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Topic 5.8: Reaction Mechanism and Rate Law

Worksheet · AP Chemistry

UNIT 5 · KINETICS

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How to Use This Worksheet

Work in order. Section A checks the vocabulary: rate-determining step, measurable species, pre-equilibrium, and the two tests a proposed mechanism must pass. Section B practises the working skills: reading a law off a slow first step, removing an intermediate through a fast equilibrium, and judging proposals against data. Section C combines everything in exam style, including a fractional order produced by a splitting equilibrium.

The overall rate law is built from the rate-determining step: if the slow step is first, its own law is the overall law. If a fast equilibrium comes before the slow step, the intermediate in the slow step's law is replaced using that equilibrium, the constants folding into one k. A finished law contains only measurable species, never an intermediate, and a mechanism is consistent only if its steps sum to the overall equation and its predicted law matches experiment.

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 M_2, I or J 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) Define the rate-determining step of a mechanism. (b) State how it can be recognised on an energy profile. (c) State why steps that come after it do not appear in the overall rate law.

A2. A slow elementary step is written 2A + B → products. (a) Write the rate law of the step. (b) State the overall order of the step. (c) State the molecularity of the step. (d) State the units of its rate constant when the rate is measured in mol L^{-1} s^{-1}.

A3. (a) State which species may appear in a finished overall rate law. (b) State why an intermediate may not appear in it. (c) State why a catalyst may appear in it, even though a catalyst cancels when the steps of a mechanism are added.

A4. The slow step has the rate law rate = k_2[I][B], where I is an intermediate formed in a fast reversible step before it. (a) State the name given to this arrangement of a fast reversible step before a slow step. (b) Describe the procedure used to turn the step law into the overall rate law. (c) State what happens to the constants k_2 and K in the finished law.

A5. A proposed mechanism sums exactly to the overall equation, but the rate law it predicts differs from the experimental rate law. (a) State the verdict on the mechanism. (b) State what could have been concluded if the predicted law had matched. (c) State the two tests a proposed mechanism must pass.

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Section B: Core Practice

B1. A mechanism is: Step 1: A + B → C (slow). Step 2: C + B → D (fast). (a) Add the steps and write the overall equation. (b) Identify the intermediate. (c) Write the overall rate law. (d) State the overall order and the units of k.

B2. A mechanism is: Step 1: 2X → Y (slow). Step 2: Y + Z → W (fast). (a) Write the overall rate law. (b) State what happens to the rate when [X] is doubled. (c) State what happens to the rate when [Z] is doubled, and why. (d) Write the overall equation.

B3. A mechanism is: Step 1: 2M ⇌ M_2 (fast equilibrium, constant K). Step 2: M_2 + N → P (slow, constant k_2). (a) Add the steps and write the overall equation. (b) Write the rate law of the slow step as it stands, and name the species that makes it unfinished. (c) Use the equilibrium to express [M_2] in terms of [M], substitute, and write the finished overall rate law. (d) State the order in each reactant, the overall order, and the units of the overall k. (e) With K = 0.25 L/mol, k_2 = 8.0 L mol^{-1} s^{-1}, [M] = 0.40 mol/L and [N] = 0.10 mol/L, calculate [M_2] and the rate, checking the rate by both laws.

B4. The experimental rate law of a reaction with overall equation A + B → P is rate = k[A][B]. Two mechanisms are proposed. Mechanism I: Step 1: A + B → I (slow). Step 2: I → P (fast). Mechanism II: Step 1: A ⇌ I (fast equilibrium, constant K). Step 2: I + B → P (slow, constant k_2). (a) Write the overall equation produced by each mechanism. (b) Write the finished rate law predicted by each mechanism. (c) Give the verdict on each mechanism. (d) State what the two verdicts together show about mechanisms and proof.

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B5. A mechanism is: Step 1: A → I (fast). Step 2: I + B → P (slow). A student writes the overall rate law as rate = k[I][B]. (a) Explain why this cannot be accepted as the overall rate law. (b) State the one change to step 1 that would allow I to be eliminated by the method of this topic, and why that change matters. (c) With that change made, step 1 has equilibrium constant K = 1.5. Derive the overall rate law, and calculate the overall k if k_2 = 0.20 L mol^{-1} s^{-1}.

