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Topic 5.2: Introduction to Rate Law

Worksheet · AP Chemistry

UNIT 5 · KINETICS

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How to Use This Worksheet

Work in order. Section A checks the language of rate laws: orders, the rate constant, and its units. Section B practises the method of initial rates, solving for k, and predicting rates from a rate law. Section C combines those skills in exam style, including a pair of runs in which both concentrations change.

Reference facts used throughout. A rate law has the form rate = $k[A]^m[B]^n$; m and n are the orders in each reactant, found from experiment only, never from the coefficients of the balanced equation; the overall order is m + n. Doubling a concentration multiplies the rate by 2 raised to that reactant's order: by 1 for zero order, by 2 for first order, by 4 for second order. Once the orders are known, k = rate ÷ ($[A]^m[B]^n$) from any one run, and the units of k are M^(1 − overall order) s^{-1}: M s^{-1} for zero order overall, s^{-1} for first, M^{-1} s^{-1} for second, M^{-2} s^{-1} for third. Carry unrounded values through each calculation and round only the final answer, to three significant figures.

Three habits protect every answer. Compare only runs that differ in one concentration when finding an order. State the units of k every time, derived from the overall order. And keep k separate from the rate: changing a concentration changes the rate, not k; only a temperature change alters k.

One method runs through Sections B and C. Find each order from a clean pair of runs, write the rate law, substitute one complete run to get k with its units, and only then predict a rate at new concentrations.

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Watch the powers as you substitute. A second order concentration is squared before it is multiplied by anything else, and a zero order term is 1 whatever the concentration, so it contributes nothing to k.

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

Section A: Recall and Concepts

A1. Define each term in one sentence. (a) Rate law. (b) Order with respect to a reactant. (c) Overall order. (d) Rate constant. (e) Initial rate. (f) Method of initial rates.

A2. A reaction has the balanced equation $2A + B \rightarrow 3C$. A student writes rate = $k[A]^2[B]$ without doing any experiments. (a) State the two mistakes built into that rate law. (b) State what information is actually needed before any rate law can be written.

A3. For each statement, state the order with respect to the named reactant. (a) Doubling [A] doubles the rate. (b) Doubling [B] quadruples the rate. (c) Tripling [C] leaves the rate unchanged. (d) Tripling [D] multiplies the rate by 9. (e) Halving [E] halves the rate. (f) Halving [F] reduces the rate to one quarter.

A4. Complete the units of k for each overall order, and show the division that produces each one. (a) Overall zero order. (b) Overall first order. (c) Overall second order. (d) Overall third order.

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A5. A rate constant is given as 3.5 M^{-2} s^{-1} for a reaction involving only A and B. (a) What is the overall order? (b) Give two different pairs of individual orders (order in A, order in B) that are consistent with those units. (c) Explain why the units alone cannot decide between your two pairs.

Section B: Core Practice

B1. The initial rate of a reaction between A and B was measured in three runs. Run 1: [A] = 0.20 M, [B] = 0.10 M, rate = 2.0×10^{-3} M/s. Run 2: [A] = 0.40 M, [B] = 0.10 M, rate = 4.0×10^{-3} M/s. Run 3: [A] = 0.20 M, [B] = 0.30 M, rate = 1.8×10^{-2} M/s. (a) Find the order with respect to A, naming the runs you compared. (b) Find the order with respect to B, naming the runs you compared. (c) Write the rate law and state the overall order. (d) Calculate k, with its units. (e) Predict the rate at [A] = 0.30 M and [B] = 0.20 M.

B2. The initial rate of a reaction between X and Y was measured in three runs. Run 1: [X] = 0.10 M, [Y] = 0.20 M, rate = 5.0×10^{-4} M/s. Run 2: [X] = 0.20 M, [Y] = 0.20 M, rate = 2.0×10^{-3} M/s. Run 3: [X] = 0.10 M, [Y] = 0.40 M, rate = 5.0×10^{-4} M/s. (a) Find the order with respect to X. (b) Find the order with respect to Y. (c) Write the rate law and state the overall order. (d) Calculate k, with its units. (e) Predict the rate at [X] = 0.30 M and [Y] = 0.50 M, and explain the part [Y] plays in your calculation.

