The Simple AP® Chemistry Unit 5 Cheat Sheet

5.1 Reaction Rates

What Rate Means

Rate (how fast [ ] changes) = Δ[conc]/Δt, in M/s; reported as a + value even when [ ] falls.
Rate of rxn for aA → bB: rate = −(1/a)Δ[A]/Δt = +(1/b)Δ[B]/Δt; divide by each coefficient.
Stoich link: $2N_2O_5 \rightarrow 4NO_2 + O_2$: NO_2 forms 2× as fast as N_2O_5 is used up, 4× as fast as O_2.
Avg rate = slope between two points on the curve; **initial rate** = tangent slope at t = 0.
Rate slows over time b/c reactant [ ] drops → fewer collisions per second → curve flattens.

Factors That Change Rate

Factor	Effect	Why
↑ [reactant]	↑ rate	more hits/s
↑ temp	↑ rate	more ≥ E_a
↑ surface	↑ rate	more exposed
catalyst	↑ rate	lower E_a

Measuring Rate

Track a property ∝ [ ]: absorbance (color), gas pressure or volume, mass lost as gas escapes, pH.
Gas-forming rxn: mass of an open flask drops as gas escapes; Δmass/Δt tracks the rate.
Worked: [A] 0.500 → 0.380 M in 40 s → avg rate = 0.120 M ÷ 40 s = 3.0×10^{-3} M/s (A used up).

⚠ Rate of A used up = rate of rxn only if A's coefficient is 1; otherwise divide by it.

✓ FRQ avg rate: Δ[ ]/Δt from two data points; always give units (M/s) and a + sign.

5.2 Introduction to Rate Law

Rate Law Basics

Rate law: rate = $k[A]^m[B]^n$; orders m, n come ONLY from experimental data, never from the eqn.
Overall order = m + n; each order is 0, 1 or 2.
k: changes w/ T & catalyst, NOT w/ [ ].

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 → m = 2.
Trials 1→3: only [B] ×2, rate same → n = 0.
Rate law: rate = $k[A]^2$, 2nd order overall; $k = 2.0\times10^{-3} \div (0.10)^2 = 0.20\ M^{-1}\ s^{-1}$ (any trial).
[ ] ×2 → rate ×1, ×2 or ×4 → order 0, 1 or 2.
No clean pair? Divide out the effect of the reactant you already know, then solve for the other.
Order meaning: 0 → [ ] has no effect; 1 → rate ∝ [ ]; 2 → rate ∝ $[ ]^2$ (×2 → ×4, ×3 → ×9).

Units of k

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

Units check: k's units always make rate = M/s.

⚠ Never take orders from the overall eqn's coefficients; they only work for elementary steps.

✓ FRQ: show the ratio ("[A] ×2, rate ×4 → 2nd order") to earn the justification point.

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: plot [A], ln[A] & 1/[A] vs time; whichever plot is a straight line gives the order.
Eqn sheet gives the 1st- & 2nd-order integrated laws and $t_{½}$ = 0.693/k; know which fits.

Half-Life

1st order: $t_{½}$ = 0.693/k, constant no matter the starting [A]; equal $t_{½}$ in data → 1st order.
Half-life counting: 3 half-lives → 1/8 = 12.5% left.
2nd order: $t_{½}$ gets longer as [A] drops, doubling each time, so $t_{½}$ isn't constant.
Radioactive decay is always 1st order.

Worked Examples

k = 0.0231 min^{-1}: $t_{½}$ = 0.693/0.0231 = 30.0 min.
Then: 0.80 M → 0.40 → 0.20 → 0.10 M after 3 half-lives (90 min), so 12.5% of A is left.
Graph example: ln[A] vs t is straight w/ slope $-0.046\ s^{-1}$ → 1st order, k = 0.046 s^{-1}.

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

✓ Justify order: name the plot that is linear and state the order that plot shows.

5.4–5.5 Elementary Rxns & Collision Model

Elementary Reactions (5.4)

Elementary step: one collision exactly as written, so its rate law comes from its coefficients.

Type	Step	Rate law
uni-	A → ...	k[A]
bi-	A + B → ...	k[A][B]
bi-	2A → ...	$k[A]^2$

Molecularity = # of particles colliding in one step; 3-body (termolecular) steps are rare.
Overall eqn: coefficients ≠ orders.

Collision Model (5.5)

Effective collision: energy ≥ E_a AND the right **orientation**; most collisions fail.
Orientation: hits must strike the reactive part of the molecule, or nothing happens.
↑T → ↑avg KE → bigger fraction of collisions w/ E ≥ E_a (main effect) + more hits/s.
Maxwell–Boltzmann: higher T → curve flattens & shifts right; more area past E_a → faster.
↑[ ] → more collisions per second, not more energy per hit; the fraction ≥ E_a stays the same.
Surface area: powder reacts faster than a chunk b/c more particles are exposed to collide.

