

Chemical Kinetics

Rate laws, integrated rate laws, half-lives, Arrhenius, mechanisms, and energy diagrams.

01 Rate of reaction

CORE RULE

For $aA + bB \rightarrow cC + dD$: $\text{rate} = -(1/a)d[A]/dt = -(1/b)d[B]/dt = +(1/c)d[C]/dt = +(1/d)d[D]/dt$. The 1/coefficient prefactor makes the single rate value independent of which species you track.

02 Rate law

CORE RULE

$\text{rate} = k[A]^m[B]^n$. Orders m, n are found by EXPERIMENT, not from coefficients (except for an elementary step). k depends only on temperature. Overall order = $m + n$.

03 Integrated rate laws

REFERENCE

Order	Integrated law	Linear plot
0	$[A]_t = [A]_0 - kt$	$[A]$ vs t (slope $-k$)
1	$\ln[A]_t = \ln[A]_0 - kt$	$\ln[A]$ vs t (slope $-k$)
2	$1/[A]_t = 1/[A]_0 + kt$	$1/[A]$ vs t (slope $+k$)

04 Half-life by order

REFERENCE

Order	$t_{1/2}$	Depends on $[A]_0$?
0	$[A]_0 / (2k)$	yes
1	$\ln 2 / k \approx 0.693/k$	no
2	$1 / (k \cdot [A]_0)$	yes

05 Fraction remaining (first order)

CORE RULE

After N half-lives, fraction left = $(1/2)^N$ (50%, 25%, 12.5%, ...), with $N = t/t_{1/2}$. For any time: $[A]_t/[A]_0 = e^{(-kt)}$. If $X\%$ decomposes, $(100-X)\%$ remains.

06 Method of initial rates

METHOD

Pick two trials where only ONE concentration changes: $\text{rate}_2/\text{rate}_1 = ([X]_2/[X]_1)^{\text{order}}$, so $\text{order} = \log(\text{rate ratio}) / \log(\text{conc ratio})$. Repeat per reactant, then get k by plugging one trial into $\text{rate} = k[A]^m[B]^n$.

07 Arrhenius equation

CORE RULE

$k = A \cdot e^{(-E_a/RT)}$. Two-temperature: $\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$. Plot $\ln k$ vs $1/T$: slope = $-E_a/R$. T in Kelvin; $R = 8.314 \text{ J/(mol} \cdot \text{K)}$ for E_a in J/mol.

08 Units of k

REFERENCE

Overall order	k units
0	M/s
1	s^{-1}
2	$M^{-1} \cdot s^{-1}$
3	$M^{-2} \cdot s^{-1}$

09 Rate-determining step

CORE RULE

The slowest (RDS) step sets the overall rate. For an ELEMENTARY step the orders DO equal its coefficients: $A + 2B \rightarrow \text{products}$ gives $\text{rate} = k[A][B]^2$. If the RDS contains an intermediate, substitute it out via the pre-equilibrium.

10 Intermediate vs catalyst

CORE RULE

Both have net-zero stoichiometry (not in the overall equation). Intermediate: produced first, then consumed. Catalyst: consumed first, then regenerated (it lowers E_a).

11 Energy diagram

CORE RULE

Peak = transition state; valley between peaks = intermediate. Forward E_a = peak - reactants; ΔH = products - reactants. A catalyst gives a lower- E_a path with the SAME ΔH . RDS = the highest peak.

12 Pre-equilibrium

METHOD

If a fast equilibrium precedes the RDS, solve the intermediate from that step: $[\text{int}] = K_{\text{eq}} \cdot [\text{reactants}]$, then substitute into the RDS rate. E.g. $2\text{NO} + \text{Cl}_2$: $\text{rate} = k_2 K_{\text{eq}} [\text{NO}]^2 [\text{Cl}_2]$.