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Topic 5.9: Steady-State Approximation

Worksheet · AP Chemistry

UNIT 5 · KINETICS

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How to Use This Worksheet

Work in order. Section A checks the ideas: the steady state, when the pre-equilibrium approximation applies, equilibrium constant expressions, and the effective constant k'. Section B practises the working skills: substitution, denominator rate laws, numerical effective constants, and a steady state with no equilibrium. Section C combines everything in exam style, including an enzyme complex, an ionic intermediate, and a step that hands back one of its own reactants.

The pattern throughout is the same. An intermediate in a steady state is consumed about as fast as it is formed, so d[I]/dt ≈ 0. If a fast reversible step before the slow step holds it at equilibrium, solve that step's K expression for [I] and substitute into the slow step's law, folding the constants into k' = kK. If no equilibrium exists, set the intermediate's formation rate equal to its consumption rate instead. A finished law contains no intermediate and only one constant.

Steps are labelled (slow) or (fast) where the label matters, and a fast reversible step is written with ⇌ and called a fast equilibrium. Species written as single formulas such as A_2, Z or I are single species that balance exactly as written.

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

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Section A: Recall and Concepts

A1. (a) State what is meant by a steady state for an intermediate in a mechanism. (b) Write the steady-state condition for the intermediate concentration [I]. (c) State why the intermediate concentration is small when a steady state holds.

A2. (a) State the conditions under which the pre-equilibrium approximation applies. (b) State two situations in which it does not apply, and what is done instead in each case.

A3. A fast step is $2NO \rightleftharpoons N_2O_2$, with equilibrium constant K. (a) Write the expression for K. (b) Rearrange it to give $[N_2O_2]$ in terms of [NO]. (c) A different fast step is $A \rightleftharpoons B + C$, with equilibrium constant K. Write the expression for K and rearrange it to give [B] in terms of [A] and [C].

A4. (a) State why an intermediate must be removed before a rate law counts as finished. (b) In a finished pre-equilibrium law, what is k', and how are its units worked out? (c) State the three checks to run on a finished rate law.

A5. An experimental rate law is rate = $k[A]^2/[B]$. (a) What feature of a mechanism can put [B] in the denominator? (b) State the order in A, the order in B, and the overall order. (c) State what happens to the rate when [B] is doubled, and explain the effect physically.

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Section B: Core Practice

B1. A mechanism is: Step 1: X + Y ⇌ Z (fast, constant K). Step 2: Z + W → P (slow, constant k_2). (a) Add the steps and write the overall equation. (b) Identify the intermediate. (c) Write the rate law of the slow step as it stands, then derive the finished overall rate law. (d) State the order in each reactant, the overall order, and the units of k'.

B2. A mechanism is: Step 1: A ⇌ B + C (fast, constant K). Step 2: B + D → E (slow, constant k_2). (a) Write the expression for K and solve it for [B]. (b) Derive the finished overall rate law. (c) State the order in A, in C, and in D, and the overall order. (d) State what happens to the rate when [C] is doubled, and why.

B3. A mechanism is: Step 1: A + B ⇌ C (fast, K = 3.0 L/mol). Step 2: C + D → E (slow, k_2 = 0.20 L mol^{-1} s^{-1}). (a) Calculate the effective constant k' of the finished law, with its units. (b) Calculate [C] when [A] = 0.10 mol/L and [B] = 0.30 mol/L. (c) Calculate the rate when [D] = 0.050 mol/L, checking it by both the slow step's law and the finished law.

B4. A mechanism is: Step 1: 2A ⇌ A_2 (fast, constant K). Step 2: A_2 + B → C (slow, constant k_2). (a) Derive the finished overall rate law. (b) State what happens to the rate when [A] is doubled. (c) State what happens to the rate when [B] is doubled. (d) State the overall order of the reaction.

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B5. A mechanism is: Step 1: P + Q → I (one-way, constant k_1 = 0.60 L mol^{-1} s^{-1}). Step 2: I + R → S (slow, constant $k_2 = 3.0 \times 10^2$ L mol^{-1} s^{-1}). (a) Explain why the pre-equilibrium approximation cannot be used for this mechanism. (b) Write the steady-state condition for I, setting its formation rate equal to its consumption rate, and solve it for [I]. (c) Substitute into the slow step's law and write the finished overall rate law. (d) Calculate [I] and the rate when [P] = 0.050, [Q] = 0.040 and [R] = 0.010 mol/L, checking the rate by both routes.