B6. The reaction $2NO_2 + F_2 \rightarrow 2NO_2F$ has experimental rate law rate = $k[NO_2][F_2]$. A proposed mechanism is: Step 1: $NO_2 + F_2 \rightarrow NO_2F + F$ (slow). Step 2: $NO_2 + F \rightarrow NO_2F$ (fast). (a) Show that the steps sum to the overall equation. (b) Identify the intermediate. (c) Write the rate law predicted by the mechanism and give the verdict on it. (d) With k = 0.40 L mol^{-1} s^{-1}, $[NO_2]$ = 0.050 mol/L and $[F_2]$ = 0.020 mol/L, calculate the rate. (e) State the effect of doubling $[F_2]$ on the rate.

Section C: Exam Style

C1. The overall reaction $2NO + Br_2 \rightarrow 2NOBr$ has experimental rate law rate = $k[NO]^2[Br_2]$. A proposed mechanism is: Step 1: $NO + Br_2 \rightleftharpoons NOBr_2$ (fast equilibrium, constant K). Step 2: $NOBr_2 + NO \rightarrow 2NOBr$ (slow, constant k_2). (a) Show that the steps sum to the overall equation. (b) Identify the intermediate. (c) Write the rate law of the slow step as it stands. (d) Use step 1 to eliminate the intermediate and derive the finished overall rate law. (e) Give the verdict on the mechanism, with the reason. (f) With K = 0.80 L/mol and $k_2 = 5.0 \times 10^2$ L mol^{-1} s^{-1}, and with $[NO] = [Br_2]$ = 0.010 mol/L, calculate the concentration of the intermediate and the rate, checking the rate by both laws.

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C2. The overall reaction $2X + Y \rightarrow P$ has experimental rate law rate = $k[X]^2$. Three mechanisms are proposed. Mechanism I: Step 1: $2X \rightarrow I$ (slow). Step 2: $I + Y \rightarrow P$ (fast). Mechanism II: Step 1: $X + Y \rightarrow I$ (slow). Step 2: $I + X \rightarrow P$ (fast). Mechanism III: Step 1: $X \rightleftharpoons I$ (fast equilibrium, constant K). Step 2: $I + X \rightarrow J$ (slow, constant k_2). Step 3: $J + Y \rightarrow P$ (fast). (a) Show that each mechanism sums to the overall equation, naming the species that cancel in each. (b) Write the finished rate law predicted by each mechanism. (c) State which mechanisms are consistent with the experimental rate law, and which is rejected. (d) State the general conclusion about mechanisms that this comparison demonstrates.

C3. Chloroform is chlorinated by the mechanism: Step 1: $Cl_2 \rightleftharpoons 2Cl$ (fast equilibrium, constant K). Step 2: $Cl + CHCl_3 \rightarrow HCl + CCl_3$ (slow, constant k_2). Step 3: $CCl_3 + Cl \rightarrow CCl_4$ (fast). (a) Add the steps and write the overall equation. (b) Identify both intermediates. (c) Write the rate law of the slow step, then use step 1 to derive the finished overall rate law, and state the order in Cl_2. (d) With K = 4.0×10^{-4} mol/L and $[Cl_2]$ = 0.010 mol/L, calculate [Cl]. (e) With $k_2 = 2.5 \times 10^3$ L mol^{-1} s^{-1} and $[CHCl_3]$ = 0.10 mol/L, calculate the rate. (f) State the overall order of the reaction.

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Answer Key

A1. (a) The rate-determining step is the slowest step of a mechanism, and it sets the overall rate of the reaction. (b) On an energy profile it is the step whose activation energy barrier, measured from the level just before its peak to the peak itself, is the highest. (c) Steps after it only process what the slow step has supplied, running fast on whatever arrives, so their reactants cannot change the overall rate and do not appear in the rate law.

A2. (a) rate = $k[A]^2[B]$, because an elementary step's law is written from its own reactants with orders equal to coefficients. (b) Overall order 3, from 2 + 1. (c) Termolecular: three reactant particles, two of A and one of B, take part in the single event. (d) Dividing rate units by concentration cubed: (mol L^{-1} s^{-1}) / (mol L^{-1})^3 = L^2 mol^{-2} s^{-1}.

A3. (a) Only species with known, measurable concentrations: the reactants placed in the vessel, and a catalyst added at the start. (b) An intermediate is produced and consumed inside the mechanism; its concentration rises and falls during the run, is never set in advance, and cannot be measured directly, so it cannot appear in a usable law. (c) A catalyst cancels in the sum because it is regenerated, but it was added at the start in a known amount, so its concentration is known throughout and may appear when it is a reactant of the slow step.

A4. (a) A pre-equilibrium: a fast equilibrium established before the rate-determining step. (b) Write the equilibrium constant expression for the fast step, rearrange it to give [I] in terms of measurable reactants, and substitute that expression into the slow step's law in place of [I]. (c) They merge into a single overall constant, $k = k_2K$.