⚠ ↑T speeds up BOTH endothermic and exothermic rxns b/c more collisions have E ≥ E_a.

✓ Explain at the particle level: more collisions w/ enough energy & right orientation.

5.6 Reaction Energy Profile

Reading the Diagram

Energy profile: energy vs rxn progress; the peak is the **transition state** (top of the hill).
E_a (activation energy) = peak − reactants; higher E_a → fewer hits get over → slower.
Reverse E_a = peak − products (right side).
ΔH = products − reactants: negative = exothermic (heat out), positive = endothermic (heat in).

Feature	Exothermic	Endothermic
products	lower	higher
ΔH sign	−	+
E_a fwd vs rev	fwd smaller	fwd larger
heat	released	absorbed

Transition State

Transition state: highest-energy arrangement, bonds half broken/half formed; can't be isolated.
Not an intermediate: a transition state sits on a peak; intermediates sit in valleys (5.10).

Temperature & k

Arrhenius (trend): ↑T → ↑k and lower activation energy → ↑k, so the rxn speeds up.
Rule of thumb: many rxns ~2× faster per +10 °C.

⚠ ΔH ≠ E_a: exothermic rxns can be slow.

✓ Explain how T & E_a change k in terms of collisions w/ enough energy, not just the eqn.

5.7–5.8 Mechanisms & Rate Law

Mechanisms (5.7)

Mechanism: series of elementary steps that add up to the overall balanced eqn; each has its own k.
Intermediate: made in one step, used up in a later one; never appears in the overall eqn.
Catalyst: used in an early step, regenerated in a later one; present at the start & end.

Species	First as	Then
intermediate	product	used up
catalyst	reactant	regenerated

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 cancels.

Rate-Determining Step (5.8)

Slow step = rate-determining step (RDS): the rxn can't go faster than its slowest step.
Slow-step orders = its coefficients.
Slow step first: rate = $k[NO_2]^2$; CO enters after the slow step, so it's not in the rate law.
Fast eq. then slow: slow-step rate law has an intermediate → swap it out using step 1 (5.9).
Valid mechanism: steps sum to the overall eqn AND match the experimental rate law.
Plausible steps: each step should be uni- or bimolecular; 3-body hits are rare.

⚠ Matching data makes a mechanism consistent, not proven; other mechanisms may also fit.

✓ FRQ: write the slow-step rate law, compare it to the data, and check that the steps add up.

5.9–5.10 Steady State & Multistep Profiles

Fast Equilibrium First (5.9)

Setup: fast reversible step first, then a slow step whose rate law holds an intermediate.
Step 1 (fast, reversible): $2NO \rightleftharpoons N_2O_2$
Step 2 (slow): $N_2O_2 + O_2 \rightarrow 2NO_2$
Slow step: rate = $k_2[N_2O_2][O_2]$
Swap out N_2O_2 using step 1: $[N_2O_2] \propto [NO]^2$.
Result: rate = $k[NO]^2[O_2]$, 3rd order overall, matching the experimental data.
Steady state: intermediate [ ] stays ~constant b/c it is made & used up at the same rate.

Multistep Energy Profile (5.10)

One hump per elementary step; valleys = **intermediates**; peaks = transition states.

Feature	Meaning
# of humps	# of steps
valley	intermediate
peak	transition state
biggest E_a climb	slow step
end below start	exothermic

Catalyzed profile: lower peaks, often extra humps; start & end levels (ΔH) stay the same.

⚠ Intermediates sit in valleys and can be detected; transition states sit on peaks.

✓ The final rate law never includes an intermediate, only species from the overall eqn.

5.11 Catalysis

How Catalysts Work

Catalyst: gives a new pathway w/ lower E_a → faster rxn; regenerated, so not used up.
No change to: ΔH, K or yield; speeds fwd & reverse equally → reaches equilibrium sooner.
Energy profile: lower peak(s), often more humps; same start & end energy levels as before.
In a mechanism: used in an early step, regenerated later; it can show up in the rate law.

Types of Catalysis

Type	How it works
acid-base	gains/loses H^+
surface	adsorb → weak bonds
enzyme	active site fit
homogeneous	same phase

Acid-base: reactant gains or loses H^+ → more reactive form; rate may depend on $[H^+]$.
Surface: reactants stick (adsorb) to a metal like Pt or Ni → bonds weaken → react faster.
Enzymes: protein catalysts; active site holds substrate in the right orientation.
Solid catalyst: ↑ surface area → ↑ rate.

Catalyst vs Intermediate

Spot it: catalyst = reactant first, product later; intermediate = product first, then used.

⚠ A catalyst does NOT shift equilibrium.

✓ FRQ: catalyst → new path w/ lower E_a → bigger fraction of collisions have E ≥ E_a.