**ANSWER KEY** Answers and explanations appear after each question, marked by a bar at the left. Answers written in table cells are in *italics*.

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# AP Chemistry Unit 5 Study Guide | ANSWER KEY

Kinetics (Topics 5.1 to 5.11)

Show all work with units and correct significant figures. When you explain, connect what the particles are doing (collision frequency, energy, orientation) to what is measured.

| | | | |
|---|---|---|---|
| **Equations** | rate = $k[A]^m[B]^n$ | For aA → bB: rate = $-(1/a)(\Delta[A]/\Delta t) = (1/b)(\Delta[B]/\Delta t)$ | Zero order: $[A]_t - [A]_0 = -kt$ |
| | First order: $\ln[A]_t - \ln[A]_0 = -kt$ | Second order: $1/[A]_t - 1/[A]_0 = kt$ | First order: $t_{1/2} = 0.693/k$ |

## Part 1. Reaction Rates (Topic 5.1)

**1.** Dinitrogen pentoxide decomposes: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. At one moment, $N_2O_5$ is being used up at a rate of 0.0060 M/s.

(a) At what rate is $NO_2$ being produced?

> Rate of $NO_2$ = (4/2)(0.0060 M/s) = **0.012 M/s**. Four $NO_2$ form for every two $N_2O_5$ used, so $NO_2$ appears twice as fast.

(b) At what rate is $O_2$ being produced?

> Rate of $O_2$ = (1/2)(0.0060 M/s) = **0.0030 M/s**. One $O_2$ forms for every two $N_2O_5$ used.

(c) What is the rate of the reaction, using the equation on the reference table?

> Rate = $-(1/2)(\Delta[N_2O_5]/\Delta t)$ = (1/2)(0.0060 M/s) = **0.0030 M/s**. Dividing by the coefficient gives the same value for every species: (1/4)(0.012) = (1/1)(0.0030).

**2.** In a separate experiment, the concentration of $N_2O_5$ was measured over time.

| **Time (s)** | **0** | **100** | **200** |
|---|---|---|---|
| $[N_2O_5]$ (M) | 0.0200 | 0.0169 | 0.0142 |

(a) Calculate the average rate at which $N_2O_5$ is used up from 0 to 200 s.

> Average rate = $-\Delta[N_2O_5]/\Delta t = -(0.0142 - 0.0200)/(200 - 0)$ = 0.0058 M/200 s = **$2.9 \times 10^{-5}$ M/s**

(b) The concentration drops by 0.0031 M in the first 100 s but only 0.0027 M in the next 100 s. Explain why at the particle level.

> As $N_2O_5$ is used up, there are fewer $N_2O_5$ molecules per liter, so there are fewer collisions per second that can react. The rate slows as the reactant concentration decreases.

**3.** Calcium carbonate chips react with hydrochloric acid: $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$. For each change, state whether the rate increases or decreases and give a particle-level reason.

| **Change** | **Rate increases or decreases?** | **Particle-level reason** |
|---|---|---|
| Crush the chips into a powder | *Increases* | *More surface area exposes more $CaCO_3$ particles, so more collisions with $H_3O^+$ per second.* |
| Use 0.5 M HCl instead of 2.0 M HCl | *Decreases* | *Fewer $H_3O^+$ ions per liter, so fewer collisions per second.* |
| Warm the acid from 20 °C to 40 °C | *Increases* | *Particles move faster: collisions happen more often and a larger fraction have energy ≥ $E_a$.* |
| Add a catalyst | *Increases* | *Provides a new pathway with a lower $E_a$, so a larger fraction of collisions are successful.* |

> Every change that raises the number of successful collisions per second raises the rate.

## Part 2. Rate Laws and Initial Rates (Topic 5.2)

**4.** Initial rates were measured at 25 °C for $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$.

| Trial | Initial [NO] (M) | Initial [$Cl_2$] (M) | Initial rate (M/s) |
|---|---|---|---|
| 1 | 0.10 | 0.10 | $1.8 \times 10^{-4}$ |
| 2 | 0.20 | 0.10 | $7.2 \times 10^{-4}$ |
| 3 | 0.10 | 0.30 | $5.4 \times 10^{-4}$ |

(a) Determine the order with respect to NO. Justify using the data.

> Compare trials 1 and 2 ([$Cl_2$] constant): [NO] doubles and the rate increases by 7.2/1.8 = 4 = $2^2$. The reaction is **second order in NO**.

(b) Determine the order with respect to $Cl_2$. Justify using the data.

