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Topic 5.3: Concentration Changes Over Time

Worksheet · AP Chemistry

UNIT 5 · KINETICS

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How to Use This Worksheet

Work in order. Section A checks the three integrated rate laws, the plot each one makes linear, and the half-life expressions. Section B practises using the laws on data and given values of k. Section C combines order identification, slopes, half-lives and predictions in exam style.

Reference facts used throughout. For A → products: zero order, $[A]t = [A]_0 - kt$, linear plot [A] against t, slope −k, intercept $[A]_0$, half-life $[A]_0 \div 2k$. First order, $\ln[A]t = \ln[A]_0 - kt$, linear plot ln[A] against t, slope −k, intercept $\ln[A]_0$, half-life $0.693 \div k$. Second order, $1/[A]t = kt + 1/[A]_0$, linear plot 1/[A] against t, slope +k, intercept $1/[A]_0$, half-life $1 \div (k[A]_0)$. Carry unrounded values through each calculation and round only the final answer, to three significant figures.

Three habits protect every answer. Test all three plots, or all three patterns in the numbers, before naming an order; two of them will curve. Take k from the slope with the correct sign: the [A] and ln[A] slopes are −k, and the 1/[A] slope is +k. And use the half-life expression belonging to the order you identified, not the one you remember first.

One method runs through Sections B and C: decide the order from the data, extract k from the slope or the half-life, then substitute into the matching integrated law to predict a concentration or a time.

Watch the starting concentration. It enters the zero and second order half-lives, it hides in the intercept of an ln[A] plot as $\ln[A]_0$, and a percentage remaining question needs only the ratio $[A]t \div [A]_0$.

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Do not look at the answer key until you have attempted every question.

Section A: Recall and Concepts

A1. For A → products, write the integrated rate law for (a) zero order, (b) first order, (c) second order. For each, name the plot against time that is linear, and state its slope and intercept.

A2. (a) Define the half-life of a reaction. (b) Write the half-life expression for zero, first and second order. (c) State which order has a half-life that does not depend on $[A]_0$, and explain why, using the form of its expression.

A3. A first order reaction starts with $[A]_0 = 0.64$ M. (a) Give [A] after one, two and three half-lives. (b) State the fraction of the original reactant remaining after three half-lives. (c) State the percentage of the reactant consumed after three half-lives.

A4. A rate constant is reported as $k = 4.2 \times 10^{-3}\ s^{-1}$ for a reaction in a single reactant A. (a) State the order of the reaction in A, and explain how the units of k tell you. (b) Calculate the half-life of the reaction.

A5. A plot of ln[A] against time for a reaction is a straight line with slope $-0.0462\ min^{-1}$ and intercept -0.511. (a) State the order of the reaction. (b) Give the value of k, with its units. (c) Calculate $[A]_0$. (d) Calculate the half-life.

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Section B: Core Practice

B1. The concentration of A was measured during a reaction: at t = 0 min, [A] = 0.600 M; at 15 min, 0.300 M; at 30 min, 0.150 M; at 45 min, 0.0750 M. (a) Show from the table that the half-life is constant, and state its value. (b) State the order of the reaction. (c) Calculate k, with its units. (d) Predict [A] at t = 60 min. (e) Calculate the time at which 87.5% of A has been consumed.

B2. A zero order reaction has $[A]_0$ = 0.900 M and k = 0.0250 M min^{-1}. (a) Calculate [A] after 20 min. (b) Calculate the half-life. (c) Calculate the time at which [A] has fallen to 0.100 M. (d) Calculate the time at which the reactant is completely consumed, and explain why the answer the integrated law gives at t = 40 min is meaningless.

B3. A second order reaction has $[A]_0$ = 0.400 M and k = 0.250 M^{-1} min^{-1}. (a) Calculate $1/[A]_0$. (b) Calculate [A] after 8.0 min. (c) Calculate the half-life. (d) Calculate the time at which [A] = 0.100 M, and state the duration of the second half-life, from [A] = 0.200 M to [A] = 0.100 M.

