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Topic 5.7: Introduction to Reaction Mechanisms

Worksheet · AP Chemistry

UNIT 5 · KINETICS

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How to Use This Worksheet

Work in order. Section A checks the vocabulary: mechanism, elementary step, intermediate, catalyst, transition state, and the two tests a proposed mechanism must pass. Section B practises the working skills: adding steps, cancelling species, spotting the step that must be multiplied, judging proposals. Section C combines everything in exam style, including a catalysed surface mechanism and a rate law error to correct.

Reference facts used throughout. The overall equation is the sum of the steps after every species that appears on both sides cancels. An intermediate is produced in one step and consumed in a later step; a catalyst is consumed in an early step and regenerated in a later step; both are absent from the overall equation. Each elementary step has exactly one transition state. The rate law of a step is written from that step's own reactants (Topic 5.4), and the overall rate law follows the slow step, never the overall equation.

Steps are labelled (slow) or (fast) where the label matters. Species written as formulas such as MP, XZ_2 or AB_2 are single species that balance exactly as written; treat each as one particle type.

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 a reaction mechanism. (b) Define an elementary step. (c) State what the overall equation of a reaction shows, and one thing it cannot show.

A2. (a) Define a reaction intermediate. (b) State the two appearances, in order, that mark a species as an intermediate. (c) State whether an intermediate appears in the overall equation, and why. (d) Describe how the concentration of an intermediate changes as the reaction proceeds.

A3. (a) Define a catalyst in terms of the steps of a mechanism. (b) State the two appearances, in order, that mark a species as a catalyst. (c) State how the amount of catalyst present at the end of a reaction compares with the amount at the start. (d) State the single question that distinguishes a catalyst from an intermediate.

A4. (a) State what a transition state is, and where it sits on an energy profile. (b) State how many transition states a mechanism of three elementary steps has. (c) State what sits in the valley between two peaks of an energy profile. (d) State which of a transition state and an intermediate can in principle be detected during a reaction, and why the other cannot.

A5. (a) State the two tests a proposed mechanism must pass. (b) State why passing both tests still does not prove the mechanism. (c) State the greatest number of reactant particles a plausible elementary step can involve, and why a step needing four particles is rejected.

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Section B: Core Practice

B1. A mechanism proposed for the decomposition $2O_3 \rightarrow 3O_2$ is: Step 1: $O_3 \rightarrow O_2 + O$. Step 2: $O + O_3 \rightarrow 2O_2$. (a) Add the steps and write the overall equation, showing what cancels. (b) Identify the intermediate, giving the two appearances that prove it. (c) State how many transition states this pathway has.

B2. In the stratosphere, nitric oxide takes part in the destruction of ozone. Step 1: $NO + O_3 \rightarrow NO_2 + O_2$. Step 2: $NO_2 + O \rightarrow NO + O_2$. (a) Add the steps and write the overall equation. (b) Identify the catalyst and the intermediate, stating the order of appearances for each. (c) State what happens to the total amount of NO as the overall reaction proceeds, and why that matters for ozone.

B3. A mechanism has two steps. Step 1: $A_2 \rightarrow 2A$. Step 2: $A + B_2 \rightarrow AB_2$. (a) Explain why step 2 must run twice for every one run of step 1 if the mechanism is to keep going. (b) Write out step 2 doubled, add it to step 1, and give the overall equation. (c) Identify the intermediate.

B4. A mechanism has three steps. Step 1: $MN + P \rightarrow MP + N$. Step 2: $MP + Q \rightarrow MPQ$. Step 3: $N + MP_2 \rightarrow MP + NP$. (a) Add the three steps and write the overall equation. (b) Identify the intermediate. (c) A student calls MP the intermediate, because it is produced in step 1 and consumed in step 2. Explain, using the sum, why the student is wrong.

