The Ultimate AP® Chemistry Unit 5 Cheat Sheet

5.1 Reaction Rates

What Rate Means

Rate = Δ[conc]/Δt in M/s (mol L^{-1} s^{-1}). Reactant [ ] ↓, product [ ] ↑, but rate is always reported as a + value.
Rate of rxn for aA + bB → cC: rate = −(1/a)Δ[A]/Δt = −(1/b)Δ[B]/Δt = +(1/c)Δ[C]/Δt: one value for all.
Stoich link: $2N_2O_5 \rightarrow 4NO_2 + O_2$: NO_2 forms 2× as fast as N_2O_5 is used & 4× as fast as O_2 forms.

Avg rate = slope of secant over an interval; **instantaneous** = tangent slope at one t; **initial** = tangent at t = 0.
Rate slows over time (order > 0) b/c reactant [ ] drops → fewer collisions per second; [A] vs t curve flattens.

Factors That Change Rate

Factor	Effect	Why
↑ [reactant]	↑ rate (order>0)	more hits/s
↑ temperature	↑ rate	more w/ E ≥ E_a
↑ surface area	↑ rate	more exposed
catalyst	↑ rate	lower-E_a path
↑ P (gases)	↑ rate	↑ conc.

Measuring Rate in the Lab

Track a property ∝ [ ]: absorbance (Beer–Lambert, A = εbc), gas pressure or volume, mass lost, pH, conductivity.
Gas-forming rxn: Δmass of an open flask or ΔV of gas collected per unit time → rate of product formation.
Gas rates: atm/s works too; P ∝ [ ] at constant T, V.
Why initial rates? [ ] known exactly, no reverse rxn yet.
Worked: [A] 0.500 → 0.380 M in 40 s → 3.0×10^{-3} M/s; if 2A → B, rate of rxn = 1.5×10^{-3} M/s (÷ coefficient 2).

⚠ Rate of disappearance of A = rate of rxn only if A's coefficient is 1. Otherwise divide by the coefficient.

✓ FRQ "calculate the avg rate": use two data points, Δ[ ]/Δt, give units (M/s), a + sign and correct sig figs.

5.2 Introduction to Rate Law

Rate Law Basics

Rate law: rate = $k[A]^m[B]^n$; m, n = **orders**, found ONLY from experiment, never from coefficients of the overall eqn.
Overall order = m + n. AP orders: 0, 1 or 2 per reactant.
k: set by T & catalyst only, NOT by [ ]. ↑T → ↑k.

Method of Initial Rates

Trial	[A] (M)	[B] (M)	Rate (M/s)
1	0.10	0.10	2.0×10^{-3}
2	0.20	0.10	8.0×10^{-3}
3	0.10	0.20	2.0×10^{-3}

Trials 1→2: only [A] ×2, rate ×4 → $2^m = 4$ → m = 2.
Trials 1→3: only [B] ×2, rate ×1 → n = 0 → rate = $k[A]^2$.
Find k: $2.0\times10^{-3} \div (0.10)^2 = 0.20$ M^{-1} s^{-1} (any trial).

Ratio rule: rate ratio = ([ ] ratio)^{order}. [ ] ×2 → rate ×1/×2/×4; [ ] ×3 → ×1/×3/×9 for order 0/1/2; works for ×½ too.

Both change? If [A] ×2 & [B] ×2 and rate ×8 → $2^{m+n} = 8$ → m + n = 3; then use the known m to get n.
No clean pair? Cancel [B]'s known effect, then solve m.

Units of k

Order	Rate law	k units
0	rate = k	M s^{-1}
1	rate = k[A]	s^{-1}
2	rate = $k[A]^2$	M^{-1} s^{-1}

Shortcut: k units = M^{1-n} s^{-1} (n = overall order).
Check: M/s = $(M^{-1}\ s^{-1})(M)^2$ for rate = $k[A]^2$.

⚠ Never read orders off the overall balanced eqn's coefficients; only an elementary step allows that.

✓ FRQ: show the ratio ("[A] doubled, rate ×4, so 2nd order in A") to earn the justification pt; a bare answer gets 0.

5.3 Concentration Changes Over Time

Graphs Reveal the Order

Order	Linear plot	Slope
0	[A] vs t	−k
1	ln[A] vs t	−k
2	1/[A] vs t	+k

Find order from data: graph [A], ln[A] & 1/[A] vs t; the straight one gives the order, its slope gives k.
Eqn sheet gives $\ln[A]_t - \ln[A]_0 = -kt$, $1/[A]_t - 1/[A]_0 = kt$ and $t_{½} = 0.693/k$. Know which order each fits.

Half-Life

1st-order $t_{½}$ = 0.693/k: constant, independent of $[A]_0$. Equal $t_{½}$ intervals in a data table → 1st order, no graph needed.

