ANSWER KEY.

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5.4 Elementary Reactions

AP Chemistry | ANSWER KEY

For an elementary step, the coefficients of the reactants become the orders. Use them only when a step is stated to be elementary.

1. Each reaction below is an elementary step. Give its molecularity (unimolecular, bimolecular, or termolecular) and write its rate law.

(a) $O_3(g) \rightarrow O_2(g) + O(g)$

(b) $NO(g) + NO_3(g) \rightarrow 2NO_2(g)$

(c) $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$

(d) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

(a) Unimolecular (1 particle). rate = $k[O_3]$

(b) Bimolecular (2 particles). rate = $k[NO][NO_3]$

(c) Bimolecular (2 NOCl particles). rate = $k[NOCl]^2$

(d) Termolecular (3 particles). rate = $k[NO]^2[O_2]$

2. In an elementary step, one molecule of nitrogen dioxide collides with one molecule of carbon monoxide. The products are nitrogen monoxide and carbon dioxide.

(a) Write the balanced equation for this step.

(b) Write the rate law and give the overall order.

(a) $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

(b) rate = $k[NO_2][CO]$. Second order overall (first order in each). The products do not appear.

3. The elementary step A + 2B → C has a rate of 3.0×10^{-4} M/s under certain conditions.

(a) Write the rate law and give the overall order.

(b) Predict the new rate if [B] is doubled and [A] stays the same.

(c) Predict the new rate if both [A] and [B] are doubled.

(a) rate = $k[A][B]^2$. Third order overall.

(b) Rate × 2^2 = × 4: $(3.0 \times 10^{-4}$ M/s)(4) = 1.2×10^{-3} M/s

(c) Rate × (2)(2^2) = × 8: $(3.0 \times 10^{-4}$ M/s)(8) = 2.4×10^{-3} M/s

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4. A student is given the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ and writes the rate law rate = $k[N_2O_5]^2$. Experiments show rate = $k[N_2O_5]$.

(a) Explain the student's error.

(b) What does the experimental rate law tell you about whether this equation is a single elementary step?

(a) The reaction was not stated to be an elementary step, so the coefficients cannot be used as orders. The rate law for an overall reaction must come from experimental data.

(b) If it were one elementary step, the rate law would be $k[N_2O_5]^2$. The experimental order is 1, not 2, so the reaction is not a single elementary step. It must happen in more than one step.

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5. For $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$, experiments show rate = $k[NO_2][F_2]$. Could this reaction happen in a single elementary step? Explain.

No. As one elementary step, the coefficients would give rate = $k[NO_2]^2[F_2]$, second order in NO_2. The experimental order in NO_2 is 1, so the predicted and experimental rate laws do not match. (It would also need a rare termolecular collision.) The reaction must happen in more than one step.

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6. Explain why termolecular elementary steps are rare and why an elementary step with four colliding particles basically never happens.

In an elementary step, every reactant particle must be in the same collision. Two particles colliding happens all the time. Three particles must arrive at the same spot at the same instant, with enough energy and the right orientation, which is unlikely. Four particles arriving together at once is so unlikely that it basically never happens.

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