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PHYSICAL

CH 01

Chemical Kinetics — Rate Laws & Integrated Forms

01

Rate laws, order and molecularity, integrated laws and half-lives for zero and first order, the Arrhenius equation and catalysis — with every numerical type solved, an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Write a rate law, find order from initial-rate data, and give the units of k for any order
- Use the integrated laws and half-life expressions for zero- and first-order reactions
- Solve first-order numericals: percentage completion, t½, gas-phase pressure data
- Use the Arrhenius equation to find Ea or k at a new temperature
- Explain collision theory, the role of a catalyst and the rate-determining step

INSIDE

A The big picture
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G Temperature and Arrhenius
H Collision theory and catalysts
I Exam trap gallery
J Practice MCQs
K Advanced problems
R One-page revision

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

Four equations answer almost every question in this chapter.

IN ONE LINE

The rate law says how rate depends on concentration; the integrated law turns that into concentration against time; the Arrhenius equation says how the rate constant depends on temperature.

1. **Rate law:** rate = $k[A]^x[B]^y$ — found by experiment, not from the equation.
2. **Integrated law:** how much reactant is left after time t.
3. **Half-life:** the time for half the reactant to go.
4. **Arrhenius:** k rises steeply with temperature because more molecules have enough energy.

THINK OF IT LIKE THIS

Picture a crowd leaving a stadium. If one gate lets out a fixed number per minute whatever the crowd size, that is zero order. If a fixed fraction of whoever is left leaves each minute, that is first order — the crowd halves in the same time again and again, however big it was.

SECTION B

Rate and rate law

B

How fast, measured how.

For aA + bB → cC + dD the rate is written so that it is the same whichever species you watch:

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Minus sign for reactants (their concentration falls); units mol L^{-1} s^{-1}

SOLVED EXAMPLE 01 — RELATING RATES

For $2N_2O_5 \rightarrow 4NO_2 + O_2$, the rate of formation of NO_2 is 0.04 mol L^{-1} s^{-1}. Find the rate of disappearance of N_2O_5 and the rate of reaction.

SOLUTION

1. Rate of reaction = (1/4) $d[NO_2]/dt$ = 0.04/4 = 0.01 mol L^{-1} s^{-1}.
2. $-d[N_2O_5]/dt$ = 2 × rate = 0.02 mol L^{-1} s^{-1}.

ANSWER N_2O_5 disappears at 0.02 mol L^{-1} s^{-1}; rate of reaction 0.01 mol L^{-1} s^{-1}.

$$\text{Rate} = k\,[A]^x\,[B]^y$$

$$\text{Order} = x + y$$

x and y come from experiment; they need not equal a and b

KEY IDEA

Units of k depend on order: (mol $L^{-1})^{(1-n)}$ s^{-1}. Zero order: mol L^{-1} s^{-1}. First order: s^{-1}. Second order: L mol^{-1} s^{-1}. Third order: L^2 mol^{-2} s^{-1}. Read the units and you know the order.

Finding order from initial rates

SOLVED EXAMPLE 02 — METHOD OF INITIAL RATES

For A + B → products: (1) [A] = 0.1, [B] = 0.1, rate = 2.0×10^{-3}; (2) [A] = 0.2, [B] = 0.1, rate = 8.0×10^{-3}; (3) [A] = 0.1, [B] = 0.2, rate = 4.0×10^{-3} (mol L^{-1} s^{-1}). Find the rate law and k.

SOLUTION

1. Experiments 1 → 2: [A] doubles, rate × 4 = 2^2 → order 2 in A.
2. Experiments 1 → 3: [B] doubles, rate × 2 → order 1 in B.
3. $k = 2.0 \times 10^{-3} / (0.1^2 \times 0.1) = 2.0$.

ANSWER Rate = $k[A]^2[B]$; overall order 3; k = 2.0 L^2 mol^{-2} s^{-1}.

SECTION C

Order and molecularity

C

Two numbers students mix up every year.

