F325: Equilibria, Energetics and Elements 5.1.1 How Fast? / 71

- 1. O_3 : Exp 2 has 4 times $[H_2]$ as Exp 1 and rate increases by 4 (1), so order = 1 with respect to O_3 (1) C_2H_4 : Exp 3 has $2 \times [C_2H_4]$ and $2 \times [O_3]$ as Exp 2; and rate has increased by 4 (1), so order = 1 with respect to C_2H_4 (1) rate = $k [O_3] [C_2H_4]$ (1) 5 use of $k = \text{rate} / [O_3] [C_2 H_4] = 1.0 \times 10^{-12} / (0.5 \times 10^{-7} \times 1.0 \times 10^{-8})$ to obtain a calculated value (1) $k = 2 \times 10^3$ (1) units: $dm^3 mol^{-1} s^{-1}$ (1) 3 (iii) rate = $1.0 \times 10^{-12} / 4 = 2.5 \times 10^{-13} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$ (1) 1 (iv) rate increases and k increases (1) 1 [10]
- 2. $1\frac{1}{2}O_2(g) \rightarrow O_3(g)/O_2(g) + \frac{1}{2}O_2(g) \rightarrow O_3(g)$ (1)

NO is a catalyst (1) as it is (used up in step 1 and) regenerated in step 2/ not used up in the overall reaction(1) allow 1 mark for 'O/NO₂ with explanation of regeneration.'

[3]

(ii) rate =
$$k[NO]^2 [H_2] (1)$$

(iii)
$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{H}_2]} / \frac{2.6}{0.10^2 \times 0.20}$$
 (1)

= 1300 (1) units: $\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ (1)
allow 1 mark for 7.69×10^{-4} or 1.3×10^{8} (x not 3)

3

[9]

4. (i) $1\frac{1}{2}O_2(g) \rightarrow O_3(g) / O_2(g) + \frac{1}{2}O_2(g) \rightarrow O_3(g)$ (1)

NO is a catalyst (1) as it is (used up in step 1 and) regenerated in step 2/
not used up in the overall reaction(1)
allow 1 mark for 'O/NO₂ with explanation of regeneration.'

3

(ii) Rate = $k[\text{NO}][O_3]$ (1)
Species in rate equation match those reactants in the slow step / rate determining step (1)

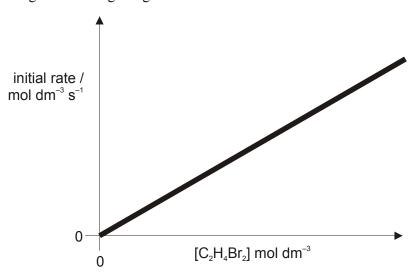
2

5. (a) (i) Curve downwards starting at t = 0 \checkmark with slope gradually levelling off with no increase \checkmark (don't worry about hitting the x axis)

(ii) Tangent shown at start \checkmark 1

(iii) Half-life is constant OR: draw tangents and then plot a 2nd graph of tangent or rate against concentration, which is a straight line through the origin. \checkmark

(iv) Straight line through origin ✓



(b) 4 times [KI], rate increases by 4 ✓, so order = 1 with respect to KI ✓ independent marks

(c) (i) rate/r = $k[C_2H_4Br_2]$ [KI] \checkmark or ecf from (b)

(ii)
$$k = \frac{\text{rate}}{[C_2H_4Br_2][KI]} / \frac{0.027}{0.50 \times 0.18} \checkmark$$

= 0.3(0) \checkmark units: dm³ mol⁻¹ s⁻¹ \checkmark

units dependent on rate equation in (i).

Mark independently.

6. From graph, constant half-life **(1)**

Therefore 1st order w.r.t. [CH₃COCH₃] (1)

From table, rate doubles when [H⁺] doubles (1)

Therefore 1^{st} order w.r.t. $[H^+]$ (1)

From table, rate stays same when $[I_2]$ doubles (1)

Therefore zero order w.r.t. $[I_2]$ (1)

Order with no justification does **not** score.

 $rate = k[H^{+}][CH_{3}COCH_{3}] (1)$

(from all three pieces of evidence)

$$k = \frac{\text{rate}}{[\text{H}^+][\text{CH}_3\text{COCH}_3]} / \frac{2.1 \times 10^{-9}}{0.02 \times 1.5 \times 10^{-3}}$$
(1)
= 7.0×10^{-5} (1) dm³ mol⁻¹ s⁻¹ (1)
accept 7×10^{-5}

Plymstock School

1

2

3

[11]

rate determining step involves species in rate equation (1) two steps that add up to give the overall equation (1) The left hand side of a step that contains the species in rate-determining step (1) i.e., for marking points 2 and 3: $CH_3COCH_3 + H^+ \rightarrow [CH_3COHCH_3]^+$ $[\mathrm{CH_3COHCH_3}^+] + \mathrm{I_2} \rightarrow \mathrm{CH_3COCH_2I} + \mathrm{HI} + \mathrm{H}^+$ 3 organises relevant information clearly and coherently, using specialist vocabulary where appropriate Use of the following four words/phrases: constant, half-life, order, doubles/x2 (1) 1 [14] 7. The slowest step (1) 1 (i) $2NO_2 \rightarrow NO + NO_3$ (1) (ii) $NO_3 + CO \rightarrow NO_2 + CO_2$ (1) 2 (or similar stage involving intermediates) [3] 8. HCl and CH₃COOH have same number of moles/ release same number of moles H⁺/ 1 mole of each acid produce ½ mol of H₂ (1) $[H^+]$ in $CH_3COOH < [H^+]$ in HCl/CH₃COOH is a weaker acid than HCl (ora) (1) $Mg + 2HCl \rightarrow MgCl_2 + H_2$ (1) $Mg + 2CH_3COOH \rightarrow (CH_3COO)_2Mg + H_2$ (1) $Mg + 2H^{+} \rightarrow Mg^{2+} + H_{2}$ (1)(1) 4 [4] 9. (i) constant half-life (1) 1 (ii) rate = $k[N_2O_5]$ (1) 1 Common error will be to use '2' from equation. (iii) curve downwards getting less steep (1) curve goes through 1200,0.30; 2400,0.15; 3600,0.075 (1) 2 (iv) tangent shown on graph at t = 1200 s (1) 1

	(v)	$3.7(2) \times 10^{-4}$ (1) mol dm ⁻³ s ⁻¹ (1) ecf possible from (ii) using $[N_2O_5]^x$ (2 nd order answer: $2.2(3) \times 10^{-4}$)	2	[7]
10.	(i)	slow step (1)	1	
	(ii)	$(CH_3)_2C=CH_2 + H_2O \rightarrow (CH_3)_3COH$ (1)	1	
	(iii)	H ⁺ is a catalyst (1)		
		H ⁺ used in first step and formed in second step/regenerated/ not used up (1)	2	
	(iv)	rate = k [(CH ₃) ₂ C=CH ₂] [H ⁺] (1) common error will be use of H ₂ O instead of H ⁺	1	
				[5]