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Topic 5.4: Elementary Reactions

Worksheet · AP Chemistry

UNIT 5 · KINETICS

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How to Use This Worksheet

Work in order. Section A checks the definitions: what an elementary step is, how molecularity is counted, and why termolecular steps are rare. Section B practises writing rate laws for steps and calculating k and rates from them. Section C combines step analysis, mechanisms and rate law matching in exam style.

Reference facts used throughout. Molecularity counts the reactant particles in one elementary step: 1 is unimolecular, 2 is bimolecular, 3 is termolecular. For an elementary step only, the rate law is written from the equation, with the order in each reactant equal to its coefficient. The units of k follow the overall order of the step: s^{-1} for first order, $M^{-1}\ s^{-1}$ for second order, $M^{-2}\ s^{-1}$ for third order.

Three habits protect every answer. First, check the question actually says a step is elementary before using any coefficients as orders; for an overall equation that move is forbidden. Second, count particles, not species and not atoms: 2A is two particles. Third, when adding steps, cancel only species that appear on both sides, and check what is left balances.

One distinction runs through the whole worksheet. An intermediate is formed in one step and consumed in a later one. A catalyst is consumed in an early step and regenerated in a later one. Both cancel from the overall equation.

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 an elementary reaction. (b) Define molecularity. (c) Explain why a molecularity can be stated for an elementary step but not for an overall reaction.

A2. State the molecularity of each elementary step, naming the reactant particles you counted: (a) $N_2O_5 \rightarrow NO_2 + NO_3$ (b) $NO + O_3 \rightarrow NO_2 + O_2$ (c) $2NO_2 \rightarrow N_2O_4$ (d) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$.

A3. Write the rate law for each elementary step and state its overall order: (a) A → products (b) A + B → products (c) 2A + B → products (d) A + A + B → products. (e) State what parts (c) and (d) show about two ways of writing the same event.

A4. (a) Explain why termolecular elementary steps are extremely rare. (b) The equation $2H_2 + O_2 \rightarrow 2H_2O$ is balanced. Explain why it still cannot represent a single elementary step, and state what must be happening instead.

A5. In a two-step mechanism, species X is formed in step 1 and consumed in step 2, while species Y is consumed in step 1 and formed again in step 2. (a) Identify X and Y as an intermediate or a catalyst. (b) State whether X or Y appears in the overall equation, and explain why. (c) State which of the two is present at the very start of the reaction mixture.

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Section B: Core Practice

B1. The elementary step $Br_2 \rightarrow 2Br$ has $k = 0.040\ s^{-1}$. (a) State its molecularity. (b) Write its rate law. (c) Explain why the units of k are s^{-1} here. (d) Calculate the rate when $[Br_2] = 0.50$ M. (e) Calculate the rate when $[Br_2] = 0.25$ M, and state the factor by which the rate changed.

B2. The elementary step $A + B \rightarrow$ products has $k = 0.20\ M^{-1}\ s^{-1}$. (a) State its molecularity and its overall order. (b) Calculate the rate when [A] = 0.30 M and [B] = 0.50 M. (c) Calculate the rate when [A] is doubled to 0.60 M and [B] stays at 0.50 M. (d) Explain why k has the same value in parts (b) and (c).

B3. The elementary step $2A \rightarrow$ products has a measured rate of 8.0×10^{-3} M/s when [A] = 0.20 M. (a) Write its rate law. (b) Calculate k, with its units. (c) Predict the rate when [A] = 0.30 M. (d) A student calls the step unimolecular because only one reactant species appears. Correct the student, and explain why doubling [A] multiplies the rate by four.

B4. A mechanism has two steps. Step 1: $NO_2 + F_2 \rightarrow NO_2F + F$. Step 2: $NO_2 + F \rightarrow NO_2F$. (a) State the molecularity of each step. (b) Write the rate law of each step. (c) Identify the species F as an intermediate or a catalyst, justifying your choice. (d) Add the two steps, cancel what appears on both sides, and write the overall equation. Check that it balances.

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B5. An overall reaction P + 2Q → products has the experimental rate law rate = k[P]. (a) Explain why this rate law could not have been predicted from the overall equation. (b) Write the rate law the reaction would have if P + 2Q occurred as a single elementary step, and state that step's molecularity and overall order. (c) State the experimental order in P, the experimental order in Q, and the experimental overall order. (d) Give the units of k for the experimental rate law.

B6. Four steps are proposed as elementary steps: (a) A → products (b) A + B → products (c) 2A + B → products (d) 2A + 3B → products. For each of (a) to (c), state the molecularity and write the rate law. (e) Explain why step (d) cannot be an elementary step, and state what its rate law would have to be if it were one.