A5. (a) The mechanism is rejected. A predicted rate law that disagrees with experiment rules the mechanism out, however well the steps sum. (b) Only that the mechanism is consistent with the data: supported by the evidence, not proved, because another mechanism might predict the same law. (c) First, the steps must add up to the overall equation. Second, the rate law predicted from the rate-determining step must match the experimental rate law.

B1. (a) Left sides sum to A + B + C + B = A + 2B + C. Right sides sum to C + D. C appears on both sides and cancels, leaving the overall equation A + 2B → D. (b) C is the intermediate: produced in step 1, consumed in step 2. (c) The slow step is first, so the overall rate law is its own law: rate = k[A][B]. (d) Overall order 2, so k has units L mol^{-1} s^{-1}.

B2. (a) rate = $k[X]^2$, the law of the slow first step. (b) The rate increases fourfold, because X appears to the second power: doubling [X] multiplies the rate by $2^2 = 4$. (c) The rate is unchanged: Z reacts in step 2, after the rate-determining step, so [Z] does not appear in the rate law. (d) Adding the steps and cancelling Y gives 2X + Z → W.

B3. (a) Left sides sum to 2M + M_2 + N. Right sides sum to M_2 + P. M_2 cancels, leaving 2M + N → P. (b) rate = $k_2[M_2][N]$. It is unfinished because M_2 is the intermediate, produced in step 1 and consumed

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in step 2, and an intermediate cannot appear in a finished law. (c) From step 1, $K = [M_2]/[M]^2$, so $[M_2] = K[M]^2$. Substituting: rate = $k_2K[M]^2[N] = k[M]^2[N]$, with $k = k_2K$. (d) Order 2 in M, order 1 in N, overall order 3, so k has units $L^2\ mol^{-2}\ s^{-1}$. (e) $[M_2] = 0.25 \times (0.40)^2 = 0.25 \times 0.16 = 0.040$ mol/L. By the step law, rate = $8.0 \times 0.040 \times 0.10 = 0.032$ mol $L^{-1}\ s^{-1}$. By the finished law, $k = 0.25 \times 8.0 = 2.0\ L^2\ mol^{-2}\ s^{-1}$, and rate = $2.0 \times (0.40)^2 \times 0.10 = 2.0 \times 0.16 \times 0.10 = 0.032$ mol $L^{-1}\ s^{-1}$. The two routes agree, as they must.

B4. (a) Mechanism I: left sides sum to A + B + I, right sides to I + P; I cancels, giving A + B → P. Mechanism II: left sides sum to A + I + B, right sides to I + P; I cancels, giving A + B → P. Both produce the stated overall equation. (b) Mechanism I: the slow step is first, so its law is the overall law, rate = k[A][B]. Mechanism II: the slow step gives rate = k_2[I][B]; from step 1, K = [I]/[A], so [I] = K[A], and substitution gives rate = k_2K[A][B] = k[A][B]. (c) Both mechanisms are consistent with the experimental rate law: each passes the sum test and the rate law test. (d) Two different mechanisms can predict the same rate law, so a matching law can never prove a mechanism. Kinetics can reject a mechanism, but between mechanisms that both fit, it cannot choose.

B5. (a) I is an intermediate, made in step 1 and consumed in step 2. Its concentration is not known, not set, and not directly measurable, so a law containing [I] is not a usable overall rate law. (b) Step 1 must be a fast equilibrium, written A ⇌ I, instead of a one-way fast step. Only then does an equilibrium constant expression tie [I] to the measurable [A] while the slow step runs. (c) From step 1, K = [I]/[A], so [I] = K[A] = 1.5[A]. Substituting into rate = k_2[I][B] gives rate = $1.5k_2$[A][B] = k[A][B]. The overall constant is $k = 1.5 \times 0.20 = 0.30\ L\ mol^{-1}\ s^{-1}$.

B6. (a) Left sides sum to $NO_2 + F_2 + NO_2 + F = 2NO_2 + F_2 + F$. Right sides sum to $NO_2F + F + NO_2F = 2NO_2F + F$. F appears on both sides and cancels, leaving $2NO_2 + F_2 \rightarrow 2NO_2F$, the overall equation. (b) F is the intermediate: produced in step 1, consumed in step 2. (c) The slow step is first, so the predicted law is rate = k[NO_2][F_2]. This matches the experimental rate law, so the mechanism is consistent with the data. (d) rate = $0.40 \times 0.050 \times 0.020 = 4.0 \times 10^{-4}$ mol $L^{-1}\ s^{-1}$. (e) The rate doubles: F_2 appears to the first power in the rate law, so doubling [F_2] doubles the rate.

