CHEMWHIZ QUICK REFERENCE

TOPIC 20

Chemical Kinetics

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

01 Rate of reaction — CORE RULE

For aA + bB → cC + dD: 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

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: $rate_2/rate_1 = ([X]_2/[X]_1)^{order}$, so order = log(rate ratio) / log(conc ratio). Repeat per reactant, then get k by plugging one trial into rate = k[A]^m[B]^n.

07 Arrhenius equation — CORE RULE

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

11 Energy diagram — CORE RULE

Peak = transition state; valley between peaks = intermediate. Forward Ea = peak − reactants; ΔH = products − reactants. A catalyst gives a lower-Ea 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: [int] = K_eq·[reactants], then substitute into the RDS rate. E.g. 2NO + Cl_2: rate = $k_2 K_{eq}[NO]^2[Cl_2]$.