	Order	Molecularity
Definition	Sum of powers in the experimental rate law	Number of particles colliding in one elementary step
Found by	Experiment	Proposed mechanism

	Order	Molecularity
Values	0, 1, 2, 3 or a fraction	Whole number 1, 2 or 3 (never 0)
Applies to	Overall reaction	Each elementary step only

- **Pseudo-first-order:** a second-order reaction looks first order when one reactant (often water) is in huge excess. Examples: acid hydrolysis of an ester ($CH_3COOC_2H_5 + H_2O$), inversion of cane sugar.
- **Rate-determining step:** in a multi-step mechanism the slowest step fixes the rate law.
- Molecularity above 3 is almost never seen: four particles colliding at once is too unlikely.

SECTION D

D

Zero-order reactions

A constant rate, independent of concentration.

$$[A] = [A]_0 - kt$$

$$t_{1/2} = [A]_0 / 2k$$

Rate = k; units of k: mol L^{-1} s^{-1}

- Examples: decomposition of NH_3 on a hot platinum surface (surface saturated), the $H_2 + Cl_2$ photochemical reaction, some enzyme reactions at high substrate concentration.
- The reaction finishes completely at $t = [A]_0/k$.
- Half-life is **proportional** to the starting concentration.

SECTION E

E

First-order reactions

The most examined section of the chapter.

$$k = (2.303 / t) \log ([A]_0 / [A])$$

Equivalently $\ln[A] = \ln[A]_0 - kt$, or $[A] = [A]_0 e^{-kt}$

$$t_{1/2} = 0.693 / k$$

Independent of starting concentration

KEY IDEA

Shortcuts worth memorising: after n half-lives, the fraction left is $(1/2)^n$. 75% complete = 2 half-lives; 87.5% = 3; 93.75% = 4. **t(99%) = 2 × t(90%)**, and **t(99.9%) ≈ 10 × t½.**

- Examples: radioactive decay, decomposition of N_2O_5, H_2O_2, and many gas-phase decompositions.
- **Gas-phase pressure data** for A(g) → B(g) + C(g): with initial pressure p_0 and total pressure p_t, $k = (2.303/t) \log [p_0 / (2p_0 - p_t)]$.

SOLVED EXAMPLE 03 — HALF-LIFE FROM K

A first-order reaction has $k = 1.155 \times 10^{-3}\ s^{-1}$. Find $t_{1/2}$ and the time for 75% completion.

SOLUTION

1. $t_{1/2} = 0.693 / (1.155 \times 10^{-3}) = 600$ s.
2. 75% complete means two half-lives.

ANSWER $t_{1/2} = 600$ s (10 min); 75% completion takes 1200 s (20 min).

SOLVED EXAMPLE 04 — PERCENTAGE COMPLETION

A first-order reaction is 20% complete in 10 min. How long for 75% completion? (log 1.25 = 0.0969, log 4 = 0.602)

SOLUTION

1. 20% complete: $[A]_0/[A] = 100/80 = 1.25$. $k = (2.303/10) \times 0.0969 = 0.0223\ min^{-1}$.
2. 75% complete: $[A]_0/[A] = 4$. $t = (2.303/0.0223) \times 0.602$.

ANSWER About 62 min.

SOLVED EXAMPLE 05 — GAS-PHASE DECOMPOSITION

For A(g) → B(g) + C(g), first order, $p_0 = 0.40$ atm and after 100 s the total pressure is 0.60 atm. Find k. (log 2 = 0.301)

SOLUTION

1. $p(A)$ left $= 2p_0 - p_t = 0.80 - 0.60 = 0.20$ atm.
2. $k = (2.303/100) \log (0.40/0.20) = 0.02303 \times 0.301$.

ANSWER $k \approx 6.93 \times 10^{-3}\ s^{-1}$ (so $t_{1/2} = 100$ s — the pressure of A has exactly halved).

CHECK YOURSELF

C1 The rate constant of a reaction is $3 \times 10^{-4}\ s^{-1}$. What is its order?

