta G = 0$ for reaction to be spontaneous) (1)

$T = \frac{1.92}{0.0067}$ (1)

T = 286.6 K (1) [3]

(ii) Changes in temperature (above or below 286.6 K) caused the tin to change form making it unstable (and causing it to disintegrate) [1]

(d) (i) (At the anode) $H_2 \longrightarrow 2H^+ + 2e^-$ (1)

(At the cathode) $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (1)

(Overall reaction) $2H_2 + O_2 \longrightarrow 2H_2O$ (1)

[3]

(ii) Hydrogen is difficult to store / takes up large volume / too flammable / explosive / produced from fossil fuels which leads to a net energy loss / Pt electrodes very expensive [1]

Total [20]

5. (a) - 705 ($kJ\ mol^{-1}$) (1) for correct sign (1) for correct number [2]

(b) (i) ..... hydration .....

..... lattice **breaking** [1]

(ii) e.g. add a small 'amount' of an alkali / sodium hydroxide / NaOH / OH^- ions (1)
this would remove / react with hydrogen ions giving water, shifting the position of equilibrium to the left (removing iodine) (1)
add $P6^{2+}$ / Ag^+ ect. [2]

(c) (i) Any TWO from
white / misty fumes (of HI)
yellow solid / solution (of sulfur)
brown / black solid / purple vapour (of iodine)
bubbles / effervescence / fizzing

One mark for each correct response [2]

(ii) The values show that chlorine is the best oxidising agent, as it has the most positive E^θ value and therefore iodide is the better reducing agent (1)
and is 'strong' enough to reduce the sulfuric acid. / OWTTE (1) [2]

(d) (i) $2\ NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$ [1]

(ii) e.g. bleach, kills bacteria [1]

Total [11]

6.

(a) Lead(II) iodide or PbI_2 (1) Bright yellow (1) [2]

(b) $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$ (1)

The precipitate is copper(I) iodide (stated or clearly indicated by state symbols) (1) [2]

(c) Bromine has a more positive $E^\ominus$ than iodine so it is a stronger oxidising agent (1)

Bromine is able to oxidise iodide (1)

Bromine has a less positive $E^\ominus$ than chlorine so it is a weaker oxidising agent (1)

Bromine is not able to oxidise chloride (1)

MAX 3

OR Calculate EMF for each reaction (1 each) and state that positive EMF means reaction is feasible (1) [3]

QWC Legibility of text, accuracy of spelling, punctuation and grammar, clarity of meaning [1]

(d) 1 mark for each two products or observations
$KHSO_4$ HI H_2S SO_2 S I_2 [MAX 2 for products]

Yellow solid rotten egg smell steamy fumes

Black solid or brown solution or purple fumes

MAX 3 [3]

(e) (i) Measure time taken for a sudden colour change (1)
Rate = 1 ÷ time (1) [2]

(ii) I. pH 1 has a concentration of H^+ ten times higher than pH 2. [1]

II. Order with respect to H_2O_2 = 1 (1)
Order with respect to I^- = 1 (1)
Order with respect to H^+ = 0 (1) [MAX 2 for the stated orders]
Rate = $k[H_2O_2][I^-]$ (1) [3]

III. k = 0.028 (1) $mol^{-1}dm^3 s^{-1}$ (1) [ecf from rate equation] [2]

IV. Rate equation is unchanged and increasing temperature increases the value of the rate constant [1]

Total [20]