Unit 3 · Chemical Kinetics

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Physical Chemistry (Units 1–5 together): 22 of 75 marks; 4 MCQs, 2 short and 1 long question
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: a first-order decomposition of N_2O_5, rate and k given → $[N_2O_5]$ = rate ÷ k; short (OR): derive $k = \frac{2.303}{t} \log \frac{a}{a-x}$, show $t_{1/2}$ doesn't depend on $[A]_0$, compare the times for 50% and 90% to react
- **MCQ (1 mark)**
  - rate; doubling [B] in a rate law; collision theory and temperature; k from rate and [A]; half-life sums (0.08 → 0.01 M)
  - average vs instantaneous; molecularity; what a rate law shows; zero-order plot; half-life depends on
  - activated complex; Arrhenius; catalyst and K; heterogeneous catalysis; enzymes; E_a when the rate doubles 300 → 310 K; powder and E_a; order from a table
- **Short (5 marks, in parts)**
  - define, and differ: rate and k, E_a and activated complex, average/instantaneous, order/molecularity, first/second order, homogeneous/heterogeneous
  - initial rate; rate expressions for $H_2 + I_2$, $N_2 + 3H_2$, $2NO + O_2$; units of k
  - N_2O_5 at 45 °C: order, molecularity, rate; orders and k from tables (Q → W + X, $NH_4^+ + NO_2^-$, $H_2 + 2NO$, $H_2O_2 + I^-$); one-eighth left; E_a from a rate ratio ($CO + Cl_2$); half-life rising as $[A]_0$ halves → order; Maxwell–Boltzmann graph
- **Long (8 marks)**: $2NO + Cl_2$ from initial rates (law, orders, k, a rate); a concentration–time plot (half-life, order, average rate, k, when complete); Haber with iron (catalysis, yield, equilibrium); zero order in X, second in Y; two energy profiles (endo/exo, E_a, faster, more stable product)

Key terms

Chemical kinetics: rates of reactions, what affects them, and their mechanisms.

Rate of reaction: change in concentration of a reactant or product per unit time, mol L^{-1} s^{-1}.

Average rate: over an interval, the slope of the **chord**; **instantaneous rate**: at a moment, the slope of the **tangent**; **initial rate**: the tangent at $t = 0$.

Rate law: rate = $k[A]^x[B]^y$, found by **experiment**, not from the equation.

Rate constant (k): the rate when every concentration is 1 mol/L; depends on the reaction and temperature, not on concentration.

Order: the sum of the powers in the experimental rate law; 0, 1, 2, a fraction or negative.

Pseudo-first-order: really second order, but one reactant (water, a catalyst) is in such excess that its concentration is constant.

Molecularity: number of particles colliding in an **elementary step**; always 1, 2 or 3 (van 't Hoff).

Rate-determining step: the slowest step, which sets the rate.

Half-life ($t_{1/2}$): time for a reactant's concentration to fall to half.

Effective collision: right **orientation** and **enough energy**.

Activation energy (E_a): the minimum energy colliding particles need to react; the barrier.

Activated complex (transition state): the short-lived arrangement at the top of the barrier, old bonds half broken, new half made.

Catalyst: speeds a reaction by a path of lower E_a, unchanged at the end; **inhibitor**: slows it (antioxidants, preservatives).

Homogeneous catalysis: catalyst in the same phase; **heterogeneous**: a different phase (usually a solid).

Enzyme: a protein catalyst with an **active site** for its **substrate**.

Formulas

$\text{rate} = -\frac{1}{a}\frac{d[\text{A}]}{dt} = +\frac{1}{c}\frac{d[\text{C}]}{dt}$	$aA + bB \to cC + dD$ **Use:** one rate for the reaction
unit of $k = (\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$	n overall order **Use:** order from the unit
$k_0 = \frac{x}{t}$, $[\text{A}] = [\text{A}]_0 - k_0 t$	straight line, slope $-k_0$ **Use:** zero order
$t_{1/2} = \frac{[\text{A}]_0}{2k_0}$	proportional to $[\text{A}]_0$ **Use:** zero order
$k_1 = \frac{2.303}{t}\log\frac{a}{a-x}$	a initial, x reacted **Use:** first order
$\log(a-x) = -\frac{k_1}{2.303}t + \log a$	log [A] against t: slope $-k_1/2.303$ **Use:** first order, graph
$t_{1/2} = \frac{0.693}{k_1}$	not on $[\text{A}]_0$; $(1/2)^n$ left after n **Use:** first order
$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$, $t_{1/2} = \frac{1}{k[\text{A}]_0}$	each half-life twice the last **Use:** second order
$k = A\,e^{-E_a/RT}$	A frequency factor, $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$ **Use:** Arrhenius
$\log k = -\frac{E_a}{2.303RT} + \log A$	ln k against $1/T$: slope $-E_a/R$ **Use:** E_a from a graph
$E_a = 2.303R\log\frac{k_2}{k_1}\left(\frac{T_1T_2}{T_2-T_1}\right)$	rate ratio for k_2/k_1 **Use:** two temperatures