B4. The concentration of A was measured during a reaction: at t = 0 min, [A] = 0.500 M; at 50 min, 0.250 M; at 100 min, 0.125 M; at 150 min, 0.0625 M. (a) Test the data three ways: the changes in [A], the values of ln[A], and the values of 1/[A] over each 50 min interval. State which quantity changes by a constant amount and hence the order of the reaction. (b) Calculate k from the slope of the linear plot, with its units. (c) State $[A]_0$ and show it agrees with the intercept of the linear plot. (d) Calculate the half-life from k, and check it against the table. (e) Predict [A] at t = 200 min.

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B5. A first order reaction has k = 5.78×10^{-3} s^{-1} and $[A]_0$ = 0.750 M. (a) Calculate the half-life. (b) Use the integrated rate law to calculate [A] at t = 240 s, showing the ln[A]t step. (c) Calculate the time at which [A] has fallen to 0.0938 M.

B6. Three reactions, P, Q and R, each start with $[A]_0$ = 0.80 M. In P, [A] falls to 0.40 M in 10 min, then to 0.20 M in a further 10 min. In Q, [A] falls to 0.40 M in 10 min, then to 0.20 M in a further 20 min. In R, [A] falls to 0.40 M in 10 min, then to 0.20 M in a further 5 min. (a) State the order of each reaction, using the pattern of its successive half-lives. (b) Calculate k for each reaction, with its units. (c) For each reaction, state how long the next halving, from 0.20 M to 0.10 M, would take.

Section C: Exam Style

C1. The decomposition of A was followed by measuring [A]: at t = 0 s, [A] = 0.2500 M; at 25 s, 0.1667 M; at 50 s, 0.1250 M; at 75 s, 0.1000 M; at 100 s, 0.0833 M. (a) Calculate ln[A] and 1/[A] at each time and use them to determine the order, stating which plot is linear and which quantities fail to change by constant amounts. (b) Calculate k from the slope of the linear plot, with its units. (c) Use the intercept of the linear plot to state $[A]_0$, and check it against the table. (d) Calculate the half-life, and verify it against the table. (e) Calculate [A] at t = 200 s. (f) A second experiment starts with $[A]_0$ = 0.100 M at the same temperature. Calculate its half-life, and explain why it differs from the value in part (d).

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C2. A first order reaction has a half-life of 18.0 min and starts with $[A]_0$ = 0.960 M. (a) Calculate k, with its units. (b) Calculate [A] after 54.0 min. (c) Calculate the time taken for 90.0% of the reactant to be consumed. (d) Use the integrated rate law to calculate [A] at t = 30.0 min. (e) Explain why part (d) cannot be answered by counting half-lives alone.

C3. The concentration of A was measured during a reaction: at t = 0 s, [A] = 1.00 M; at 10 s, 0.90 M; at 20 s, 0.80 M; at 30 s, 0.70 M; at 40 s, 0.60 M; at 50 s, 0.50 M. (a) Determine the order of the reaction, giving the evidence from the table. (b) Calculate k, with its units, stating how the slope of the linear plot gives it. (c) Calculate the half-life. (d) A second run starts with $[A]_0$ = 0.60 M at the same temperature. Calculate its half-life and the time at which the reactant is completely consumed. (e) The integrated law for the first run gives [A] = −0.20 M at t = 120 s. Explain why this value is impossible and what it tells you about the range over which the law can be applied.

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Answer Key

A1. (a) Zero order: [A]t = $[A]_0$ − kt. The plot of [A] against t is linear, with slope −k and intercept $[A]_0$. (b) First order: ln[A]t = ln$[A]_0$ − kt. The plot of ln[A] against t is linear, with slope −k and intercept ln$[A]_0$. (c) Second order: 1/[A]t = kt + 1/$[A]_0$. The plot of 1/[A] against t is linear, with slope +k and intercept 1/$[A]_0$. In each case the equation is already in the form y = mx + b for its own plotted variable.

