

Reaction Rates and Rate Laws

Answer key with worked solutions

A. Understanding

1. Collision theory.

(a) Powder has a much **larger surface area**, so more particles are exposed to the acid and **collisions happen more often**. (b) A higher concentration means **more particles per litre**, so collisions are **more frequent**; the fraction of collisions with enough energy is unchanged, but there are more of them per second.

B. Rates and stoichiometry

2. Rates of formation.

NO_2 : $0.0060 \text{ M/s} \times (4 \text{ mol NO}_2 / 2 \text{ mol N}_2\text{O}_5) = \mathbf{0.012 \text{ M/s}}$. O_2 : $0.0060 \text{ M/s} \times (1 \text{ mol O}_2 / 2 \text{ mol N}_2\text{O}_5) = \mathbf{0.0030 \text{ M/s}}$.

3. Average rate.

$$-\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.560 \text{ M} - 0.800 \text{ M}}{120 \text{ s}} = \frac{0.240 \text{ M}}{120 \text{ s}} = 2.00 \times 10^{-3} \text{ M/s}$$

C. Rate laws

4. $\text{rate} = k[\text{NO}]^2[\text{H}_2]$.

(a) **second order** in NO, **first order** in H_2 (b) **third order** overall (c) $k = \text{rate} \div ([\text{NO}]^2[\text{H}_2]) = \text{M s}^{-1} \div \text{M}^3 = \mathbf{\text{M}^{-2} \text{ s}^{-1}}$ (d) the rate is multiplied by $2^2 = 4$

5. Method of initial rates.

Experiments 1 → 2: [NO] doubles, [O₂] constant; rate ratio = $\frac{1.12 \times 10^{-5} \text{ M/s}}{2.8 \times 10^{-6} \text{ M/s}} = 4$, so **second order in NO**.

Experiments 1 → 3: [O₂] doubles; rate ratio = $\frac{5.6 \times 10^{-6} \text{ M/s}}{2.8 \times 10^{-6} \text{ M/s}} = 2$, so **first order in O₂**.

Rate law: **rate = k[NO]²[O₂]**. From experiment 1:

$$k = \frac{2.8 \times 10^{-6} \text{ M s}^{-1}}{(0.020 \text{ M})^2(0.010 \text{ M})} = 0.70 \text{ M}^{-2} \text{ s}^{-1}$$

6. Double [NO], halve [O₂].

Rate is multiplied by $2^2 \times \frac{1}{2} = 2$: the rate doubles.

7. Units of k.

Zero order: **M s⁻¹**; first order: **s⁻¹**; second order: **M⁻¹ s⁻¹**

D. Half-life

8. $k = 2.31 \times 10^{-3} \text{ s}^{-1}$.

$$(a) t_{1/2} = \frac{0.693}{2.31 \times 10^{-3} \text{ s}^{-1}} = \mathbf{300. \text{ s}}$$

$$(b) 900. \text{ s} \div 300. \text{ s} = 3 \text{ half-lives, so } [A] = 0.400 \text{ M} \times \left(\frac{1}{2}\right)^3 = \mathbf{0.0500 \text{ M}}$$

E. Challenge

9. $k = 0.0150 \text{ min}^{-1}$, $[A]_0 = 0.200 \text{ M}$.

$$(a) kt = 0.0150 \text{ min}^{-1} \times 60.0 \text{ min} = 0.900 \text{ (no unit)}. [A] = 0.200 \text{ M} \times e^{-0.900} = \mathbf{0.0813 \text{ M}}$$

$$(b) \text{ From } \ln \frac{[A]_0}{[A]_t} = kt:$$

$$t = \frac{\ln(0.200 \text{ M}/0.0500 \text{ M})}{0.0150 \text{ min}^{-1}} = \frac{1.386}{0.0150 \text{ min}^{-1}} = 92.4 \text{ min}$$

(The concentration falls to a quarter, which is exactly 2 half-lives: $2 \times 46.2 \text{ min} = 92.4 \text{ min}$.)