B6. The overall reaction $2NO + O_2 \rightarrow 2NO_2$ has experimental rate law rate = $k[NO]^2[O_2]$. Two mechanisms are proposed. Mechanism I: Step 1: $2NO \rightleftharpoons N_2O_2$ (fast, constant K). Step 2: $N_2O_2 + O_2 \rightarrow 2NO_2$ (slow, constant k_2). Mechanism II: Step 1: $NO + O_2 \rightarrow NO_3$ (slow). Step 2: $NO_3 + NO \rightarrow 2NO_2$ (fast). (a) Show that the steps of each mechanism sum to the overall equation. (b) Identify the intermediate in each mechanism. (c) Write the finished rate law predicted by each mechanism. (d) Give the verdict on each mechanism.

Section C: Exam Style

C1. An enzyme E binds its substrate S in the mechanism: Step 1: E + S ⇌ ES (fast, K = 20 L/mol). Step 2: ES → E + P (slow, k_2 = 10 s^{-1}). (a) Add the steps and write the overall equation. Identify the intermediate, and the species acting as a catalyst, with a reason for each. (b) Write the rate law of the slow step, then derive the finished rate law for the formation of P. (c) Calculate k' and state its units. (d) Calculate [ES] and the rate of product formation when [E] = 1.0×10^{-4} mol/L and [S] = 0.020 mol/L, checking the rate by both laws.

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C2. Nitrous acid is protonated before it reacts with bromide ions: Step 1: $H^+ + HNO_2 \rightleftharpoons H_2NO_2^+$ (fast, constant K). Step 2: $H_2NO_2^+ + Br^- \rightarrow NOBr + H_2O$ (slow, constant k_2). (a) Write the equilibrium constant expression for step 1. (b) Solve it for $[H_2NO_2^+]$. (c) Derive the finished overall rate law and state its overall order. (d) State the effect on the rate of doubling $[H^+]$, and of doubling $[Br^-]$, with a reason for each.

C3. A mechanism is proposed for the reaction of nitrogen dioxide with carbon monoxide: Step 1: $2NO_2 \rightleftharpoons N_2O_4$ (fast, K = 1.5 L/mol). Step 2: $N_2O_4 + CO \rightarrow NO + CO_2 + NO_2$ (slow, $k_2 = 50$ L mol^{-1} s^{-1}). (a) Add the steps and write the overall equation, naming every species that cancels, in whole or in part. (b) Identify the intermediate. (c) Write the rate law of the slow step as it stands, then derive the finished overall rate law. (d) Calculate $[N_2O_4]$ and the rate when $[NO_2] = 0.020$ mol/L and $[CO] = 0.010$ mol/L, checking the rate by both laws. (e) State the overall order of the reaction.

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Answer Key

A1. (a) A steady state means the intermediate is consumed about as fast as it is formed, so after a short opening period its concentration stops changing appreciably and stays nearly constant for most of the reaction. (b) d[I]/dt ≈ 0: the net rate of change of [I] is treated as zero. (c) The intermediate is removed by a fast or slow-but-ready consumption step as quickly as it appears, so it never gets the chance to build up; only a small standing concentration is needed to keep the consumption rate matched to the formation rate.

A2. (a) A fast reversible step must come before the slow step, and it must reach equilibrium quickly and stay at equilibrium while the slow step runs, which holds because the slow step drains the intermediate only slowly. (b) First, if the slow step comes first, there is nothing to substitute: its own rate law is already the finished law. Second, if the step before the slow step is fast but one-way, no equilibrium constant exists; the general steady-state treatment is used instead, setting the intermediate's formation rate equal to its consumption rate and solving for [I].

A3. (a) $K = [N_2O_2]/[NO]^2$: products over reactants, and [NO] is squared because two NO particles form one N_2O_2. (b) $[N_2O_2] = K[NO]^2$. (c) K = [B][C]/[A]. Multiplying both sides by [A] and dividing by [C] gives [B] = K[A]/[C]. Note how the co-product C ends up underneath: any species made alongside the intermediate in the fast step appears in the denominator of the rearranged expression.

