

Orders, rate constants and activation energy

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Worksheet answers

Each answer shows how the order was deduced, the substitution into the rate equation or Arrhenius expression, and the result with its unit. Check particularly the units of k and whether you used kelvin and joules in the Arrhenius calculations.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** IB R2.2

Problem 1 Rate words

1. The change in concentration of a reactant or product per unit time.
2. $\text{mol dm}^{-3} \text{ s}^{-1}$.
3. Temperature and a catalyst change k . Changing the concentration of a reactant does not change k .

Problem 2 Reading a rate equation

1. NO second order, O_2 first order, overall **third order**.
2. Doubling $[\text{O}_2]$: rate $\times 2$. Doubling $[\text{NO}]$: rate $\times 4$.
3. $\text{mol dm}^{-3} \text{ s}^{-1} = k \times (\text{mol dm}^{-3})^3$, so k has units $\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

Problem 3 Doubling and tripling

1. $\times 1$ and $\times 1$.
2. $\times 2$ and $\times 3$.
3. $\times 4$ and $\times 9$.
4. $(\frac{1}{2})^2 = \times 0.25$.

Problem 4 Units of k

1. $\text{mol dm}^{-3} \text{ s}^{-1}$.
2. s^{-1} .
3. $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
4. $\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. Each extra order divides by another mol dm^{-3} .

Problem 5 Rate against concentration

1. **First order**: the graph is a straight line through the origin, so rate $\propto [\text{A}]$.
2. Gradient = $1.5 \times 10^{-3} / 0.50 = 3.0 \times 10^{-3} \text{ s}^{-1}$.
3. Rate = $3.0 \times 10^{-3} \times 0.35 = 1.05 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Problem 6 Using a rate equation

1. Rate = $0.030 \times 0.15^2 = 6.75 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.
2. Rate = $0.030 \times 0.30^2 = 2.7 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.
3. The second is 4 times the first because the concentration doubled and the order is 2.

Problem 7 Initial rates, one reactant

1. Doubling [X] multiplies the rate by 4 and quadrupling by 16, so **second order**.
2. Rate = $k[X]^2$.
3. $k = 1.6 \times 10^{-3} / 0.20^2 = 0.040 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Problem 8 Half-life calculation

1. $t_{1/2} = 0.693 / 4.6 \times 10^{-3} = 151 \text{ s}$.
2. 12.5 % is three half-lives: $3 \times 150.7 = 452 \text{ s}$.
3. **50 %** and **25 %**.

Problem 9 Half-lives from a graph

1. 60 s and 60 s (0.40 at 60 s, 0.20 at 120 s).
2. The half-life is constant, so the reaction is **first order**.
3. $k = 0.693 / 60 = 1.16 \times 10^{-2} \text{ s}^{-1}$.

Problem 10 Two reactants

1. Doubling [A] gives rate $\times 4$: second order in A. Tripling [B] gives rate $\times 3$: first order in B.
2. Rate = $k[A]^2[B]$; overall **third order**.
3. $k = 1.0 \times 10^{-5} / (0.050^2 \times 0.020) = 0.20 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

Problem 11 Slow step

1. Adding: $2\text{NO}_2 + \text{NO}_3 + \text{CO} \rightarrow \text{NO}_3 + \text{NO} + \text{NO}_2 + \text{CO}_2$; cancelling gives **$\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$** . The intermediate is **NO_3** .
2. Rate = $k[\text{NO}_2]^2$.
3. CO reacts only in the fast step after the rate-determining step, so its concentration does not affect the overall rate.

Problem 12 Doubling every ten degrees

1. $3.3557 \times 10^{-3} - 3.2468 \times 10^{-3} = 1.0895 \times 10^{-4} \text{ K}^{-1}$.
2. $E_a = 8.314 \times \ln 2 / 1.0895 \times 10^{-4} = 52\,890 \text{ J/mol} = 52.9 \text{ kJ/mol}$.
3. E_a and A are constant over the range, and the rate constant (not the rate) doubles.

Problem 13 Effect of a catalyst

1. $25.0 \text{ kJ/mol} = \mathbf{25\,000 \text{ J/mol}}$.
2. Factor = $e^{(25\,000 / (8.314 \times 300))} = e^{10.02} = \mathbf{2.25 \times 10^4}$.
3. A larger fraction of collisions have energy at least equal to the lower activation energy.

Problem 14 Reading an Arrhenius plot

1. Gradient = $(-7.40 - (-5.00)) / (0.00340 - 0.00300) = -2.40 / 0.00040 = \mathbf{-6000 \text{ K}}$.
2. $E_a = 6000 \times 8.314 = 49\,884 \text{ J/mol} = \mathbf{49.9 \text{ kJ/mol}}$.
3. $\ln A = -5.00 + 6000 \times 0.00300 = 13.0$, so $A = e^{13} = \mathbf{4.4 \times 10^5 \text{ s}^{-1}}$.

Problem 15 A drug in the body

1. $k = 0.693 / 6.0 = \mathbf{0.1155 \text{ h}^{-1}}$.
2. Fraction = $e^{(-0.1155 \times 15)} = e^{-1.733} = 0.177$, so **17.7 %**.
3. 10 % remains: $t = \ln 10 / k = 2.303 / 0.1155 = \mathbf{19.9 \text{ h}}$.

Problem 16 Three reactants

1. P: doubling doubles the rate, first order. Q: tripling gives $\times 9$, second order. R: quadrupling has no effect, zero order.
2. Rate = $k[P][Q]^2$; $k = 3.0 \times 10^{-5} / (0.10 \times 0.10^2) = \mathbf{0.030 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}}$.
3. Rate = $0.030 \times 0.25 \times 0.15^2 = \mathbf{1.7 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}}$.

Problem 17 Which mechanism?

1. $\text{ICl} + \text{H}_2 + \text{HI} + \text{ICl} \rightarrow \text{HI} + \text{HCl} + \text{I}_2 + \text{HCl}$; cancelling HI gives **$2\text{ICl} + \text{H}_2 \rightarrow \text{I}_2 + 2\text{HCl}$** .
2. A: rate = $k[\text{ICl}][\text{H}_2]$. B: rate = $k[\text{ICl}]^2$.
3. **Mechanism A** fits; the intermediate is HI.

Problem 18 Rate constant at a new temperature

1. $\ln(k_2/k_1) = (65\,000 / 8.314)(1/298 - 1/318) = 7818 \times 2.1105 \times 10^{-4} = \mathbf{1.650}$.
2. $k_2 = 2.5 \times 10^{-4} \times e^{1.650} = 2.5 \times 10^{-4} \times 5.207 = \mathbf{1.30 \times 10^{-3} \text{ s}^{-1}}$.
3. **5.2 times** faster.

Problem 19 Decomposition on a surface

1. [A] falls by 0.015 mol/dm^3 every 100 s, a straight line, so **zero order**.
2. $k = 0.015 / 100 = \mathbf{1.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}}$.
3. $t_{1/2} = [A]_0 / 2k$: $0.100 / (3.0 \times 10^{-4}) = \mathbf{333 \text{ s}}$ and $0.050 / (3.0 \times 10^{-4}) = \mathbf{167 \text{ s}}$. The half-life halves as the concentration halves.

Problem 20 Spot the errors

1. Orders come from experiment, not from coefficients: the rate equation **cannot be written from the balanced equation**.
2. Units are **$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$** ; s^{-1} is for first order.
3. A catalyst provides an alternative route with **lower activation energy**.
4. It is the **slowest step**.