A2. (a) The half-life is the time for a reactant's concentration to fall to half of its value at the start of that interval. (b) Zero order: $t_1/_2$ = $[A]_0$ ÷ 2k. First order: $t_1/_2$ = ln 2 ÷ k = 0.693 ÷ k. Second order: $t_1/_2$ = 1 ÷ (k$[A]_0$). (c) First order. Its expression, 0.693 ÷ k, contains only k, so the time to halve is the same whatever the concentration at the start of the interval. The other two expressions contain $[A]_0$, so their half-lives change with the starting concentration.

A3. (a) Each half-life halves the concentration: after one half-life, 0.32 M; after two, 0.16 M; after three, 0.080 M. (b) The fraction remaining is $(1/2)^3$ = 1/8. (c) The fraction consumed is 1 − 1/8 = 7/8, which is 87.5%.

A4. (a) First order. The units of k follow M^(1 − overall order) s^{-1}, and s^{-1} matches an overall order of 1; with A the only reactant, the reaction is first order in A. (b) $t_1/_2$ = 0.693 ÷ k = 0.693 ÷ (4.2×10^{-3}) = 165 s.

A5. (a) First order: a linear ln[A] against time plot is the signature of first order kinetics. (b) The slope of the ln[A] plot is −k, so k = 0.0462 min^{-1}. (c) The intercept is ln$[A]_0$ = −0.511, so $[A]_0$ = e^(−0.511) = 0.600 M. (d) $t_1/_2$ = 0.693 ÷ 0.0462 = 15.0 min.

B1. (a) The concentration halves every 15 min: 0.600 M to 0.300 M, then to 0.150 M, then to 0.0750 M. Equal halving times mean a constant half-life of 15 min. (b) First order: only the first order half-life expression contains no concentration term. (c) k = 0.693 ÷ $t_1/_2$ = 0.693 ÷ 15 = 0.0462 min^{-1}. (d) At 60 min four half-lives have passed, so [A] = 0.600 × $(1/2)^4$ = 0.600 ÷ 16 = 0.0375 M. (e) Consuming 87.5% leaves 12.5%, which is 1/8 of the start, or three half-lives: t = 3 × 15 = 45 min, agreeing with the 0.0750 M reading in the table.

B2. (a) [A]t = $[A]_0$ − kt = 0.900 − (0.0250)(20) = 0.900 − 0.500 = 0.400 M. (b) $t_1/_2$ = $[A]_0$ ÷ 2k = 0.900 ÷ (2 × 0.0250) = 0.900 ÷ 0.0500 = 18.0 min. (c) Rearranging, t = ($[A]_0$ − [A]t) ÷ k = (0.900 − 0.100) ÷ 0.0250 = 0.800 ÷ 0.0250 = 32.0 min. (d) Setting [A]t = 0 gives t = 0.900 ÷ 0.0250 = 36.0 min. At t = 40 min the law gives [A]t = 0.900 − (0.0250)(40) = −0.100 M, which is meaningless: a concentration cannot be negative, the reactant was exhausted at 36.0 min, and the law describes the reaction only while reactant remains.

B3. (a) 1/$[A]_0$ = 1 ÷ 0.400 = 2.50 M^{-1}. (b) 1/[A]t = kt + 1/$[A]_0$ = (0.250)(8.0) + 2.50 = 2.00 + 2.50 = 4.50 M^{-1}, so [A]t = 1 ÷ 4.50 = 0.222 M. (c) $t_1/_2$ = 1 ÷ (k$[A]_0$) = 1 ÷ (0.250 × 0.400) = 1 ÷ 0.100 = 10.0 min. (d) Setting 1/[A]t = 1 ÷ 0.100 = 10.0 M^{-1} gives t = (10.0 − 2.50) ÷ 0.250 = 30.0 min. The second half-life

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runs from 0.200 M (reached at 10.0 min) to 0.100 M at 30.0 min, so it lasts 20.0 min, twice the first, as second order half-lives double.