> Compare trials 1 and 3 ([NO] constant): [$Cl_2$] triples and the rate triples (5.4/1.8 = 3). The reaction is **first order in $Cl_2$**.

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

> **Rate = $k[NO]^2[Cl_2]$**, third order overall (2 + 1 = 3).

(d) Calculate k, including units.

> Trial 1: $k = \text{rate}/([NO]^2[Cl_2]) = (1.8 \times 10^{-4}\ M/s)/((0.10\ M)^2(0.10\ M)) =$ **$0.18\ M^{-2}\ s^{-1}$**

(e) Predict the initial rate when [NO] = 0.30 M and [$Cl_2$] = 0.20 M.

> Rate = $(0.18\ M^{-2}\ s^{-1})(0.30\ M)^2(0.20\ M) =$ **$3.2 \times 10^{-3}$ M/s**

**5.** Complete the table of rate constant units (concentration in M, time in s).

| Rate law | Overall order | Units of k |
|---|---|---|
| rate = k | *0* | $M\ s^{-1}$ |
| rate = k[A] | *1* | $s^{-1}$ |
| rate = k[A][B] | *2* | $M^{-1}\ s^{-1}$ |
| rate = $k[A]^2[B]$ | *3* | $M^{-2}\ s^{-1}$ |

> The units of k must make the rate come out in M/s, so k has units of $M^{1-n}\ s^{-1}$, where n is the overall order.

**6.** For a reaction with rate = $k[A]^2[B]$, [A] is tripled and [B] is cut in half at the same temperature. By what factor does the rate change? Does the value of k change? Explain.

> Rate changes by $(3)^2(1/2) =$ **4.5 times faster**.
> k does **not** change. It depends on temperature (and on whether a catalyst is present), not on concentration.

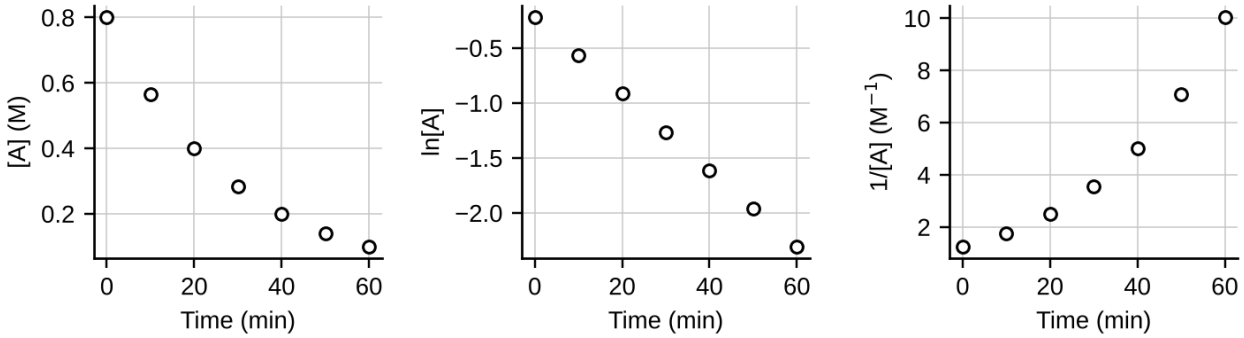
## Part 3. Concentration Changes Over Time (Topic 5.3)

**7.** Complete the summary of integrated rate laws.

| Order | Plot that gives a straight line | Slope of that line | Is the half-life constant? |
|---|---|---|---|
| Zero | *[A] vs. time* | *−k* | *No* |
| First | *ln[A] vs. time* | *−k* | *Yes, $t_{1/2} = 0.693/k$* |
| Second | *1/[A] vs. time* | *+k* | *No* |

> Only a first-order reaction has a half-life that does not depend on the starting concentration.

**8.** The decomposition A → products was monitored at 25 °C, starting with $[A]_0$ = 0.800 M. The same data are graphed three ways.




(a) What is the order of the reaction with respect to A? Justify using the graphs.

> **First order.** Only the graph of ln[A] versus time is a straight line.

(b) The best-fit line of the linear graph has a slope of −0.0347 $min^{-1}$. Write the rate law and give k with units.

> For first order, slope = −k, so k = 0.0347 $min^{-1}$. **Rate = (0.0347 $min^{-1}$)[A]**

(c) Calculate the half-life. Check your answer against the first graph.

> $t_{1/2}$ = 0.693/k = 0.693/(0.0347 $min^{-1}$) = **20.0 min**. The first graph agrees: [A] drops from 0.800 M to about 0.400 M at 20 min and to about 0.200 M at 40 min.