C2 A first-order reaction has $t_{1/2} = 20$ min. What fraction remains after 1 hour?

Answers at the end of the chapter.

SECTION F

Reading the graphs

F

Plot the right thing and get a straight line.

Order	Straight-line plot	Slope	Half-life vs $[A]_0$
Zero	[A] against t	−k	$t_{1/2} \propto [A]_0$
First	ln[A] against t	−k	Independent
First	log[A] against t	−k / 2.303	Independent
First	$\log([A]_0/[A])$ against t	+k / 2.303	—
Second (one reactant)	1/[A] against t	+k	$t_{1/2} \propto 1/[A]_0$

KEY IDEA

Rate against concentration: zero order gives a horizontal line; first order gives a straight line through the origin with slope k.

SECTION G

Temperature and the Arrhenius equation

G

Why a 10 K rise can double the rate.

$$k = A \cdot \exp(-Ea / RT)$$

$$\log k = \log A - Ea / (2.303\ RT)$$

A = frequency (pre-exponential) factor; Ea = activation energy; plot log k vs 1/T: slope = −Ea / 2.303R

$$\log (k_2 / k_1) = [Ea / (2.303\ R)] \times [(T_2 - T_1) / (T_1\ T_2)]$$

The two-temperature form used in nearly every numerical

- **Temperature coefficient:** k(T + 10)/k(T) is usually about 2 to 3 near room temperature.
- The factor exp(−Ea/RT) is the **fraction of collisions with energy ≥ Ea**. A small rise in T greatly increases this fraction — that, not collision frequency, is why rate rises so fast.
- Higher Ea → rate more sensitive to temperature.

SOLVED EXAMPLE 06 — ACTIVATION ENERGY FROM TWO TEMPERATURES

The rate constant doubles when the temperature rises from 298 K to 308 K. Find Ea. (R = 8.314 J K^{-1} mol^{-1}, log 2 = 0.301)

SOLUTION

1. log 2 = [Ea / (2.303 × 8.314)] × [10 / (298 × 308)].
2. Ea = 0.301 × 2.303 × 8.314 × 298 × 308 / 10.
3. = 0.301 × 19.147 × 9178.4 J mol^{-1}.

ANSWER Ea ≈ 52.9 kJ mol^{-1}.

SECTION H

Collision theory and catalysts

H

What has to happen for molecules to react.

- A reaction happens only when molecules collide **with energy at least Ea** and in the **right orientation**.
- Rate = P × Z × exp(−Ea/RT), where Z is collision frequency and P the steric (orientation) factor.
- **Effective collisions** are a tiny fraction of all collisions.

KEY IDEA

A catalyst provides a new path with lower Ea. It speeds the forward and backward reactions equally, so it does **not** change ΔH, ΔG or the equilibrium constant K — it only helps equilibrium arrive sooner. It is unchanged in mass and composition at the end.

CHECK YOURSELF

C3 Does a catalyst change the value of the equilibrium constant?

C4 Why does a 10 K rise often double the rate though collision frequency rises only about 2%?

Answers at the end of the chapter.

SECTION I

Exam trap gallery

I

Where marks are lost in kinetics.

✗ TRAP 01 · WHAT STUDENTS WRITE

Order = stoichiometric coefficients.

✓ WHAT IS ACTUALLY CORRECT

Order comes from experiment.

WHY The balanced equation does not show the mechanism.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Molecularity can be zero or fractional.	Molecularity is a whole number 1, 2 or 3; order can be zero or fractional.

WHY Molecularity counts colliding particles.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$t_{1/2}$ of a first-order reaction depends on starting concentration.	It is independent: $t_{1/2} = 0.693/k$.

WHY Only zero- and second-order half-lives depend on $[A]_0$.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
A catalyst shifts the equilibrium to the right.	A catalyst does not change K.

WHY It lowers Ea for both directions equally.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Rate rises with T mainly because molecules collide more often.	Mainly because more collisions have energy ≥ Ea.