B3. A reaction follows rate = $k[P]^2[Q]$, and in one run the rate is 8.0×10^{-3} M/s. Without finding k, calculate the new rate when (a) [P] is doubled and [Q] is unchanged, (b) [Q] is doubled and [P] is unchanged, (c) both [P] and [Q] are doubled, (d) [P] is halved and [Q] is tripled. Show the factor you apply in each case.

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B4. A reaction follows rate = k[M]^2 with k = 0.25 M^{-1} s^{-1}. (a) Calculate the initial rate at [M] = 0.20 M. (b) Calculate the initial rate at [M] = 0.60 M. (c) By what factor has the rate changed between the two runs, and which feature of the rate law fixes that factor? (d) A student calculates the rate at [M] = 0.60 M as 0.25 × 0.60 × 2 = 0.30 M/s. Identify the error.

B5. Derive the units of k for each rate law, showing the division in each case. (a) rate = k[A]. (b) rate = k[A][B]. (c) rate = k[A]^2[B]. (d) rate = k.

B6. For the reaction 2NO(g) + O_2(g) → 2NO_2(g), a student argues: "NO has coefficient 2, so the reaction must be second order in NO, and O_2 has coefficient 1, so it must be first order in O_2." (a) Explain why the argument fails even though, for this particular reaction, the stated orders turn out to match experiment. (b) Describe the set of experiments that would settle both orders. (c) Tripling [O_2] at constant [NO] triples the rate, and doubling [NO] at constant [O_2] quadruples the rate. Write the rate law and state the overall order.

Section C: Exam Style

C1. The initial rate of a reaction between U and V was measured in three runs. Run 1: [U] = 0.10 M, [V] = 0.10 M, rate = 1.2 × 10^{-3} M/s. Run 2: [U] = 0.10 M, [V] = 0.30 M, rate = 3.6 × 10^{-3} M/s. Run 3: [U] = 0.30 M, [V] = 0.10 M, rate = 1.08 × 10^{-2} M/s. (a) Find the order with respect to V. (b) Find the order with respect to U. (c) Write the rate law and state the overall order. (d) Calculate k, with its units. (e) Calculate the rate at [U] = 0.20 M and [V] = 0.20 M. (f) Starting from run 1, [U] is halved and [V] is doubled. Calculate the new rate, showing the combined factor.

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C2. A reaction follows rate = k[A][B] with k = 0.040 M^{-1} s^{-1} at a fixed temperature. (a) Calculate the rate at [A] = 0.50 M and [B] = 0.25 M. (b) [A] is doubled to 1.00 M at the same temperature. State the value of k and calculate the new rate. (c) The mixture is warmed and k rises to 0.12 M^{-1} s^{-1}. Calculate the rate at the original concentrations. (d) Explain why k changed in part (c) but not in part (b).

C3. The initial rate of a reaction between A and B was measured in three runs. Run 1: [A] = 0.10 M, [B] = 0.10 M, rate = 2.5×10^{-3} M/s. Run 2: [A] = 0.20 M, [B] = 0.20 M, rate = 2.0×10^{-2} M/s. Run 3: [A] = 0.20 M, [B] = 0.10 M, rate = 1.0×10^{-2} M/s. (a) Explain why runs 1 and 2 alone cannot give the order in either reactant. (b) Use runs 1 and 3 to find the order in A. (c) Use runs 2 and 3 to find the order in B, and check that your two orders are consistent with the change from run 1 to run 2. (d) Write the rate law, state the overall order, and calculate k with its units. (e) Predict the rate at [A] = 0.15 M and [B] = 0.30 M.

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Answer Key

A1. (a) An equation linking the rate of a reaction to the reactant concentrations, of the form rate = $k[A]^m[B]^n$. (b) The power to which that reactant's concentration is raised in the rate law; it states the factor by which the rate responds when that concentration changes alone. (c) The sum of the individual orders. (d) The constant k in the rate law, fixed for a reaction at a fixed temperature and independent of the concentrations. (e) The rate at the very start of a run, while the concentrations are still the known starting values. (f) Finding the orders by measuring initial rates in several runs that change one concentration at a time and comparing the rate ratios.

A2. (a) First, the powers have been copied from the coefficients: the 2 in front of A has been used as the order in A and the implied 1 in front of B as the order in B, but orders are experimental quantities and need not equal coefficients. Second, the law has been written with no measured data behind it at all, so neither the orders nor the value of k is known. (b) Initial rate measurements from runs in which one concentration at a time is changed; those data fix the orders first, and then any one run fixes k.