Rates (3.1–3.2)

- slow: diamond from carbon, ^{238}U half-life 4.5 billion years, rusting; fast: precipitation, neutralization, a match
- uses: factory conditions, a medicine's expiry date, pressure cooking, the fridge
- reactant falls (minus sign), product rises (plus)
- concentration followed by pH, conductivity, mass or gas volume, color (colorimeter)
- A falls 0.5 → 0.3 mol/L in 10 s: 0.02 mol $\text{L}^{-1}\ \text{s}^{-1}$
- $2\,H_2O \longrightarrow 2\,H_2 + O_2$: rate = $-\frac{1}{2}\frac{d[H_2O]}{dt} = \frac{1}{2}\frac{d[H_2]}{dt} = \frac{d[O_2]}{dt}$
- $2NO + O_2 \to 2NO_2$: NO_2 forms twice as fast as O_2 is used

Rate law, k, order (3.3–3.5)

- $NO_2 + CO$ (100 °C): rate = $k[NO_2]^2$; power 2 for coefficient 1, CO zero order; slow step $NO_2 + NO_2$
- doubling $[NO_2] \to 4\times$ rate; doubling [CO] → no change; rate law gives clues to the mechanism, the speed and industry's conditions

Order	Rate law	Unit of k
zero	rate = k	mol $\text{L}^{-1}\ \text{s}^{-1}$
first	$k[\text{A}]$	s^{-1}
second	$k[\text{A}]^2$ or $k[\text{A}][\text{B}]$	L $\text{mol}^{-1}\ \text{s}^{-1}$
third	$k[\text{A}]^2[\text{B}]$	$\text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$

- negative order: more of it slows the reaction (O_2 in $2O_3 \to 3O_2$)

Zero order: [A] falls in a straight line; rate = k throughout; often pseudo-zero

- $H_2 + Cl_2$ in light (rate set by the light)
- $2\,N_2O \xrightarrow{Pt} 2\,N_2 + O_2$ on a covered surface
- iodination of acetone: rate = k[acetone][H^+], zero order in $\mathbf{I_2}$ only
- alcohol cleared by the liver at a steady rate (enzyme saturated)

First order: rate = k[A]; halves in equal times

- $2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$; radioactive decay
- k doesn't depend on the concentration unit; same fraction in the same time from any start
- pseudo-first-order: $CH_3I + H_2O \longrightarrow CH_3OH + H^+ + I^-$, rate = $k'[CH_3I]$, $k' = k[H_2O]$ (water ~55.5 M); ester hydrolysis in acid; sucrose inversion

Second order: rate = $k[\text{A}]^2$; doubling [A] → 4×; $2\,NO_2 \longrightarrow 2\,NO + O_2$

Finding the order

- differential: rate at several [A]
- **initial rates**: change one concentration at a time; ln(rate) against ln[A], slope = order
- integral: which plot is straight, [A] (zero), ln[A] (first), 1/[A] (second)
- $2NO + Cl_2$: [NO] ×1.5 → rate ×2.25 (order 2); $[Cl_2]$ ×1.5 → ×1.5 (order 1)
- rate = $k[NO]^2[Cl_2]$, $k = 0.00300/(0.10^2 \times 0.10) = 3.0\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$

Integrated equations, half-life (3.6–3.7)

- zero: $dx/dt = k_0 \to x = k_0t + I$, $I = 0$ at $t = 0 \to k_0 = x/t$
- first: $\frac{dx}{a-x} = k_1\,dt \to -\ln(a-x) = k_1t + C$, $C = -\ln a \to k_1 = \frac{1}{t}\ln\frac{a}{a-x}$
- half-life, first order: $x = a/2 \to t_{1/2} = 2.303\log 2/k_1 = 0.693/k_1$
- **90% reacted**: $a/(a-x) = 10 \to t = 2.303/k_1 = 3.32\,t_{1/2}$; 99.9%: $6.909/k_1 \approx 10$ half-lives
- 87.5% (one-eighth left) = 3 half-lives; 0.08 → 0.01 M with $t_{1/2}$ 20 min: 60 min
- H_2O_2, $k = 0.0410\ \text{min}^{-1}$, 0.500 M: 0.220 M after 20.0 min; 75% gone in 33.8 min (2 × 16.9)
- half-life rises as $[\text{A}]_0$ falls (1.20 → 0.60 M, 2.0 → 4.0 min): second order

	Zero	First	Second
$t_{1/2}$	$[\text{A}]_0/2k$	$0.693/k$	$1/k[\text{A}]_0$
with $[\text{A}]_0$	$\propto [\text{A}]_0$	constant	$\propto 1/[\text{A}]_0$
straight line	[A] vs t	log [A] vs t	1/[A] vs t