A4. (a) An intermediate's concentration is not known, not set in advance, and not directly measurable, so a law containing it cannot be used to predict or compare rates; it describes one step, not the overall reaction. (b) k' is the single overall constant formed by multiplying the slow step's rate constant by the fast step's equilibrium constant, k' = kK. Its units are the product of the two constants' units, and they must match the overall order of the finished law. (c) No intermediate appears anywhere; every species in the law is measurable; and only one constant remains.

A5. (a) B can land in the denominator if B is produced in the fast equilibrium step alongside the intermediate: solving that step's K expression for the intermediate puts [B] underneath. (b) Order 2 in A, order −1 in B, and overall order 2 + (−1) = 1. (c) Doubling [B] halves the rate. Physically, extra B pushes the fast equilibrium backwards towards reactants, so less intermediate is present at equilibrium, and the slow step that feeds on the intermediate runs more slowly.

B1. (a) Left sides sum to X + Y + Z + W. Right sides sum to Z + P. Z appears on both sides and cancels, leaving the overall equation X + Y + W → P. (b) Z is the intermediate: produced in step 1, consumed in step 2, and absent from the overall equation. (c) The slow step gives rate = $k_2[Z][W]$, which still contains the intermediate. From step 1, K = [Z]/([X][Y]), so [Z] = K[X][Y]. Substituting: rate = $k_2K[X][Y][W] = k'[X][Y][W]$. (d) First order in X, in Y and in W; overall order 3; so k' has units $L^2\ mol^{-2}\ s^{-1}$.

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B2. (a) K = [B][C]/[A], so [B] = K[A]/[C]. (b) The slow step gives rate = k_2[B][D]. Substituting for [B]: rate = k_2K[A][D]/[C] = k'[A][D]/[C]. (c) Order 1 in A, order 1 in D, order −1 in C; overall order 1 + 1 − 1 = 1. (d) Doubling [C] halves the rate: C is a product of the fast equilibrium, so adding C shifts that equilibrium back towards A, lowering [B], and the slow step slows in proportion.

B3. (a) k' = k_2K = 0.20 × 3.0 = 0.60 L^2 mol^{-2} s^{-1}, the units multiplying along with the values and matching the third order law rate = k'[A][B][D]. (b) [C] = K[A][B] = 3.0 × 0.10 × 0.30 = 0.090 mol/L. (c) By the slow step's law: rate = 0.20 × 0.090 × 0.050 = 9.0×10^{-4} mol L^{-1} s^{-1}. By the finished law: rate = 0.60 × 0.10 × 0.30 × 0.050 = 9.0×10^{-4} mol L^{-1} s^{-1}. The two routes agree, as they must.

B4. (a) The slow step gives rate = k_2[A_2][B]. From step 1, K = [A_2]/$[A]^2$, so [A_2] = K$[A]^2$. Substituting: rate = k_2K$[A]^2$[B] = k'$[A]^2$[B]. (b) The rate increases fourfold: A appears to the second power, so doubling [A] multiplies the rate by 2^2 = 4. (c) The rate doubles: B appears to the first power. (d) Overall order 3.

B5. (a) Step 1 is written with a one-way arrow: it is not reversible, so it never reaches equilibrium and has no equilibrium constant expression to solve for [I]. (b) Steady state: rate of formation = rate of consumption, so k_1[P][Q] = k_2[I][R]. Solving: [I] = k_1[P][Q]/(k_2[R]). (c) The slow step gives rate = k_2[I][R]. Substituting: rate = k_2 × k_1[P][Q]/(k_2[R]) × [R] = k_1[P][Q]. The k_2 and the [R] cancel completely: the finished law is rate = k_1[P][Q], and the overall rate is set entirely by the formation step. (d) Formation rate = 0.60 × 0.050 × 0.040 = 1.2×10^{-3} mol L^{-1} s^{-1}. Then [I] = 1.2×10^{-3}/(3.0×10^2 × 0.010) = 1.2×10^{-3}/3.0 = 4.0×10^{-4} mol/L, far below the reactant concentrations, as a steady-state intermediate should be. Rate by the slow step: 3.0×10^2 × 4.0×10^{-4} × 0.010 = 1.2×10^{-3} mol L^{-1} s^{-1}. Rate by the finished law: 0.60 × 0.050 × 0.040 = 1.2×10^{-3} mol L^{-1} s^{-1}. The routes agree.