A3. (a) First order in A: the rate factor equals the concentration factor. (b) Second order in B: 2 raised to the order gives 4. (c) Zero order in C: no change in concentration produces no change in rate because the term equals 1. (d) Second order in D: $3^2 = 9$. (e) First order in E: the rate tracks the concentration exactly. (f) Second order in F: $(1/2)^2 = 1/4$.

A4. (a) Overall zero: rate = k, so k = M/s, units M s^{-1}. (b) Overall first: k = (M/s) ÷ M = s^{-1}. (c) Overall second: k = (M/s) ÷ M^2 = M^{-1} s^{-1}. (d) Overall third: k = (M/s) ÷ M^3 = M^{-2} s^{-1}. In each case the units of k are whatever turns the concentration product into M/s.

A5. (a) M^{-2} s^{-1} matches M^(1 − overall order) s^{-1} with 1 − overall order = −2, so the overall order is 3. (b) Any pair summing to 3, for example order 2 in A and 1 in B, or order 1 in A and 2 in B (order 3 in A and 0 in B is also consistent). (c) The units of k depend only on the sum of the orders, because the units calculation sees the total power of concentration, M^3, and not how that power is split between A and B. Only initial rate experiments, changing one concentration at a time, can split the total.

B1. (a) Compare runs 1 and 2, where [B] is constant at 0.10 M. [A] doubles from 0.20 M to 0.40 M and the rate doubles from 2.0×10^{-3} to 4.0×10^{-3} M/s, a factor of 2, so the order in A is 1. (b) Compare runs 1 and 3, where [A] is constant at 0.20 M. [B] triples from 0.10 M to 0.30 M and the rate multiplies by $1.8 \times 10^{-2} \div 2.0 \times 10^{-3} = 9$, and $3^2 = 9$, so the order in B is 2. (c) rate = $k[A][B]^2$; overall order = 1 + 2 = 3. (d) From run 1, $k = 2.0 \times 10^{-3} \div (0.20 \times (0.10)^2) = 2.0 \times 10^{-3} \div 2.0 \times 10^{-3} = 1.0$ M^{-2} s^{-1}, the third order unit. (e) rate = $1.0 \times 0.30 \times (0.20)^2 = 1.0 \times 0.30 \times 0.040 = 0.012$ M/s.

B2. (a) Compare runs 1 and 2, where [Y] is constant. [X] doubles and the rate multiplies by $2.0 \times 10^{-3} \div 5.0 \times 10^{-4} = 4 = 2^2$, so the order in X is 2. (b) Compare runs 1 and 3, where [X] is constant. [Y]

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doubles and the rate is unchanged, so the order in Y is 0. (c) rate = k[X]^2, with [Y]^0 = 1 dropping out; overall order = 2. (d) From run 1, k = 5.0 × 10^{-4} ÷ (0.10)^2 = 5.0 × 10^{-4} ÷ 0.010 = 0.050 M^{-1} s^{-1}, the second order unit. (e) rate = 0.050 × (0.30)^2 = 0.050 × 0.090 = 4.5 × 10^{-3} M/s. [Y] plays no part: its term is [Y]^0 = 1 at 0.50 M just as at any other concentration, so the value of [Y] never enters the multiplication.

B3. (a) [P] is second order, so doubling it applies a factor of 2^2 = 4: rate = 4 × 8.0 × 10^{-3} = 0.032 M/s. (b) [Q] is first order, so doubling it applies a factor of 2: rate = 0.016 M/s. (c) The factors combine: 4 × 2 = 8, so rate = 8 × 8.0 × 10^{-3} = 0.064 M/s. (d) Halving [P] applies (1/2)^2 = 1/4 and tripling [Q] applies 3, a combined factor of 3/4, so rate = 0.75 × 8.0 × 10^{-3} = 6.0 × 10^{-3} M/s. In every case k cancels because it is the same at the same temperature, so the ratios need only the orders.

B4. (a) rate = 0.25 × (0.20)^2 = 0.25 × 0.040 = 0.010 M/s. (b) rate = 0.25 × (0.60)^2 = 0.25 × 0.36 = 0.090 M/s. (c) The rate multiplies by 0.090 ÷ 0.010 = 9. Tripling [M] fixes the factor, and the second order power turns that factor of 3 into 3^2 = 9. (d) The student multiplied [M] by the order instead of raising [M] to the power of the order: the term is (0.60)^2, not 0.60 × 2.