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B5. A three-step mechanism produces an intermediate I. Measurements during one run give the concentration of I in mol/L: 0.000 at 0 s, 0.018 at 10 s, 0.027 at 20 s, 0.015 at 30 s and 0.000 at 40 s. (a) State the maximum concentration of I reached, and the time at which it is reached. (b) Explain the rise and then the fall of the concentration in terms of the steps that form and consume I. (c) State how many peaks and how many valleys the energy profile of a three-step mechanism has. (d) State how the concentration record of a catalyst over the same run would differ from the record of I.

B6. The overall equation of a reaction is $2NO + Br_2 \rightarrow 2NOBr$, and two mechanisms are proposed. Proposal A: Step 1: $NO + Br_2 \rightarrow NOBr_2$; Step 2: $NOBr_2 \rightarrow NOBr + Br$. Proposal B: a single elementary step, $2NO + Br_2 \rightarrow 2NOBr$. (a) Add the steps of Proposal A and state the equation they actually sum to. (b) Give the verdict on Proposal A, with the reason. (c) Proposal B sums to the overall equation by construction. Give the verdict on Proposal B, with the reason. (d) State the general lesson the two verdicts teach about the sum test.

Section C: Exam Style

C1. A three-step mechanism is: Step 1: $H_2 + NO \rightarrow H_2O + N$ (slow). Step 2: $N + NO \rightarrow N_2O$ (fast). Step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast). (a) Add the steps and write the overall equation, showing every cancellation. (b) Identify all the intermediates. (c) State whether the mechanism contains a catalyst, and how you can tell. (d) State how many transition states the pathway has. (e) Write the rate law of step 1 as an elementary step, and state the molecularity of each of the three steps.

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C2. Platinum catalyses the reaction of hydrogen with oxygen at its surface. Step 1: $Pt + O_2 \rightarrow PtO_2$ (fast). Step 2: $PtO_2 + 2H_2 \rightarrow Pt + 2H_2O$ (slow). (a) Add the steps and write the overall equation. (b) Identify the catalyst, stating the two appearances that mark it. (c) Identify the intermediate. (d) State which two species are absent from the overall equation, and explain why the reason for the absence differs between them. (e) A run begins with 0.250 mol of Pt. State how many moles of Pt, and how many moles of PtO_2, are present when the reaction is complete.

C3. For the overall reaction $2O_3 \rightarrow 3O_2$, a student writes rate = $k[O_3]^2$ straight from the balanced equation. The mechanism is: Step 1: $O_3 \rightarrow O_2 + O$ (slow). Step 2: $O + O_3 \rightarrow 2O_2$ (fast). (a) Explain what is wrong with the student's rate law. (b) Show that the mechanism sums to the overall equation. (c) Identify the intermediate. (d) Write the rate law that follows from the slow step, and state the molecularity of that step. (e) The student then argues that O should appear in the rate law because it appears in the mechanism. Correct the claim.

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Answer Key

A1. (a) A mechanism is the sequence of elementary steps by which a reaction actually takes place, whose sum is the overall equation. (b) An elementary step is a single molecular event that occurs exactly as its equation is written, with no hidden sub-steps. (c) The overall equation shows the net change only: reactants consumed overall and products formed overall. It cannot show the route: nothing about the steps, the intermediates, or any catalyst involved.

A2. (a) An intermediate is a species formed in one step of a mechanism and consumed in a later step. (b) It appears first as a product of one step, later as a reactant of another. (c) No. It is produced and then consumed inside the sequence, so it cancels when the steps are added together. (d) It starts at zero, rises while the forming step runs ahead of the consuming step, then falls as consumption catches up, returning to zero by the end.

A3. (a) A catalyst is a species that takes part in the steps, speeds the reaction up, and is regenerated by a later step, so it is not used up overall. (b) It appears first as a reactant, consumed in an early step, and later as a product, regenerated in a later step. (c) The amounts are identical: all of the catalyst present at the start is present again at the end. (d) Ask which came first for that species: if it was made first, it is an intermediate; if it was used first, it is a catalyst.

