

F325: Equilibria, Energetics and Elements

5.1.1 How Fast? / 71

1. (i) O₃: Exp 2 has 4 times [H₂] as Exp 1
and rate increases by 4 (1),
so order = 1 with respect to O₃ (1)
C₂H₄: Exp 3 has 2 × [C₂H₄] and 2 × [O₃] as Exp 2;
and rate has increased by 4 (1),
so order = 1 with respect to C₂H₄ (1)
rate = $k [\text{O}_3] [\text{C}_2\text{H}_4]$ (1) 5
- (ii) use of $k = \text{rate} / [\text{O}_3] [\text{C}_2\text{H}_4] = 1.0 \times 10^{-12} / (0.5 \times 10^{-7} \times 1.0 \times 10^{-8})$
to obtain a calculated value (1)
 $k = 2 \times 10^3$ (1)
units: $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (1) 3
- (iii) rate = $1.0 \times 10^{-12} / 4 = 2.5 \times 10^{-13} (\text{mol dm}^{-3} \text{s}^{-1})$ (1) 1
- (iv) rate increases and k increases (1) 1

[10]

2. $1\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})/$
 $\text{O}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$ (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]

3. (i) H₂: Exp 2 has 2.5 times [H₂] as Exp 1
and rate increases by 2.5 (1),
so order = 1 with respect to H₂ (1) 2
NO: Exp 3 has 3 x [NO] as Exp 2;
and rate has increased by 9 = 3² (1),
so order = 2 with respect to NO (1) 2
QWC At least two complete sentences where the meaning is clear. 1
- (ii) rate = $k[\text{NO}]^2 [\text{H}_2]$ (1) 1

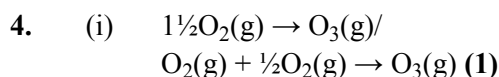
$$(iii) \quad k = \frac{\text{rate}}{[\text{NO}]^2[\text{H}_2]} / \frac{2.6}{0.10^2 \times 0.20} \quad (1)$$

$$= 1300 \quad (1) \quad \text{units: dm}^6 \text{ mol}^{-2} \text{ s}^{-1} \quad (1)$$

allow 1 mark for 7.69×10^{-4} or 1.3×10^x (x not 3)

3

[9]



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) $\text{Rate} = k[\text{NO}] [\text{O}_3] \quad (1)$

Species in rate equation match those reactants in the slow
 step / rate determining step (1)

2

[5]

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

2

(ii) Tangent shown at start ✓

1

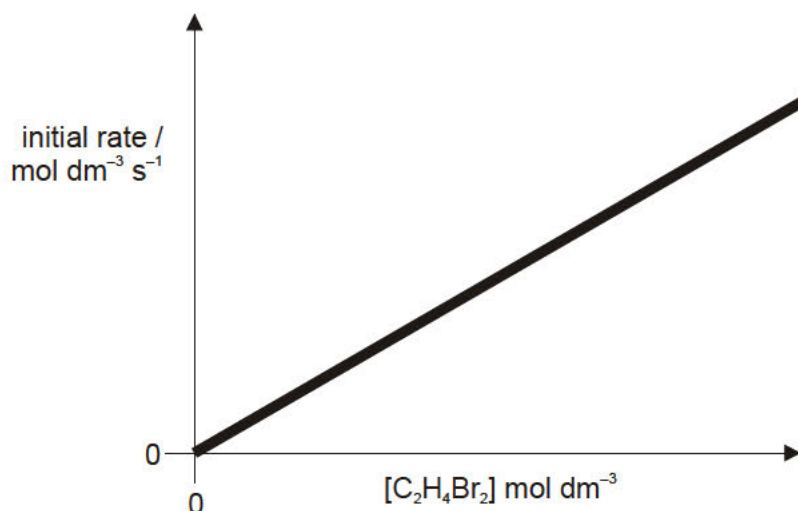
(iii) Half-life is constant

1

OR: draw tangents and then plot a 2nd graph of tangent
 or rate against concentration, which is a straight line
 through the origin. ✓

(iv) Straight line through origin ✓

1



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

2

(c) (i) $\text{rate}/r = k[\text{C}_2\text{H}_4\text{Br}_2][\text{KI}]$ ✓ or ecf from (b)

1

(ii) $k = \frac{\text{rate}}{[\text{C}_2\text{H}_4\text{Br}_2][\text{KI}]} / \frac{0.027}{0.50 \times 0.18}$ ✓
 $= 0.3(0)$ ✓ units: $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ✓
 units dependent on rate equation in (i).
 Mark independently.

3

[11]

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

Therefore 1st order w.r.t. $[\text{CH}_3\text{COCH}_3]$ (1)

2

From table, rate doubles when $[\text{H}^+]$ doubles (1)

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

2

From table, rate stays same when $[\text{I}_2]$ doubles (1)

Therefore zero order w.r.t. $[\text{I}_2]$ (1)

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

2

$\text{rate} = k[\text{H}^+][\text{CH}_3\text{COCH}_3]$ (1)

(from all three pieces of evidence)

$$k = \frac{\text{rate}}{[\text{H}^+][\text{CH}_3\text{COCH}_3]} / \frac{2.1 \times 10^{-9}}{0.02 \times 1.5 \times 10^{-3}} \text{ (1)}$$

$$= 7.0 \times 10^{-5} \text{ (1) } \text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ (1)}$$

accept 7×10^{-5}

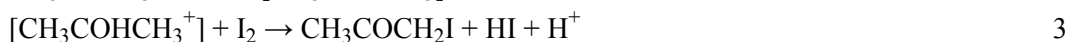
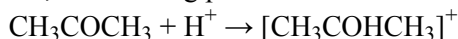
4

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:



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. (i) The slowest step (1) 1



(or similar stage involving intermediates)

[3]

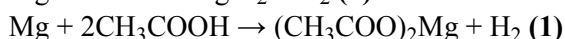
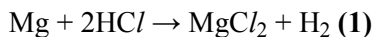
8. HCl and CH_3COOH have same number of moles/

release same number of moles H^+ /

1 mole of each acid produce $\frac{1}{2}$ mol of H_2 (1)

$[\text{H}^+]$ in $\text{CH}_3\text{COOH} < [\text{H}^+]$ in HCl //

CH_3COOH is a weaker acid than HCl (ora) (1)



or



[4]

9. (i) constant half-life (1) 1

(ii) rate = $k[\text{N}_2\text{O}_5]$ (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 $t = 1200 \text{ s}$ (1) 1

- (v) $3.7(2) \times 10^{-4}$ **(1)** mol dm⁻³ s⁻¹ **(1)**
 ecf possible from (ii) using [N₂O₅]^x
 (2nd order answer: $2.2(3) \times 10^{-4}$) 2 **[7]**

- 10.** (i) slow step **(1)** 1
- (ii) $(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH}$ **(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 [(CH₃)₂C=CH₂] [H⁺] **(1)**
 common error will be use of H₂O instead of H⁺ 1 **[5]**