

Rate laws, orders and half-lives

AP Chemistry · Worksheet answers

Full methods are given: formula, substitution and result in bold. Compare your reasoning with the model, not only the final number, because AP graders award marks for method. Small differences in the last digit come from rounding, so keep an extra figure until the end.

Level: AP Chemistry · **Curriculum:** AP Chem Unit 5

Problem 1 Reading a rate law

- Order in A = **2**, order in B = **1**, overall order = **3**.
- rate (M s^{-1}) = $k \text{ M}^3$, so k has units **$\text{M}^{-2} \text{ s}^{-1}$** .
- The rate is proportional to [B], so doubling [B] **doubles the rate**.

Problem 2 Units of the rate constant

- (X) **M s^{-1}** ; (Y) **s^{-1}** ; (Z) **$\text{M}^{-1} \text{ s}^{-1}$** .
- Reaction X** (zero order) has a rate that does not depend on concentration.

Problem 3 What the change in rate tells you

- Factor 2 gives factor $2 = 2^1$: order **1**.
- Factor 3 gives factor $9 = 3^2$: order **2**.
- Factor 2 gives factor $1 = 2^0$: order **0**.

Problem 4 Half-life of a first-order reaction

- $t_{1/2} = 0.693/0.0462 = \mathbf{15.0 \text{ min}}$.
- $45.0 \text{ min} = 3 \text{ half-lives}$, so the fraction left is $(\frac{1}{2})^3 = 1/8 = \mathbf{0.125 (12.5 \%)}$.

Problem 5 Reading a concentration-time graph

- The graph is a straight line falling steadily: **zero order**.
- Slope = $(0.30 - 0.90)/(60 - 0) = -0.010 \text{ M/s}$.
- For zero order slope = $-k$, so $k = \mathbf{0.010 \text{ M s}^{-1}}$.

Problem 6 Choosing the straight-line plot

- A straight $\ln[A]$ plot means **first order**.
- $k = -\text{slope} = \mathbf{0.025 \text{ s}^{-1}}$.
- $t_{1/2} = 0.693/0.025 = \mathbf{28 \text{ s} (27.7 \text{ s})}$.

Problem 7 Second-order half-life

1. $t_{1/2} = 1/(0.25 \times 0.40) = \mathbf{10\ s}$.
2. $t_{1/2} = 1/(0.25 \times 0.20) = \mathbf{20\ s}$.
3. In a second-order reaction $t_{1/2} \propto 1/[A]_0$. With less reactant, collisions between A molecules are rarer, so the halving takes longer.

Problem 8 Initial rates with two reactants

1. Experiments 1 and 2: $[P] \times 2$, rate $\times 2$, so the order in P is **1**.
2. Experiments 2 and 3: $[Q] \times 3$, rate $\times (5.4 \times 10^{-3}/6.0 \times 10^{-4} = 9)$, so the order in Q is **2**.
3. rate = $k[P][Q]^2$. $k = 3.0 \times 10^{-4}/(0.20 \times 0.10^2) = \mathbf{0.15\ M^{-2}\ s^{-1}}$.

Problem 9 Time for a first-order change

1. $t = \ln(0.60/0.15)/k = \ln 4/(2.5 \times 10^{-3}) = 1.386/(2.5 \times 10^{-3}) = \mathbf{5.5 \times 10^2\ s}$ (554 s).
2. $t_{1/2} = 0.693/(2.5 \times 10^{-3}) = 277\ s$. $0.60 \rightarrow 0.30 \rightarrow 0.15\ M$ is two half-lives = 554 s. ✓

Problem 10 Finding k from two measurements

1. $k = \ln(0.80/0.50)/120 = 0.470/120 = \mathbf{3.9 \times 10^{-3}\ s^{-1}}$.
2. $t_{1/2} = 0.693/3.92 \times 10^{-3} = \mathbf{1.8 \times 10^2\ s}$.
3. $[A] = 0.80 \times e^{(-3.92 \times 10^{-3} \times 300)} = 0.80 \times e^{(-1.176)} = 0.80 \times 0.3085 = \mathbf{0.25\ M}$.

Problem 11 Pesticide breakdown on a farm

1. $k = 0.693/8.0 = \mathbf{0.0866\ day^{-1}}$.
2. $t = \ln(5.0/1.0)/0.0866 = 1.609/0.0866 = \mathbf{19\ days}$ (18.6).