Half-life counting: each $t_{½}$ halves [A]: 3 half-lives → 1/8 = 12.5% left, 87.5% gone; 5 → 3.1% left.
Radioactive decay: always 1st order, fixed $t_{½}$.

2nd order: $t_{½}$ doubles as [A] halves. **Zero order**: $t_{½}$ shrinks as [A] drops; rate = k, constant until A runs out.

Worked Examples

1st order, k = 0.0231 min^{-1}: $t_{½} = 0.693/0.0231 = 30.0$ min.
From 0.80 M, after 90 min (3 $t_{½}$) → 0.10 M.

Using ln form: $\ln[A]_{60} = \ln(0.80) - (0.0231)(60) = -1.609$ → [A] = 0.20 M at 60 min (2 $t_{½}$, checks out).

k from a slope: ln[A] vs t slope = −0.046 s^{-1} → k = 0.046 s^{-1} and $t_{½} = 0.693/0.046 \approx 15$ s (1st order).

⚠ On an ln[A] plot, slope = −k, so k = −slope (k is always +). On a 1/[A] plot, slope = +k directly.

✓ "Justify the order using the graph": name which plot is linear and state the order that it implies.

5.4–5.5 Elementary Rxns & Collision Model

Elementary Reactions (5.4)

Elementary step: one collision or event exactly as written; its rate law comes straight from its coefficients.

Molecularity	Step	Rate law
unimolecular	A → products	k[A]
bimolecular	A + B → ...	k[A][B]
bimolecular	2A → ...	$k[A]^2$
termolecular	A + B + C →	rare (3-body)

Molecularity = # of particles colliding in one step: 1, 2, rarely 3 (3-body collisions are very unlikely).
Overall rxn ≠ elementary unless the Q says so. Only elementary steps let coefficients = orders.

Collision Model (5.5)

Effective collision: E ≥ E_a AND correct **orientation**.

Most collisions fail: too little energy or wrong orientation, so only a tiny fraction of hits make products.
↑T → ↑avg KE → bigger fraction of collisions w/ E ≥ E_a (main effect) + slightly more collisions per second.
Maxwell–Boltzmann: higher T → curve flattens, shifts right; more area past E_a → ↑rate; total area unchanged.

↑[ ] → more collisions/s, NOT a bigger fraction ≥ E_a.

Orientation: only hits at the reactive site count; big molecules waste many energetic collisions on the wrong side.
Surface area: only particles at a solid's surface can collide → powder reacts faster than a chunk of the same mass.
Pressure (gases): ↑P = ↑[ ] → more collisions/s.

⚠ ↑T speeds up BOTH endo- and exothermic rxns: it ↑ the fraction of collisions ≥ E_a, not just hit frequency.

✓ Explain rate changes at the particle level: "more collisions per second w/ enough energy and proper orientation."

5.6 Reaction Energy Profile

Reading the Diagram

Energy profile: PE (y) vs rxn progress (x); reactants → peak (**transition state**) → products; peak height sets rate.
$E_{a,fwd}$ = peak − reactants; **$E_{a,rev}$** = peak − products.
ΔH = products − reactants: negative if products lower (exothermic), positive if higher (endothermic).
Link: $\Delta H = E_{a,fwd} - E_{a,rev}$. Exothermic → $E_{a,rev} > E_{a,fwd}$.

Feature	Exothermic	Endothermic
products level	lower	higher
ΔH sign	−	+
$E_{a,fwd}$ vs rev	fwd smaller	fwd larger
heat	released	absorbed

Transition State

Transition state (activated complex): top-PE arrangement, bonds half broken/half formed; can't be isolated.
Not an intermediate: a transition state sits at a peak; intermediates sit in valleys between peaks (5.10).

Temperature & k

Activation energy = min. collision energy to reach the transition state; bigger E_a → smaller k.

Arrhenius (trend): $k = Ae^{-Ea/RT}$, so ↑T → ↑k and lower activation energy → ↑k (how catalysts work).
A (frequency factor) covers collision rate & orientation; $e^{-Ea/RT}$ = fraction of collisions w/ enough energy.
Rule of thumb: many rxns run ~2× faster per +10 °C; the higher the E_a, the bigger the jump per degree.

⚠ ΔH and E_a are independent: a very exothermic rxn can still be slow (high E_a). Thermo ≠ kinetics.

✓ AP tests Arrhenius trends: explain how T & E_a shift k.

5.7–5.8 Mechanisms & Rate Law

Mechanisms (5.7)

Mechanism: series of elementary steps that add up to the overall balanced eqn; each step has its own k.
Intermediate: made in one step, used up in a later one; cancels in the sum, so it's not in the overall eqn.
Catalyst: used in an early step, regenerated in a later one; cancels too, but it is present at the start.