(d) Calculate [A] at t = 75 min.

> $\ln[A]_t = \ln(0.800) - (0.0347\ min^{-1})(75\ min) = -0.223 - 2.603 = -2.826$, so $[A]_t = e^{-2.826}$ = **0.0593 M**

**9.** Iodine-131, used to treat thyroid disease, decays by a first-order process with a half-life of 8.02 days.

(a) Calculate the rate constant k.

> $k = 0.693/t_{1/2}$ = 0.693/(8.02 days) = **0.0864 $day^{-1}$**

(b) A 40.0 mg sample is prepared. How much I-131 remains after 24.06 days?

> 24.06 days ÷ 8.02 days = 3.00 half-lives. 40.0 mg → 20.0 mg → 10.0 mg → **5.00 mg**.

(c) How many days does it take for 90.0% of the sample to decay (10.0% remains)?

> ln(10.0/100.0) = −kt, so t = ln(10.0)/k = 2.303/(0.0864 $day^{-1}$) = **26.7 days**

**10.** The decomposition $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ is second order in $NO_2$ with k = 0.54 $M^{-1}\ s^{-1}$ at 300 °C. The initial concentration of $NO_2$ is 0.0100 M.

(a) Calculate $[NO_2]$ after 100. s.

> $1/[NO_2]_t = 1/[NO_2]_0 + kt = 1/(0.0100\ M) + (0.54\ M^{-1}\ s^{-1})(100.\ s) = 100. + 54 = 154\ M^{-1}$, so $[NO_2]_t$ = **0.0065 M**

(b) Does it take the same time for $[NO_2]$ to fall from 0.0100 M to 0.0050 M as from 0.0050 M to 0.0025 M? Explain.

> **No.** Use $1/[NO_2]_t - 1/[NO_2]_0 = kt$ for each halving.
> First halving: $t = (200. - 100.)/0.54 = 1.9 \times 10^2$ s. Second halving: $t = (400. - 200.)/0.54 = 3.7 \times 10^2$ s. Each halving takes longer because at lower concentration, collisions between two $NO_2$ molecules happen less often.

## Part 4. Elementary Reactions and the Collision Model (Topics 5.4 to 5.5)

**11.** Each equation below is an elementary step. Write its rate law and classify its molecularity.

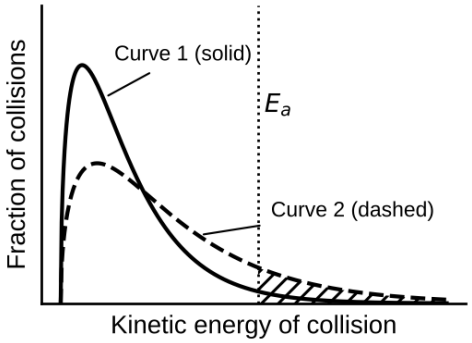
| Elementary step | Rate law | Molecularity |
|---|---|---|
| $O_3(g) \rightarrow O_2(g) + O(g)$ | $rate = k[O_3]$ | *Unimolecular* |
| $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$ | $rate = k[NO_2]^2$ | *Bimolecular* |
| $H_2(g) + I_2(g) \rightarrow 2HI(g)$ | $rate = k[H_2][I_2]$ | *Bimolecular* |
| $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$ | $rate = k[NO]^2[Br_2]$ | *Termolecular* |

> For an elementary step only, the coefficients become the exponents, because they count the particles that collide. Termolecular steps are rare: three particles must collide at the same instant with enough energy and the right orientation.

**12.** In the elementary step $Cl(g) + NOCl(g) \rightarrow Cl_2(g) + NO(g)$, two collisions have the same energy, which is greater than $E_a$. In collision 1 the Cl atom strikes the Cl end of NOCl. In collision 2 it strikes the O end. Which collision is more likely to form products? Explain.

> **Collision 1.** The new Cl–Cl bond can only form if the Cl atom hits the Cl end of NOCl. A collision needs both enough energy and the correct orientation, so collision 2 just bounces apart.

**13.** The graph shows the distribution of collision energies for the same gas mixture at two temperatures.




(a) Which curve is at the higher temperature? How do you know?

> **Curve 2.** Its peak is lower and shifted to higher energy, so the collisions have a higher average energy.

(b) On the graph, hatch the area that represents collisions with enough energy to react at the higher temperature.