Section C: Exam Style

C1. An overall reaction has the experimental rate law rate = $k[NO]^2[O_2]$. Three steps are proposed as possible single steps for it: (i) $NO + O_2 \rightarrow NO_2 + O$ (ii) $2NO + O_2 \rightarrow 2NO_2$ (iii) $2NO \rightarrow N_2O_2$. (a) For each proposed step, state the molecularity and write the rate law it would have as an elementary step. (b) State which step is consistent with the experimental rate law, and why each of the others is ruled out. (c) Taking k = 1.5 M^{-2} s^{-1} for the consistent step, calculate the rate when [NO] = 0.20 M and $[O_2]$ = 0.10 M. (d) State the new rate if $[O_2]$ alone is doubled, and explain the factor. (e) Explain why consistency with the rate law does not prove the reaction really happens in that single step.

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C2. The decomposition of ozone follows two steps. Step 1: $O_3 \rightarrow O_2 + O$. Step 2: $O + O_3 \rightarrow 2O_2$. (a) State the molecularity of each step. (b) Write the rate law of each step, giving the units of each rate constant. (c) Identify the species O as an intermediate or a catalyst, justifying your choice. (d) Add the steps and cancel to obtain the overall equation. (e) Step 1 has $k = 0.030\ s^{-1}$. Calculate the rate of step 1 when $[O_3] = 0.60$ M.

C3. The step A + 2B → products is stated to be elementary. In one run, [A] = 0.10 M, [B] = 0.10 M and the rate is 2.0×10^{-3} M/s. (a) Write the rate law from the equation, and state why this is allowed here. (b) State the molecularity and the overall order. (c) Calculate k, with its units. (d) Predict the rate when [A] = 0.20 M and [B] = 0.30 M. (e) Suppose instead that A + 2B → products were the overall equation of a multi-step reaction. State how its rate law would then have to be obtained, and why the value of k from part (c) would no longer follow.

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Answer Key

A1. (a) An elementary reaction is a reaction that occurs in a single molecular event, exactly as its equation is written, with no hidden sub-steps. (b) Molecularity is the number of reactant particles that take part in that one event, counted from the reactant side of the step's equation, coefficients included. (c) An overall reaction is the sum of several steps, so no single collision or single breaking-apart event corresponds to it. With no single event to count particles in, molecularity has no meaning for it; only its individual steps have molecularities.

A2. (a) Unimolecular: one reactant particle, a single N_2O_5 molecule breaking apart. (b) Bimolecular: two reactant particles, one NO and one O_3. (c) Bimolecular: two reactant particles, two NO_2 molecules; one reactant species still means two particles. (d) Bimolecular: two reactant particles, two HO_2 radicals. The products, and the atoms inside each particle, are never counted.

A3. (a) rate = k[A], overall order 1. (b) rate = k[A][B], overall order 2. (c) rate = $k[A]^2[B]$, overall order 3. (d) rate = $k[A]^2[B]$, overall order 3. (e) Parts (c) and (d) are the same event written two ways: two A particles and one B particle. Collecting the two A particles into a coefficient of 2 changes neither the molecularity, which is 3, nor the rate law, in which [A] is squared either way.

A4. (a) A termolecular step needs three particles to arrive at the same place at the same moment, each with enough energy and the correct orientation. Two-particle collisions are common, but the chance of a third particle arriving at exactly that instant, suitably energetic and oriented, is vanishingly small, so such steps almost never occur. (b) As one step it would require two H_2 molecules and one O_2 molecule to collide simultaneously, a termolecular event. Being balanced only shows the atoms are accounted for; it says nothing about a single event. Instead, the reaction proceeds as a sequence of unimolecular and bimolecular steps whose sum is this equation.

A5. (a) X is an intermediate: it is formed in one step and consumed in a later step. Y is a catalyst: it is consumed in an early step and regenerated in a later step. (b) Neither appears in the overall equation. When the steps are added, X is produced and then used up in equal amounts, and Y is used up and then remade in equal amounts, so both cancel from the two sides. (c) The catalyst, Y: it must be present at the start to be consumed in step 1, whereas the intermediate X does not exist until step 1 creates it.

B1. (a) Unimolecular: one Br_2 particle breaks apart. (b) rate = $k[Br_2]$. (c) The step is first order overall, and k for a first order rate law carries units s^{-1}, so that k × M gives a rate in M/s. (d) rate = 0.040 × 0.50 = 0.020 M/s. (e) rate = 0.040 × 0.25 = 0.010 M/s. Halving $[Br_2]$ halved the rate, a factor of 2, because the step is first order in Br_2.

B2. (a) Bimolecular (two reactant particles), overall order 2. (b) rate = 0.20 × 0.30 × 0.50 = 0.030 M/s. (c) rate = 0.20 × 0.60 × 0.50 = 0.060 M/s. (d) k is a constant for the step at a given temperature.

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Changing a concentration changes the rate through the rate law; it does not change k, so the same k is used in both calculations.