B6. (a) Mechanism I: left sides sum to 2NO + N_2O_2 + O_2, right sides to N_2O_2 + 2NO_2; N_2O_2 cancels, leaving 2NO + O_2 → 2NO_2. Mechanism II: left sides sum to NO + O_2 + NO_3 + NO, right sides to NO_3 + 2NO_2; NO_3 cancels, leaving 2NO + O_2 → 2NO_2. Both pass the sum test. (b) N_2O_2 in Mechanism I; NO_3 in Mechanism II: each is produced in one step and consumed in the next. (c) Mechanism I: the slow step gives rate = k_2[N_2O_2][O_2], and [N_2O_2] = K$[NO]^2$, so the finished law is rate = k'$[NO]^2$[O_2]. Mechanism II: the slow step is first, so its own law is the finished law, rate = k[NO][O_2]. (d) Mechanism I is consistent with the data: its predicted law matches the experimental law exactly. Mechanism II is rejected: it predicts first order in NO and no second NO dependence, disagreeing with experiment, even though its steps sum correctly.

C1. (a) Left sides sum to E + S + ES. Right sides sum to ES + E + P. ES cancels completely and E cancels completely, leaving the overall equation S → P. ES is the intermediate: formed in step 1, consumed in step 2, absent overall. E is the catalyst: it is consumed in step 1 and regenerated in step 2, so it cancels overall yet takes part in the mechanism, and it was added at the start in a known amount. (b) The slow step gives rate = k_2[ES]. From step 1, K = [ES]/([E][S]), so [ES] = K[E][S]. Substituting: rate = k_2K[E][S] = k'[E][S]. E may appear in the finished law because, as a catalyst added at the start, its concentration is known and measurable. (c) k' = k_2K = 10 × 20 = 2.0×10^2 L

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mol^{-1} s^{-1}, matching a second order law. (d) [ES] = 20 × 1.0 × 10^{-4} × 0.020 = 4.0 × 10^{-5} mol/L. By the slow step's law: rate = 10 × 4.0 × 10^{-5} = 4.0 × 10^{-4} mol L^{-1} s^{-1}. By the finished law: rate = 2.0 × 10^{2} × 1.0 × 10^{-4} × 0.020 = 4.0 × 10^{-4} mol L^{-1} s^{-1}. The routes agree.

C2. (a) $K = [H_2NO_2^+]/([H^+][HNO_2])$: the product ion over the two reactants, each to the first power. The charges balance across step 1, +1 on each side, as they must in a real elementary step. (b) $[H_2NO_2^+] = K[H^+][HNO_2]$. (c) The slow step gives rate = $k_2[H_2NO_2^+][Br^-]$. Substituting: rate = $k_2K[H^+][HNO_2][Br^-] = k'[H^+][HNO_2][Br^-]$, with no intermediate remaining. Overall order 3. (d) Doubling $[H^+]$ doubles the rate: H^+ appears to the first power, because more H^+ drives the fast equilibrium to make more $H_2NO_2^+$. Doubling $[Br^-]$ also doubles the rate: Br^- is a reactant of the slow step itself and appears to the first power in its law.

C3. (a) Left sides sum to $2NO_2 + N_2O_4 + CO$. Right sides sum to $N_2O_4 + NO + CO_2 + NO_2$. N_2O_4 cancels completely. NO_2 appears twice on the left and once on the right, so one NO_2 cancels, leaving the overall equation $NO_2 + CO \rightarrow NO + CO_2$. (b) N_2O_4 is the intermediate: produced in step 1, consumed in step 2, and absent from the overall equation. (c) The slow step gives rate = $k_2[N_2O_4][CO]$. From step 1, $K = [N_2O_4]/[NO_2]^2$, so $[N_2O_4] = K[NO_2]^2$. Substituting: rate = $k_2K[NO_2]^2[CO] = k'[NO_2]^2[CO]$. (d) $[N_2O_4] = 1.5 \times (0.020)^2 = 1.5 \times 4.0 \times 10^{-4} = 6.0 \times 10^{-4}$ mol/L. By the slow step's law: rate = 50 × 6.0 × 10^{-4} × 0.010 = 3.0 × 10^{-4} mol L^{-1} s^{-1}. By the finished law, k' = 50 × 1.5 = 75 L^2 mol^{-2} s^{-1}, so rate = 75 × $(0.020)^2$ × 0.010 = 3.0 × 10^{-4} mol L^{-1} s^{-1}. The routes agree. (e) Overall order 3: second order in NO_2 and first order in CO.

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