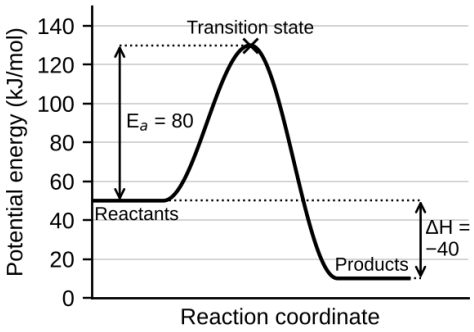
> Hatch the area under Curve 2 to the right of the $E_a$ line (shown on the graph).

(c) Use the graph to explain why a small rise in temperature can make a reaction much faster.

> At higher temperature, a much larger fraction of collisions have energy ≥ $E_a$ (more area to the right of the line), and collisions also happen more often. Both raise k and the rate.

## Part 5. Reaction Energy Profiles (Topic 5.6)

**14.** The energy profile is for a one-step (elementary) reaction.




(a) What is the activation energy for the forward reaction?

> $E_a = 130 - 50 =$ **80 kJ/mol**

(b) What is ΔH? Is the reaction endothermic or exothermic?

> $\Delta H = 10 - 50 =$ **−40 kJ/mol, exothermic**

(c) What is the activation energy for the reverse reaction?

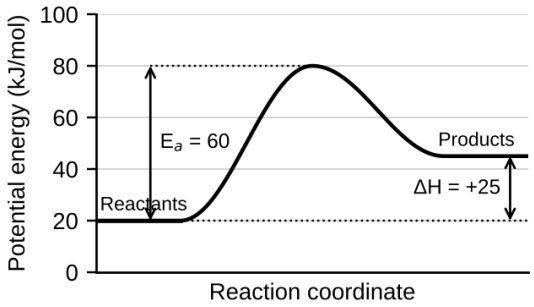
> $E_{a,reverse} = 130 - 10 =$ **120 kJ/mol**

(d) Mark the transition state with an X. What happens to bonds at this point?

> The transition state is the top of the curve. Old bonds are partly broken and new bonds are partly formed.

**15.** An elementary reaction is endothermic with $E_a$ = 60 kJ/mol and ΔH = +25 kJ/mol. The reactant energy is drawn. Sketch the energy profile and label $E_a$ and ΔH.

> The curve rises from 20 kJ/mol to a peak at 80 kJ/mol ($E_a$ = 60) and ends at 45 kJ/mol (ΔH = +25), above the reactants.




## Part 6. Reaction Mechanisms (Topics 5.7 to 5.8)

**16.** A proposed mechanism for the reaction of nitrogen dioxide with carbon monoxide is shown.
Step 1: $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$ (slow)
Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (fast)

(a) Write the overall balanced equation.

> Add the steps and cancel $NO_3$ and one $NO_2$: **$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$**

(b) Identify the intermediate. How do you know?

> **$NO_3$.** It is produced in step 1 and used up in step 2, so it does not appear in the overall equation.

(c) Write the rate law predicted by this mechanism.

> The slow step sets the rate: **rate = $k[NO_2]^2$**

(d) Changing [CO] does not change the rate. Explain why this supports the mechanism.

> CO reacts only in the fast step, after the rate-determining step. The overall rate is limited by step 1, so CO does not appear in the rate law.

**17.** The reaction $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$ has the experimental rate law rate = $k[NO]^2[H_2]$. Two mechanisms are proposed.
Mechanism I: one step, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$
Mechanism II: Step 1: $2NO + H_2 \rightarrow N_2O + H_2O$ (slow); Step 2: $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

(a) Which mechanism is consistent with the rate law? Justify.

> **Mechanism II.** Its slow step gives rate = $k[NO]^2[H_2]$, which matches the experiment.
> Mechanism I predicts rate = $k[NO]^2[H_2]^2$, which does not match.

(b) Give a second reason that Mechanism I is unlikely.

> It requires four molecules to collide at the same instant with the right energy and orientation, which almost never happens.

(c) $N_2O$ is detected while the reaction runs. Which mechanism does this support? Explain.

> **Mechanism II.** $N_2O$ is its intermediate. Mechanism I has no intermediate, so it cannot explain $N_2O$.

## Part 7. Pre-Equilibrium Approximation (Topic 5.9)

**18.** For $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, this mechanism is proposed.
Step 1: $2NO(g) \rightleftharpoons N_2O_2(g)$ (fast, reversible; forward $k_1$, reverse $k_{-1}$)
Step 2: $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$ (slow, $k_2$)

(a) Write the rate law for the slow step. Why can't it be the final rate law?

> Rate = $k_2[N_2O_2][O_2]$. $N_2O_2$ is an intermediate, so its concentration cannot be controlled or measured directly. The rate law must use reactants only.