B4. (a) The changes in [A] per interval are −0.250, −0.125 and −0.0625 M, not constant, so not zero order. The ln[A] values are −0.693, −1.386, −2.079 and −2.773, changing by −0.693 in every interval, which is constant. The 1/[A] values are 2.00, 4.00, 8.00 and 16.0 M^{-1}, changing by 2.00, 4.00 and 8.00 M^{-1}, which are not constant. Only ln[A] changes by a constant amount, so its plot is the linear one and the reaction is first order. (b) Slope = (−2.773 − (−0.693)) ÷ 150 = −2.080 ÷ 150 = −0.01386 min^{-1}. The slope equals −k, so k = 0.0139 min^{-1}, or 0.01386 min^{-1} before rounding. (c) $[A]_0$ = 0.500 M from the table at t = 0. The intercept of the ln[A] plot is $\ln[A]_0 = \ln(0.500)$ = −0.693, matching the first ln[A] value in part (a). (d) $t_1/_2$ = 0.693 ÷ 0.01386 = 50.0 min. The table shows [A] falling from 0.500 M to exactly half, 0.250 M, in the first 50 min, and halving again in each following 50 min, confirming the constant half-life. (e) At 200 min, four half-lives have passed: [A] = 0.500 × $(1/2)^4$ = 0.500 ÷ 16 = 0.0313 M.

B5. (a) $t_1/_2$ = 0.693 ÷ k = 0.693 ÷ (5.78 × 10^{-3}) = 120 s. (b) ln[A]t = $\ln[A]_0$ − kt = ln(0.750) − (5.78 × 10^{-3})(240) = −0.288 − 1.387 = −1.675, so [A]t = e^(−1.675) = 0.187 M. (c) Rearranging for time, t = ($\ln[A]_0$ − ln[A]t) ÷ k = ln(0.750 ÷ 0.0938) ÷ (5.78 × 10^{-3}) = ln(8.00) ÷ (5.78 × 10^{-3}) = 2.079 ÷ (5.78 × 10^{-3}) = 360 s. This is three half-lives, 3 × 120 s, because 0.0938 M is 0.750 M halved three times, which checks the result.

B6. (a) P has equal successive half-lives of 10 min, so P is first order. Q has successive half-lives of 10 min then 20 min, doubling as the concentration falls, so Q is second order. R has successive half-lives of 10 min then 5 min, halving as the concentration falls, so R is zero order. (b) For P, k = 0.693 ÷ $t_1/_2$ = 0.693 ÷ 10 = 0.0693 min^{-1}. For Q, $t_1/_2 = 1 \div (k[A]_0)$ gives k = 1 ÷ ($t_1/_2$ × $[A]_0$) = 1 ÷ (10 × 0.80) = 1 ÷ 8.0 = 0.125 M^{-1} min^{-1}. For R, the rate is the constant fall in [A]: k = (0.80 − 0.40) ÷ 10 = 0.040 M min^{-1}, which the zero order half-life confirms: $t_1/_2 = [A]_0 \div 2k$ = 0.80 ÷ 0.080 = 10 min. (c) For P the half-life never changes, so the next halving takes 10 min. For Q, $t_1/_2 = 1 \div (k[A]_0)$ with $[A]_0$ now 0.20 M: 1 ÷ (0.125 × 0.20) = 1 ÷ 0.0250 = 40 min. For R, the remaining 0.20 M is consumed at the constant rate 0.040 M min^{-1} down to 0.10 M, a fall of 0.10 M, taking 0.10 ÷ 0.040 = 2.5 min.