Species	Shows up 1st as	Then
intermediate	product	consumed
catalyst	reactant	regenerated

Ex. step 1 (slow): $NO_2 + NO_2 \rightarrow NO_3 + NO$
Step 2 (fast): $NO_3 + CO \rightarrow NO_2 + CO_2$
Sum: $NO_2 + CO \rightarrow NO + CO_2$; NO_3 = intermediate.

Rate-Determining Step (5.8)

Slow step = rate-determining step (RDS): the rxn can't go faster than its slowest step (a bottleneck).
Slow step first: rate law = that step's: rate = $k[NO_2]^2$; CO is zero order though it reacts (fast step 2).
Fast eq. then slow: slow-step rate law holds an intermediate → swap it out using the fast equilibrium (5.9).
Catalyst in rate law? Yes if it reacts in or before the slow step; it is a real species you can measure.
Valid mechanism test: (1) steps sum to the overall eqn, (2) predicted rate law = experimental rate law, (3) each step plausible (uni- or bimolecular). Fails any → reject it.
Data can't prove a mechanism: a matching rate law makes it consistent; other mechanisms may fit too.

⚠ A reactant that enters only AFTER the slow step (CO above) does not show up in the rate law.

✓ FRQ "is the mechanism consistent?": write the slow-step rate law, compare it to the data, and check the steps sum.

5.9–5.10 Steady State & Multistep Profiles

Fast Equilibrium First (5.9)

Setup: fast reversible step 1, then slow step 2. The slow-step rate law holds an intermediate → must remove it.
Step 1 (fast, reversible): $2NO \rightleftharpoons N_2O_2$
Step 2 (slow): $N_2O_2 + O_2 \rightarrow 2NO_2$ (rate-determining)
Slow step: rate = $k_2[N_2O_2][O_2]$, has an intermediate.
Fast eq.: $k_1[NO]^2 = k_{-1}[N_2O_2]$ (fwd = rev)
Solve: $[N_2O_2] = (k_1/k_{-1})[NO]^2$, then sub into slow step
Why it works: $k_1/k_{-1} = K$ for step 1, so [intermediate] tracks reactant [ ] like any equilibrium; it all folds into one k.
Result: rate = $k[NO]^2[O_2]$, where $k = k_2k_1/k_{-1}$.
Steady-state idea: intermediate [ ] stays ~constant b/c it forms and is used up at about the same rate.

Multistep Energy Profile (5.10)

One hump per elementary step; valleys between humps = **intermediates**; peaks = transition states.
RDS = step w/ the largest E_a (tallest climb from its own valley), not always the highest peak overall.

Profile feature	Meaning
# of humps	# of elementary steps
valley	intermediate
peak	transition state
largest E_a climb	rate-determining step
end below start	exothermic overall

Catalyzed profile: lower peaks, often extra humps; start & end levels unchanged, so ΔH is the same.

⚠ Intermediates (valleys) can be detected in principle; transition states (peaks) can't be isolated.

✓ The final rate law holds only species from the overall eqn (or a catalyst), never an intermediate.

5.11 Catalysis

How Catalysts Work

Catalyst: ↑rate by giving a new mechanism w/ lower E_a; regenerated at the end, so not used up.
No change to: ΔH, K, or yield at equilibrium. Speeds fwd & rev rxns equally → reaches eq. sooner.
Energy profile: catalyzed path has lower peak(s), often more steps; reactant & product levels stay the same.
In a mechanism: consumed in an early step, regenerated later; it can appear in the experimental rate law.

Types of Catalysis

Type	How it works
acid-base	reactant gains/loses H^+
surface (hetero.)	adsorb → weaken bonds
enzyme	active site binds substrate
homogeneous	same phase as reactants

Acid-base catalysis: reactant gains or loses H^+ → more reactive form; rate may depend on $[H^+]$.
Surface catalysis: reactants adsorb onto a metal (Pt, Pd, Ni) → bonds weaken, new intermediates form.
Enzymes: protein catalysts; substrate binds the active site in the right orientation → much lower E_a.

Catalyst vs Intermediate

Spot it: catalyst = reactant first, product later; intermediate = product first, reactant later; both cancel.
Solid catalyst: ↑ surface area → more active sites → ↑rate.
Homogeneous vs heterogeneous: same phase as reactants (H^+ in solution) vs different phase (solid metal + gases).
vs heating: heat ↑KE, catalyst ↓E_a; both ↑ fraction ≥ E_a.

⚠ A catalyst does NOT shift equilibrium or raise yield; it only gets the system to equilibrium faster.

✓ FRQ: "catalyst gives an alternate pathway w/ lower E_a, so a greater fraction of collisions have E ≥ E_a."