(b) Step 1 is a fast equilibrium, so its forward and reverse rates are equal. Use this to write an expression for $[N_2O_2]$.

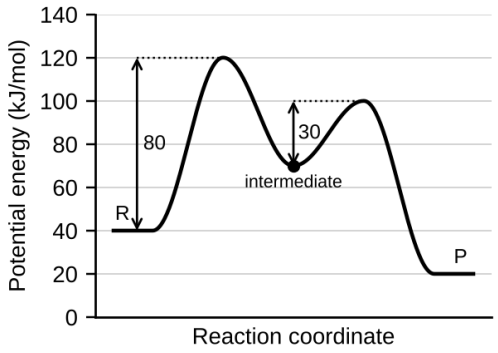
> $k_1[NO]^2 = k_{-1}[N_2O_2]$, so **$[N_2O_2] = (k_1/k_{-1})[NO]^2$**

(c) Substitute to find the rate law predicted by the mechanism.

> Rate = $k_2(k_1/k_{-1})[NO]^2[O_2]$ = **$k[NO]^2[O_2]$**, where $k = k_1k_2/k_{-1}$

## Part 8. Multistep Reaction Energy Profiles (Topic 5.10)

**19.** The energy profile shows a reaction that goes from reactants (R) to products (P).




(a) How many elementary steps does the mechanism have? How can you tell?

> **Two.** There are two peaks (transition states), one for each step.

(b) Mark the intermediate on the graph with a dot.

> The intermediate is the valley between the two peaks, at 70 kJ/mol (shown on the graph).

(c) Which step is rate determining? Justify with activation energies.

> **Step 1.** $E_{a1}$ = 120 − 40 = 80 kJ/mol is larger than $E_{a2}$ = 100 − 70 = 30 kJ/mol, so step 1 is the slow step.

(d) Is the overall reaction exothermic or endothermic?

> **Exothermic.** ΔH = 20 − 40 = −20 kJ/mol. P is lower than R.

## Part 9. Catalysis (Topic 5.11)

**20.** Iodide ions speed up the decomposition of hydrogen peroxide.

Step 1: $H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq)$ (slow)

Step 2: $H_2O_2(aq) + IO^-(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq)$ (fast)

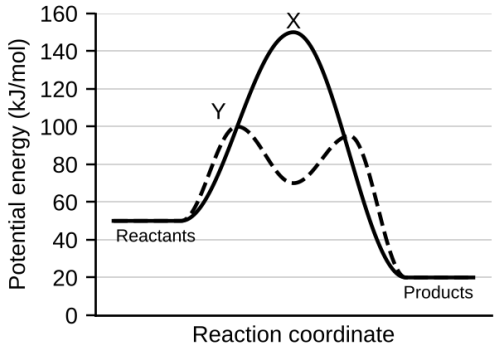
(a) Write the overall equation. Identify the catalyst and the intermediate, and explain the difference.

> Overall: **$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$**
> Catalyst: **$I^-$**, used in step 1 and regenerated in step 2. Intermediate: **$IO^-$**, made in step 1 and used in step 2. A catalyst is present at the start and end; an intermediate is not.

(b) Write the rate law. Why does it include $I^-$ even though $I^-$ is not used up?

> **Rate = $k[H_2O_2][I^-]$**. $I^-$ is a reactant in the slow step, so more $I^-$ means more successful collisions in that step per second.

**21.** Curves X and Y show the same reaction with and without a catalyst.




(a) Which curve is the catalyzed pathway? Justify.

> **Curve Y.** It has a lower activation energy and a new mechanism with two steps and an intermediate.

(b) Does the catalyst change ΔH? Explain.

> **No.** Both paths start at the same reactants and end at the same products, so ΔH = −30 kJ/mol either way.

(c) Explain why the catalyzed reaction is faster at the same temperature.

> The collision energy distribution is the same, but $E_a$ is lower, so a larger fraction of collisions have enough energy to react.

**22.** Complete the table of catalyst types.

| **Type of catalyst** | **How it speeds up the reaction** |
|---|---|
| Surface catalyst (Pt in a catalytic converter) | *Reactants bind to the surface, which weakens bonds and holds them close together, giving new steps with lower $E_a$.* |
| Enzyme (catalase breaking down $H_2O_2$) | *The reactant binds to the active site, which orients it favorably and lowers $E_a$.* |
| Acid-base catalyst ($H^+$ in ester hydrolysis) | *A proton is added to (or removed from) a reactant, forming a new intermediate that reacts faster.* |

> Each type gives a new reaction path with new intermediates and a lower activation energy.