B3. (a) rate = $k[A]^2$. (b) $k = \text{rate} \div [A]^2 = 8.0 \times 10^{-3} \div (0.20)^2 = 8.0 \times 10^{-3} \div 0.040 = 0.20\ M^{-1}\ s^{-1}$, the units for an overall order of 2. (c) rate = $0.20 \times (0.30)^2 = 0.20 \times 0.090 = 0.018$ M/s. (d) The step is bimolecular, not unimolecular: two A particles must collide in the single event, even though they are the same species. Because [A] supplies both colliding particles, [A] appears twice in the rate law, so doubling [A] multiplies the rate by $2^2 = 4$.

B4. (a) Both steps are bimolecular: step 1 has one NO_2 particle and one F_2 particle, step 2 has one NO_2 particle and one F atom. (b) Step 1: rate = $k[NO_2][F_2]$. Step 2: rate = $k[NO_2][F]$. (c) F is an intermediate: it is formed in step 1 and consumed in step 2, and it is not present at the start. (d) Adding gives $2NO_2 + F_2 + F \rightarrow 2NO_2F + F$. Cancelling the F that appears on both sides leaves $2NO_2 + F_2 \rightarrow 2NO_2F$. It balances: 2 N, 4 O and 2 F on each side.

B5. (a) The overall equation is the sum of the reaction's steps, so its coefficients balance atoms for the net change only. They describe no single collision, so they cannot give the orders; the orders had to be measured, and measurement gave first order in P and zero order in Q. (b) As a single elementary step it would have rate = $k[P][Q]^2$, with molecularity 3 (one P particle and two Q particles) and overall order 3. (c) Order in P is 1, order in Q is 0, overall order is 1. (d) s^{-1}, the units of k for an overall order of 1.

B6. (a) Unimolecular, rate = $k[A]$. (b) Bimolecular, rate = $k[A][B]$. (c) Termolecular, rate = $k[A]^2[B]$. (e) Step (d) would need five reactant particles, two A and three B, to collide at the same instant with enough energy and correct orientation. Even three-particle collisions are extremely rare; a five-particle collision is not a realistic single event, so the step cannot be elementary and the change must occur through a sequence of simpler steps. If it were elementary, its rate law would be rate = $k[A]^2[B]^3$, fifth order overall.

C1. (a) (i) Bimolecular, rate = $k[NO][O_2]$. (ii) Termolecular, rate = $k[NO]^2[O_2]$. (iii) Bimolecular, rate = $k[NO]^2$. (b) Step (ii) is consistent: its rate law matches the experimental law exactly, term for term. Step (i) is only first order in NO and second order overall, and step (iii) contains no $[O_2]$ term and is second order overall, so neither can produce a rate that depends on $[NO]^2$ and $[O_2]$. (c) rate = $1.5 \times (0.20)^2 \times 0.10 = 1.5 \times 0.040 \times 0.10 = 6.0 \times 10^{-3}$ M/s. (d) The step is first order in O_2, so doubling $[O_2]$ doubles the rate, to 0.012 M/s. (e) A rate law records how the rate depends on concentrations; more than one route can generate the same dependence. A single termolecular collision is extremely improbable, so a sequence of unimolecular and bimolecular steps whose combined behaviour gives the same law is more likely. Consistency is a necessary test for a proposed step, not a proof of it.

C2. (a) Step 1 is unimolecular (one O_3 particle). Step 2 is bimolecular (one O atom and one O_3 particle). (b) Step 1: rate = $k[O_3]$, with k in s^{-1}. Step 2: rate = $k[O][O_3]$, with k in $M^{-1}\ s^{-1}$. (c) O is an intermediate: it is formed in step 1 and consumed in step 2, and it does not appear in the overall

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equation. (d) Adding gives $O_3 + O + O_3 \rightarrow O_2 + O + 2O_2$. Cancelling the O on both sides leaves $2O_3 \rightarrow 3O_2$. (e) rate = 0.030 × 0.60 = 0.018 M/s.

C3. (a) rate = $k[A][B]^2$. This is allowed because the step is stated to be elementary: it is a single molecular event, so the order in each reactant equals its coefficient in the step's equation. (b) Molecularity 3 (one A particle and two B particles, a termolecular step), overall order 3. (c) k = rate ÷ ($[A][B]^2$) = $2.0 \times 10^{-3} \div (0.10 \times (0.10)^2) = 2.0 \times 10^{-3} \div 1.0 \times 10^{-3} = 2.0\ M^{-2}\ s^{-1}$, the units for an overall order of 3. (d) rate = $2.0 \times 0.20 \times (0.30)^2 = 2.0 \times 0.20 \times 0.090 = 0.036$ M/s. (e) As an overall equation, its rate law would have to be determined by experiment, from initial rate measurements, because the coefficients of an overall equation describe no single event. The experimental orders need not equal 1 and 2, so the calculation in part (c), which assumed those orders, would have no basis and its k value could not be trusted.

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