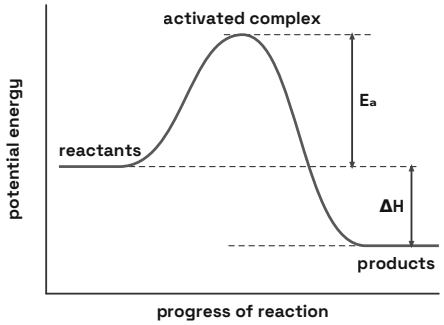
Molecularity: uni ($O_3 \longrightarrow O_2 + O$, cyclopropane → propene), bi ($NO + O_3 \longrightarrow NO_2 + O_2$), ter ($2\,NO + O_2 \longrightarrow 2\,NO_2$); never above 3 (four at once too rare)

- elementary step: order = molecularity; overall equation in steps: no molecularity
- $H_2 + Br_2 \rightarrow 2HBr$: rate = $k[H_2][Br_2]^{1/2}$, order 3/2, a chain of steps

Order	Molecularity
experimental	from the mechanism
0, fraction, negative possible	1, 2 or 3
overall reaction	each step

Collisions and energy (3.8)

- collision theory (Trautz 1916, Lewis 1918): molecules as hard spheres; only **effective** collisions react
- low E_a: goes by itself, fast; high: slow (wood doesn't light itself; a flame activates a few, their heat the rest)

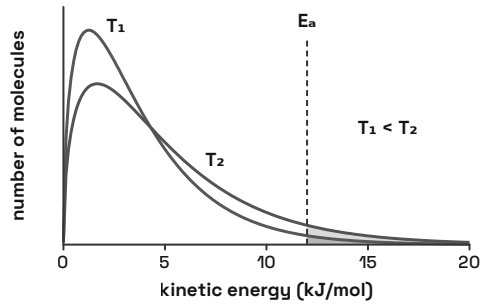


Energy profile of an exothermic reaction: E_a up to the activated complex, ΔH below.

- exothermic: products below reactants; endothermic: above; E_a(backward) = E_a(forward) − ΔH

Factors and catalysts (3.9–3.10)

- **nature**: ions react fast (no bonds to break); covalent bonds slow
- **concentration** (pressure for gases): more collisions a second; **surface area**: powder faster (flour dust explodes)
- **temperature**: a much larger **fraction** with $E \geq E_a$ (not mainly more collisions); +10 °C roughly doubles the rate ($E_a \approx 53$ kJ/mol between 300 and 310 K), more for higher E_a



Maxwell–Boltzmann at two temperatures: the same area; the hotter curve flatter and wider, more molecules past E_a.

- N_2O_5 (Daniels and Johnston, 1921): slope -12.46×10^3 K → $E_a = 8.314 \times 12.46 \times 10^3 =$ **104 kJ/mol**
- sour milk, 8 h at 30 °C, 64 h at 4 °C: $E_a = 2.303 \times 8.314 \times \log 8 \times (277 \times 303/26) \approx$ **56 kJ/mol**
- **catalyst**: another path, lower E_a; ΔH unchanged; speeds forward and backward equally: equilibrium sooner, K **unchanged**
- marcha: molds turn starch to sugar, yeast's **zymase** sugar to ethanol + CO_2

Homogeneous:

$CH_3COOH + CH_3OH \overset{H^+}{\rightleftharpoons} CH_3COOCH_3 + H_2O$; H_2O_2 with I^-

Heterogeneous

- catalytic converter (Pt, Pd, Rh; works from ~250 °C): $2\,CO + O_2 \longrightarrow 2\,CO_2$, $2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2$
- Haber (Fe); contact process (V_2O_5); cracking (zeolites); hydrogenating oils (Ni)
- steps: adsorbed → bonds weakened → react → product desorbs

Enzymes: amylase (starch, saliva), protease, lactase, zymase; carbonic anhydrase ~10^6 CO_2 a second

- **specific** (active site), **efficient** (millions of times faster), small amounts, unchanged
- **optimum** temperature (~37 °C) and pH (pepsin ~2); denatured when hot
- usually counted homogeneous (some books: microheterogeneous)
- $E + S \rightleftharpoons ES \longrightarrow E + P$: lock and key (Fischer 1894), induced fit (Koshland 1958)
- much substrate: enzyme **saturated**, rate at its maximum, zero order

COMMON MISTAKES

✗ zero order: [A] doesn't change
✓ it falls in a straight line; the **rate** doesn't change.

✗ powers in the rate law = coefficients
✓ found by experiment.

✗ k changes as the reaction goes
✓ constant at a given temperature.

✗ iodination of acetone is zero order
✓ zero order in I_2 only.

✗ molecularity of $H_2 + Br_2$ is two
✓ no molecularity for a chain; order 3/2.

✗ slope of log(a − x) against t is $k_1/2.303$
✓ $-k_1/2.303$.

✗ a catalyst shifts equilibrium, raises yield
✓ reaches it sooner, K the same.

✗ heat raises the rate mainly by more collisions
✓ by more collisions **past** E_a.

✗ a powder lowers E_a
✓ more surface, more collisions; E_a the same.

✗ doubling 300 → 310 K needs 57.9 kJ/mol
✓ 53.6 kJ/mol.

✗ enzymes speed reactions ~1000 times
✓ millions of times or more.