Problem 12 Second-order concentration

1. $1/[A]_0 = 1/0.50 = \mathbf{2.0\ M^{-1}}$.
2. $1/[A] = 2.0 + 0.80 \times 25 = 22.0\ M^{-1}$, so $[A] = \mathbf{0.045\ M}$.

Problem 13 Zero-order surface reaction

1. $t = [A]_0/k = 0.0600/(1.5 \times 10^{-4}) = \mathbf{4.0 \times 10^2\ s}$.
2. $t_{1/2} = [A]_0/(2k) = \mathbf{2.0 \times 10^2\ s}$.
3. The surface sites of the metal are saturated with ammonia; they work at full capacity, so adding more gas does not speed the reaction.

Problem 14 Reading half-lives from a graph

1. $0.80 \rightarrow 0.40\ M$ takes 20 s and $0.40 \rightarrow 0.20\ M$ takes another 20 s: **20 s, 20 s**.
2. The half-life is constant, so the reaction is **first order**.

3. $k = 0.693/20 = \mathbf{0.035\ s^{-1}}$ (0.0347).
4. 60 s is three half-lives: $0.80/8 = \mathbf{0.10\ M}$.

Problem 15 Converting the rate constant

1. $k = 3.6 \times 10^{-2}/60 = \mathbf{6.0 \times 10^{-4}\ s^{-1}}$.
2. $t_{1/2} = 0.693/0.036 = \mathbf{19\ min}$ (19.25), which is $0.693/6.0 \times 10^{-4} = 1.2 \times 10^3\ s$.

Problem 16 Deciding the order from data

1. $1/[A] = 1.00, 2.0, 3.0, 4.0\ M^{-1}$ (to two figures: $1/0.33 = 3.0$ and $1/0.25 = 4.0$).
2. $1/[A]$ increases by $1.0\ M^{-1}$ every 50 s: a straight line, so **second order**.
3. $k = \text{slope} = 1.0/50 = \mathbf{0.020\ M^{-1}\ s^{-1}}$.
4. $t_{1/2} = 1/(0.020 \times 1.00) = \mathbf{50\ s}$, and the data show 0.50 M at 50 s. ✓

Problem 17 Three reactants

1. (1)→(2): $[X] \times 2$, rate $\times 2$, order 1. (1)→(3): $[Y] \times 2$, rate $\times 4$, order 2. (1)→(4): $[Z] \times 3$, rate unchanged, order 0.
2. rate = $k[X][Y]^2$. $k = 4.0 \times 10^{-3}/(0.10 \times 0.10^2) = \mathbf{4.0\ M^{-2}\ s^{-1}}$.
3. rate = $4.0 \times 0.30 \times (0.05)^2 = 4.0 \times 0.30 \times 0.0025 = \mathbf{3.0 \times 10^{-3}\ M/s}$.

Problem 18 Gas pressure and first order

1. $t = \ln(80.0/25.0)/1.2 \times 10^{-3} = 1.163/1.2 \times 10^{-3} = \mathbf{9.7 \times 10^2\ s}$.
2. 10.0 min = 600 s; fraction left = $e^{(-1.2 \times 10^{-3} \times 600)} = e^{(-0.72)} = 0.487$, so **51 % reacted**.
3. At constant temperature and volume, the pressure of a gas is proportional to its concentration ($p = cRT$), so the ratio is the same.

Problem 19 Pseudo-first-order kinetics

1. B is in 500-fold excess, so even when all A reacts, $[B]$ changes by only 0.2 %.
2. Slope magnitude = $k[B]$: $k = 3.0 \times 10^{-3}/0.50 = \mathbf{6.0 \times 10^{-3}\ M^{-1}\ s^{-1}}$.
3. $k[B] = 6.0 \times 10^{-3} \times 0.25 = \mathbf{1.5 \times 10^{-3}\ s^{-1}}$.
4. $t_{1/2} = 0.693/1.5 \times 10^{-3} = \mathbf{4.6 \times 10^2\ s}$.

Problem 20 Two first-order reactions racing

1. Reaction 1: 4 half-lives, fraction $(1/2)^4 = \mathbf{1/16}$. Reaction 2: 1 half-life, fraction **1/2**.
2. Ratio = $2^{(t/10)} \div 2^{(t/40)} = 2^{(3t/40)} = 4 = 2^2$, so $3t/40 = 2$ and $t = \mathbf{27\ min}$ (26.7).