A4. (a) A transition state is the highest-energy arrangement of atoms passed through during one elementary step; on an energy profile it sits at the top of a peak. (b) Three: exactly one transition state per elementary step. (c) An intermediate: a real species resting at a local energy minimum between the two steps. (d) The intermediate can in principle be detected, because it is a real species that builds up to a measurable concentration. The transition state cannot: it is a fleeting energy maximum that falls apart at once into reactants or products, so it never exists as a substance to detect or isolate.

A5. (a) First, the steps must add up to the overall equation, with every intermediate and catalyst cancelling. Second, the mechanism must agree with the experimental evidence, above all the measured rate law, which is governed by the slowest step. (b) A different sequence of steps might fit the same overall equation and the same evidence equally well, so evidence can support a mechanism and can rule one out, but never prove one sequence is the only possible route. (c) Three at the very most, and three-particle steps are already extremely rare; two-particle steps are the norm. A step needing four particles would require all four to arrive at one point at the same instant, with enough energy and correct orientation: so improbable it is treated as impossible.

B1. (a) Left sides sum to $O_3 + O + O_3 = 2O_3 + O$. Right sides sum to $O_2 + O + 2O_2 = 3O_2 + O$. O appears on both sides and cancels, leaving $2O_3 \rightarrow 3O_2$, the overall equation. (b) O is the intermediate: produced in step 1, consumed in step 2, made first and used later. (c) Two, one for each elementary step.

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B2. (a) Left sides sum to NO + O_3 + NO_2 + O. Right sides sum to NO_2 + O_2 + NO + O_2. Both NO and NO_2 appear on both sides and cancel, leaving O_3 + O → $2O_2$. (b) NO is the catalyst: consumed in step 1, regenerated in step 2, used first and remade later. NO_2 is the intermediate: produced in step 1, consumed in step 2, made first and used later. (c) The total amount of NO does not change: every NO consumed in step 1 is remade in step 2. That is why a small amount of NO can destroy a large amount of ozone, cycling through the two steps repeatedly.

B3. (a) Step 1 releases two A particles, and each run of step 2 consumes only one A. If step 2 ran only once per step 1, one A would be left over with no step to consume it. Running it twice consumes both A particles. (b) Step 2 doubled: 2A + $2B_2$ → $2AB_2$. Adding step 1 gives A_2 + 2A + $2B_2$ on the left and 2A + $2AB_2$ on the right. Cancelling 2A from both sides leaves the overall equation A_2 + $2B_2$ → $2AB_2$. (c) A is the intermediate: produced in step 1, consumed in step 2, fully cancelled in the sum.

B4. (a) Left sides sum to MN + P + MP + Q + N + MP_2. Right sides sum to MP + N + MPQ + MP + NP. N appears once on each side and cancels completely. MP appears once on the left and twice on the right, so one MP survives as a product. The overall equation is MN + P + Q + MP_2 → MP + MPQ + NP. (b) N is the intermediate: produced in step 1, consumed in step 3, fully cancelled. (c) MP is produced twice, in step 1 and again in step 3, but consumed only once, in step 2. The cancellation therefore leaves one MP standing in the overall equation, which makes MP a net product. An intermediate must cancel completely; a species that survives into the overall equation is a product, however intermediate-like its first two appearances look.

B5. (a) The maximum is 0.027 mol/L, reached at 20 s. (b) At first the step forming I produces it faster than the consuming step removes it, so I builds up. As reactants are used up, formation slows while the accumulated I keeps being consumed, so the concentration falls. By 40 s every I formed has been consumed, back to zero, exactly as an intermediate must behave. (c) Three peaks, one transition state per step, and two valleys, one between each pair of peaks. (d) A catalyst starts at its full initial concentration, not at zero. Its concentration dips while some of it is tied up inside the steps, then returns to exactly its starting value at the end: it neither starts nor ends at zero.