C1. (a) Left sides sum to $NO + Br_2 + NOBr_2 + NO = 2NO + Br_2 + NOBr_2$. Right sides sum to $NOBr_2 + 2NOBr$. $NOBr_2$ appears on both sides and cancels, leaving $2NO + Br_2 \rightarrow 2NOBr$, the overall equation. (b) $NOBr_2$ is the intermediate: produced in step 1, consumed in step 2, and absent from the overall equation. (c) rate = k_2[$NOBr_2$][NO], the law of the slow step written from its own reactants. (d) From step 1, $K = [NOBr_2]/([NO][Br_2])$, so $[NOBr_2] = K[NO][Br_2]$. Substituting into the step law: rate = $k_2K[NO][Br_2][NO] = k[NO]^2[Br_2]$, with $k = k_2K$. (e) The mechanism is consistent: its steps sum to the overall equation and its predicted law, rate = $k[NO]^2[Br_2]$, matches the experimental rate law. (f) $[NOBr_2] = 0.80 \times 0.010 \times 0.010 = 8.0 \times 10^{-5}$ mol/L. By the step law, rate = $5.0 \times 10^2 \times 8.0 \times 10^{-5} \times 0.010 = 4.0 \times 10^{-4}$ mol $L^{-1}\ s^{-1}$. By the finished law, $k = 0.80 \times 5.0 \times 10^2 = 4.0 \times 10^2\ L^2\ mol^{-2}\ s^{-1}$, and rate = $4.0 \times 10^2 \times (0.010)^2 \times 0.010 = 4.0 \times 10^{-4}$ mol $L^{-1}\ s^{-1}$. Both routes agree.

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C2. (a) Mechanism I: left sides sum to 2X + I + Y, right sides to I + P; I cancels, leaving 2X + Y → P. Mechanism II: left sides sum to X + Y + I + X, right sides to I + P; I cancels, leaving 2X + Y → P. Mechanism III: left sides sum to X + I + X + J + Y, right sides to I + J + P; both I and J cancel, leaving 2X + Y → P. All three pass the sum test. (b) Mechanism I: the slow step is first, so rate = $k[X]^2$. Mechanism II: the slow step is first, so rate = k[X][Y]. Mechanism III: the slow step gives rate = $k_2[I][X]$; from step 1, [I] = K[X], so substitution gives rate = $k_2K[X]^2 = k[X]^2$. (c) Mechanisms I and III are consistent with the experimental rate law rate = $k[X]^2$. Mechanism II predicts rate = k[X][Y], which contains Y and disagrees with experiment, so Mechanism II is rejected. (d) Passing both tests still is not proof: two quite different mechanisms, I and III, fit the same overall equation and the same rate law. Agreement can support a mechanism and can eliminate one, but it can never establish that a mechanism is the only possible route.

C3. (a) Left sides sum to $Cl_2 + Cl + CHCl_3 + CCl_3 + Cl = Cl_2 + CHCl_3 + 2Cl + CCl_3$. Right sides sum to $2Cl + HCl + CCl_3 + CCl_4$. Both Cl and CCl_3 appear on both sides: cancelling 2Cl and CCl_3 leaves the overall equation $Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$. (b) Cl, produced in step 1 and consumed in steps 2 and 3, and CCl_3, produced in step 2 and consumed in step 3. (c) The slow step gives rate = $k_2[Cl][CHCl_3]$. From step 1, $K = [Cl]^2/[Cl_2]$, so $[Cl] = (K[Cl_2])^{1/2}$, taking the positive square root. Substituting: rate = $k_2K^{1/2}[Cl_2]^{1/2}[CHCl_3] = k[Cl_2]^{1/2}[CHCl_3]$. The order in Cl_2 is one half: a fractional order, created because the equilibrium splits one Cl_2 into two Cl while the slow step uses only one of them. (d) $[Cl] = (4.0 \times 10^{-4} \times 0.010)^{1/2} = (4.0 \times 10^{-6})^{1/2} = 2.0 \times 10^{-3}$ mol/L. (e) rate = $2.5 \times 10^3 \times 2.0 \times 10^{-3} \times 0.10 = 0.50$ mol L^{-1} s^{-1}. (f) The overall order is ½ + 1 = 3/2, one and a half: half order in Cl_2 and first order in $CHCl_3$.

Continue Revising

Topic 5.8 Revision Notes

Topic 5.8 Quiz: Reaction Mechanism and Rate Law

Previous Worksheet: Topic 5.7 Introduction to Reaction Mechanisms

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