C1. (a) The ln[A] values at 0, 25, 50, 75 and 100 s are −1.386, −1.792, −2.079, −2.303 and −2.485, changing by −0.406, −0.287, −0.224 and −0.182, which are not constant, so the ln[A] plot curves. The changes in [A] itself are −0.0833, −0.0417, −0.0250 and −0.0167 M, also not constant. The 1/[A] values are 4.00, 6.00, 8.00, 10.0 and 12.0 M^{-1}, rising by exactly 2.00 M^{-1} in every 25 s interval. Only the 1/[A] against time plot is linear, so the reaction is second order. (b) Slope = (12.0 − 4.00) ÷ 100 = 8.00 ÷ 100 = 0.0800 M^{-1} s^{-1}. The slope of a 1/[A] plot is +k, so k = 0.0800 M^{-1} s^{-1}. (c) The intercept is $1/[A]_0$ = 4.00 M^{-1}, so $[A]_0$ = 1 ÷ 4.00 = 0.250 M, matching the measured 0.2500 M at t = 0. (d) $t_1/_2 = 1 \div (k[A]_0)$ = 1 ÷ (0.0800 × 0.250) = 1 ÷ 0.0200 = 50.0 s. The table shows [A] = 0.1250 M at t = 50 s, exactly half of 0.2500 M, confirming it. (e) At t = 200 s, 1/[A]t = 4.00 + (0.0800)(200) = 4.00 + 16.0 = 20.0 M^{-1}, so [A]t = 1 ÷ 20.0 = 0.0500 M. (f) $t_1/_2 = 1 \div (k[A]_0)$ = 1 ÷ (0.0800 × 0.100) = 125 s. The

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half-life has $[A]_0$ in its denominator, so a smaller starting concentration gives a longer half-life: the rate is lower throughout, so halving what is present takes more time.

C2. (a) $k = 0.693 \div t_{1/2} = 0.693 \div 18.0 = 0.0385\ \text{min}^{-1}$. (b) 54.0 min is $54.0 \div 18.0 = 3$ half-lives, so $[A] = 0.960 \times (1/2)^3 = 0.960 \div 8 = 0.120$ M. (c) Consuming 90.0% leaves 10.0%, a ratio $[A]t \div [A]_0$ of 0.100, so $t = \ln(1 \div 0.100) \div k = \ln 10 \div 0.0385 = 2.303 \div 0.0385 = 59.8$ min. That is $\ln 10 \div \ln 2 = 3.32$ half-lives, and $3.32 \times 18.0 = 59.8$ min, which checks. (d) $\ln[A]t = \ln[A]_0 - kt = \ln(0.960) - (0.0385)(30.0) = -0.0408 - 1.155 = -1.196$, so [A]t = e^(−1.196) = 0.302 M. (e) Counting half-lives gives [A] only at whole numbers of half-lives: 18.0, 36.0, 54.0 min. Since 30.0 min is 1.67 half-lives, not a whole number, the halving shortcut cannot land on it, and the integrated law, which works for any t, is needed.

C3. (a) Zero order. [A] falls by exactly 0.10 M in every 10 s interval, so [A] against time is a straight line; neither ln[A] nor 1/[A] changes by a constant amount over these intervals, so those plots curve. (b) The slope of the [A] plot is $(0.50 - 1.00) \div 50 = -0.0100\ \text{M s}^{-1}$. For zero order the slope is $-k$, so $k = 0.0100\ \text{M s}^{-1}$. (c) $t_{1/2} = [A]_0 \div 2k = 1.00 \div (2 \times 0.0100) = 1.00 \div 0.0200 = 50.0$ s, matching the table, where [A] reaches 0.50 M, half of 1.00 M, at t = 50 s. (d) $t_{1/2} = 0.60 \div (2 \times 0.0100) = 0.60 \div 0.0200 = 30.0$ s, shorter than the first run because the zero order half-life is proportional to $[A]_0$. Complete consumption takes $t = [A]_0 \div k = 0.60 \div 0.0100 = 60.0$ s. (e) A concentration of −0.20 M would mean less than none of the reactant present, which is impossible. The law returns it because the straight line simply continues past zero; in reality the reactant runs out at t = 100 s, the reaction stops, and the law is valid only up to complete consumption.

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