Mark Scheme - PI3 Chemical Kinetics

1 *(a)* (i) tangent drawn at t = 40 (1)

rate calculated 0.017 to 0.027 (ignore units) (1) **[2]**

(ii) as reaction proceeds less collisions (per unit time) occur **[1]**

(b) (i) 1st order shown by:

calculation of rates at at least 2 concentrations (1)

statement rate α concentration (1)

OR

constant half-life (1)

half-life is 24 minutes (1) **[2]**

(ii) rate = k$[N_2O_5]$ (1) **[1]**

(iii) k = rate (from (i))/ $[N_2O_5]$ (from graph) (1)
(mark correct numbers – no need to check evaluation)

units = minutes^{-1} (1) ft from (ii) **[2]**

(iv) (student A more likely to be correct) reaction is 1st order and 1 $[N_2O_5]$ involved in rate determining step **[1]**

(c) correct curve starting at 100 kPa and becoming horizontal (1)

horizontal at 250 kPa (1) **[2]**

Total [11]

2 (a) (i) $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$

Acid 1 Base 2 Base 1 Acid 2 [2]

(1 mark for each pair)

(b) (i)

	$[NH_4^+(aq)]$/mol dm^{-3}	$[NO_2^-(aq)]$/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
1	0.200	0.010	4.00×10^{-7}
2	**0.100**	0.010	2.00×10^{-7}
3	0.200	**0.030**	1.20×10^{-6}
4	0.100	0.020	**4.00×10^{-7}**

(1 mark for each correct answer) [3]

(ii) $k = \dfrac{4.00 \times 10^{-7}}{0.200 \times 0.010} = 2.0 \times 10^{-4}$ (1)

Units = mol^{-1} dm^3 s^{-1} (1) [2]

(iii) No change [1]

(iv) Increases

If temperature is increased rate increases (1)

and since concentrations do not change the rate constant must increase (or similar) (1) [2]

Total [10]

3 (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]

4 (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]

5 (a) Plotting (2)

Best fit line (1) [3]

(b) (i) C (1)

Curve steeper (1) [2]

(ii) Concentration of acid is greatest [1]

(c) 44 cm^3 (±1 cm^3) [1]

(d) Moles Mg = 0.101/24.3 = 0.00416 (1)

Moles HCl = 2 x 0.02 = 0.04 (1) [2]

(e) (i) Mg is not the limiting factor /

Mg now in excess / HCl not in excess [1]

(ii) Moles acid = 0.5 x 0.04 = 0.02 (1)

Volume H_2 = 0.01 x 24 = 0.24 dm^3

- correct unit needed (1) [2]

(f) Lower the temperature of the acid (1)

Reactants collide with less energy (1)

Fewer molecules that have the required activation energy (1)[3]

or Use pieces of magnesium (1) less surface area (1) less chance of successful collisions (1)

QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter. [1]

Total [16]

6	(a)		Use weighing scales to weigh the metal oxide (1) Use measuring cylinder to pour hydrogen peroxide solution and water into a conical flask (1) Immerse flask in water bath at 35 °C (1) Add oxide to flask and connect flask to gas syringe (1) Measure volume of oxygen every minute for 10 minutes / at regular time intervals (1) (any 4 of above, credit possible from labelled diagram)	[4]
	(b)		Oxide **A** because reaction is faster	[1]
	(c)	(i)	18 cm^3	[1]
		(ii)	10 cm^3	[1]
	(d)		Concentration of hydrogen peroxide has decreased (1) reaction rate decreases / fewer successful collisions (1)	[2]
	(e)		All the hydrogen peroxide has decomposed / the same quantity of hydrogen peroxide was used	[1]
	(f)		25 cm^3	[1]
	(g)		Reaction will take less time (1) Reactants collide with more (kinetic) energy (1) More molecules have the required activation energy (1)	[3]
			QWC Selection of a form and style of writing appropriate to purpose and to complexity of subject matter	[1]

Total [15]

7 (a) (i) He may have lost carbon dioxide through leaks, this would have given a lower volume than expected. (1)
He used lower concentration of acid / diluted the acid with water and the rate of carbon dioxide evolution was slower than expected. (1) [2]

(ii) The concentration of acid is higher in the first half (1) the collision rate is higher (1) [2]

(iii) eg $k = \frac{V}{T}$ (1) $\therefore k = \frac{130}{298}$ / 0.436

$\therefore V = 0.436 \times 323 = 141\ (cm^3)$ (1)

or $\frac{V_1}{V_2} = \frac{T_1}{T_2}$ (1) $\therefore V_1 = \frac{323 \times 130}{298} = 141\ (cm^3)$ (1) [2]

(b) (i) 260 (cm^3) [1]

(ii) 0.45 (g) (0.43–0.48) [1]

(c) The diagram shows two reasonable distribution curves with T_2 flatter and 'more to the right' than T_1. (1)
Activation energy correctly labelled, or mentioned in the writing (1)
Fraction of molecules having the required activation energy is much greater at a higher temperature (thus increasing the frequency of successful collisions) (in words) (1) [3]

The candidate has selected a form and style of writing that is appropriate to purpose and complexity of the subject matter QWC [1]

(d) Place the mixture on a balance and measure the (loss in) mass (1) at appropriate time intervals (1)

OR BY OTHER SUITABLE METHOD

eg. sample at intervals / quench (1) titration (1) [2]

Total [14]

8 (a) to increase rate of reaction / to increase surface area [1]

(b) $MgCO_3 + 2HCl \rightarrow MgCl_2 + CO_2 + H_2O$ (ignore state symbols) [1]

(c) rate starts fast and gradually slows (1)

because concentration becomes less so fewer collisions (per unit time) / less frequent collisions / lower probability of collisions (1)

at time = 17/18 min rate = 0 (1) [3]

(d) all the solid would all have disappeared / if more carbonate is added further effervescence is seen [1]

(e) (i) volume CO_2 = 200 cm^3 (1)

moles CO_2 = 200 / 24000 = 0.008333 = moles $MgCO_3$ (1)
[minimum 2 sf] [2]

(ii) mass $MgCO_3$ = 0.008333 × 84.3 = 0.702 g (1)

% $MgCO_3 = \frac{0.702}{0.889} \times 100$ = 79.0% / 79% [2]

(e) carbon dioxide is soluble in water / reacts with water (1)

volume collected less therefore % / moles of $MgCO_3$ less (1) [2]

(f) use of 40.3 and 84.3 (1)

atom economy = 40.3 / 84.3 × 100 = 47.8% (1) [2]

Total [14]