B5. (a) k = (M/s) ÷ M = s^{-1}. (b) The concentration product is M × M = M^2, so k = (M/s) ÷ M^2 = M^{-1} s^{-1}. (c) The concentration product is M^2 × M = M^3, so k = (M/s) ÷ M^3 = M^{-2} s^{-1}. (d) There is no concentration term, so k equals the rate itself and carries the units M s^{-1}. The four results match the overall orders 1, 2, 3 and 0 in turn.

B6. (a) The argument treats coefficients as orders, and no reasoning from the balanced equation can establish an order: the equation records the atom balance of the overall change, while an order records how the measured rate responds to concentration. The match here is luck, and the same style of argument applied to another reaction gives the wrong rate law. (b) Measure initial rates in at least three runs: a pair that changes [NO] while [O_2] is held constant, and a pair that changes [O_2] while [NO] is held constant, all at the same temperature; compare the rate ratios within each pair. (c) Tripling [O_2] triples the rate, so the order in O_2 is 1; doubling [NO] quadruples the rate, so the order in NO is 2. rate = k[NO]^2[O_2], overall order 3.

C1. (a) Compare runs 1 and 2, where [U] is constant. [V] triples and the rate multiplies by 3.6 × 10^{-3} ÷ 1.2 × 10^{-3} = 3, so the order in V is 1. (b) Compare runs 1 and 3, where [V] is constant. [U] triples and the rate multiplies by 1.08 × 10^{-2} ÷ 1.2 × 10^{-3} = 9 = 3^2, so the order in U is 2. (c) rate = k[U]^2[V]; overall order = 3. (d) From run 1, k = 1.2 × 10^{-3} ÷ ((0.10)^2 × 0.10) = 1.2 × 10^{-3} ÷ 1.0 × 10^{-3} = 1.2 M^{-2} s^{-1}. (e) rate = 1.2 × (0.20)^2 × 0.20 = 1.2 × 0.040 × 0.20 = 9.6 × 10^{-3} M/s. (f) Halving [U] applies (1/2)^2 = 1/4 and doubling [V] applies 2, a combined factor of 1/2, so the new rate is 1.2 × 10^{-3} ÷ 2 = 6.0 × 10^{-4} M/s.

C2. (a) rate = 0.040 × 0.50 × 0.25 = 0.040 × 0.125 = 5.0 × 10^{-3} M/s. (b) k is unchanged at 0.040 M^{-1} s^{-1}, because concentration changes do not alter k. rate = 0.040 × 1.00 × 0.25 = 0.010 M/s, exactly double the rate in part (a), as expected for a reaction first order in A. (c) rate = 0.12 × 0.50 × 0.25 = 0.12 × 0.125 = 0.015 M/s. (d) k is a property of the reaction at a given temperature: raising the

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temperature makes the same concentrations react faster, which the rate law registers as a larger k, while changing a concentration only moves along the fixed rate law, changing the rate and leaving k alone.

C3. (a) Between runs 1 and 2 both [A] and [B] double, and the rate multiplies by 8. That factor is the product of the two separate effects, 2^(order in A) × 2^(order in B), and one combined number cannot be split into two unknown orders without another comparison. (b) Runs 1 and 3 hold [B] constant at 0.10 M. [A] doubles and the rate multiplies by $1.0 \times 10^{-2} \div 2.5 \times 10^{-3} = 4 = 2^2$, so the order in A is 2. (c) Runs 2 and 3 hold [A] constant at 0.20 M. [B] doubles from 0.10 M to 0.20 M and the rate doubles from 1.0×10^{-2} to 2.0×10^{-2} M/s, so the order in B is 1. Check: doubling both concentrations should multiply the rate by $2^2 \times 2 = 8$, and run 2 ÷ run 1 = $2.0 \times 10^{-2} \div 2.5 \times 10^{-3} = 8$, as required. (d) rate = $k[A]^2[B]$; overall order = 3. From run 1, $k = 2.5 \times 10^{-3} \div ((0.10)^2 \times 0.10) = 2.5 \times 10^{-3} \div 1.0 \times 10^{-3} = 2.5\ M^{-2}\ s^{-1}$. (e) rate = $2.5 \times (0.15)^2 \times 0.30 = 2.5 \times 0.0225 \times 0.30 = 0.0169$ M/s.

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