B6. (a) Left sides sum to NO + Br_2 + $NOBr_2$. Right sides sum to $NOBr_2$ + NOBr + Br. Cancelling $NOBr_2$ leaves NO + Br_2 → NOBr + Br. (b) Proposal A is rejected. Its steps sum to the wrong equation: they consume only one NO and produce NOBr and a free Br atom, not 2NOBr. A mechanism whose steps do not add up to the overall equation fails the first test, however reasonable each step looks alone. (c) Proposal B is also rejected. Written as one elementary step, it would need two NO particles and one Br_2 particle to collide at the same instant: a termolecular event so improbable that it is not accepted as a real step. The reaction must instead proceed through a sequence of one- and two-particle steps. (d) Summing to the overall equation is necessary but not sufficient. Proposal A fails even that test, while Proposal B passes it and is still rejected, because every step must also be a plausible single event, and the mechanism must agree with experimental evidence.

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C1. (a) Left sides sum to $H_2 + NO + N + NO + N_2O + H_2 = 2H_2 + 2NO + N + N_2O$. Right sides sum to $H_2O + N + N_2O + N_2 + H_2O = 2H_2O + N_2 + N + N_2O$. N and N_2O each appear on both sides and cancel. The overall equation is $2H_2 + 2NO \rightarrow N_2 + 2H_2O$. (b) N, formed in step 1 and consumed in step 2, and N_2O, formed in step 2 and consumed in step 3. Both cancel fully. (c) No. A catalyst must be consumed in an early step and regenerated later, and no species follows that pattern here: every species that cancels, N and N_2O, was produced before it was consumed. (d) Three transition states, one per elementary step. (e) Step 1 has reactants H_2 and NO, so its rate law is rate = $k[H_2][NO]$. Each of the three steps has two reactant particles, so all three steps are bimolecular.

C2. (a) Left sides sum to $Pt + O_2 + PtO_2 + 2H_2$. Right sides sum to $PtO_2 + Pt + 2H_2O$. Pt appears on both sides and cancels; PtO_2 appears on both sides and cancels. The overall equation is $O_2 + 2H_2 \rightarrow 2H_2O$. (b) Pt is the catalyst: it appears first as a reactant in step 1, consumed, and then as a product in step 2, regenerated. Used first, remade later is the catalyst pattern. (c) PtO_2 is the intermediate: produced in step 1 and consumed in step 2. (d) Pt and PtO_2 are both absent from the overall equation, but for opposite reasons. Pt is absent because it is given back: it survives the reaction unchanged in amount. PtO_2 is absent because it is used up: it existed only mid-reaction and none remains at the end. (e) Pt: 0.250 mol, the full starting amount, because a catalyst is regenerated. PtO_2: 0 mol, because an intermediate is completely consumed by the end.

C3. (a) The overall equation is the sum of the steps, not a single molecular event, so its coefficients are not orders in a rate law. A rate law comes from experiment and the mechanism: here it is governed by the slow step, step 1. The coefficient 2 in front of O_3 says only that two O_3 are consumed overall; it is not an exponent. (b) Left sides sum to $O_3 + O + O_3 = 2O_3 + O$. Right sides sum to $O_2 + O + 2O_2 = 3O_2 + O$. Cancelling O from both sides leaves $2O_3 \rightarrow 3O_2$, the overall equation, as required. (c) O is the intermediate: produced in step 1 and consumed in step 2. (d) Step 1 is an elementary step whose only reactant is O_3, so its rate law is rate = $k[O_3]$. With one reactant particle, the step is unimolecular. (e) A step's rate law contains only the reactants of that step, because they alone set how often the event can happen. O is a product of step 1, not a reactant, so it cannot appear in that law. Appearing somewhere in a mechanism earns a species no place in a rate law; only being a reactant of the step in question does.

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