WHY The exp(−Ea/RT) term changes far faster than Z.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Using ln with 2.303.	$k = (2.303/t) \log(\ldots)$ or $k = (1/t) \ln(\ldots)$.

WHY Use 2.303 only with log (base 10).

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
75% completion takes 1.5 half-lives.	It takes 2 half-lives (50% then half of the remaining 50%).

WHY First-order decay is geometric, not linear.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Pseudo-first-order reactions are truly first order.	They are higher order; one reactant is in large excess.

WHY Its concentration hardly changes, so it hides in k.

MEMORY HOOK

"**Units tell order:** s^{-1} is one, mol L^{-1} s^{-1} is zero, L mol^{-1} s^{-1} is two."

"**Point six nine three over k**" — first-order half-life.

"**Ninety-nine is twice ninety**" — t(99%) = 2 t(90%).

"**Catalyst: faster, not further.**"

SECTION J

Practice MCQs

J

Levels: Easy, Moderate, Tough.

Q01 The unit of k for a first-order reaction is: [EASY]

(a) mol L^{-1} s^{-1}
(b) s^{-1}
(c) L mol^{-1} s^{-1}
(d) L^2 mol^{-2} s^{-1}

Q02 The half-life of a first-order reaction is: [EASY]

(a) proportional to $[A]_0$
(b) inversely proportional to $[A]_0$
(c) independent of $[A]_0$
(d) proportional to $[A]_0^2$

Q03 Molecularity of a reaction cannot be: [EASY]

(a) 1
(b) 2
(c) 3
(d) 0

Q04 A catalyst increases the rate by: [EASY]

(a) increasing Ea
(b) decreasing Ea
(c) increasing ΔH
(d) changing K

Q05 For a zero-order reaction, the plot that is a straight line is: [EASY]

(a) [A] vs t
(b) ln[A] vs t
(c) 1/[A] vs t
(d) log k vs 1/T

Q06 For 2A → B, if $-d[A]/dt = 0.2$ mol L^{-1} s^{-1}, then $d[B]/dt$ is: [MODERATE]

(a) 0.4
(b) 0.2
(c) 0.1
(d) 0.05

Q07 A first-order reaction has $t_{1/2}$ = 30 min. The fraction remaining after 90 min is: [MODERATE]

(a) 1/3
(b) 1/4
(c) 1/8
(d) 1/9

Q08 Doubling [A] quadruples the rate. The order in A is: [MODERATE]

(a) 0
(b) 1
(c) 2
(d) 4

Q09 The slope of log k against 1/T is: [MODERATE]

(a) -Ea/R
(b) -Ea/2.303R
(c) Ea/2.303R
(d) -2.303Ea/R

Q10 Acid hydrolysis of ethyl acetate is: [MODERATE]

(a) zero order
(b) pseudo-first order
(c) true second order
(d) third order

Q11 For a zero-order reaction, t½ is: [MODERATE]

(a) 0.693/k (b) $[A]_0/2k$
(c) $1/k[A]_0$ (d) $2k/[A]_0$

Q12 If t(90%) of a first-order reaction is 20 min, t(99%) is: [MODERATE]

(a) 22 min (b) 30 min
(c) 40 min (d) 200 min

Q13 Total pressure for A(g) → B(g) + C(g) after one half-life, starting from p_0, is: [TOUGH]

(a) p_0 (b) 1.5 p_0
(c) 2 p_0 (d) 0.5 p_0

Q14 Ea of a reaction is zero. Its rate constant: [TOUGH]

(a) increases with T (b) decreases with T
(c) is independent of T (d) is zero

Q15 Rate = $k[A]^{0.5}[B]^{1.5}$ — the overall order is: [TOUGH]

(a) 1 (b) 1.5
(c) 2 (d) 3

Answer key with explanations

Q01 **(b) s^{-1}** — $(mol\ L^{-1})^0\ s^{-1}$.

Q02 **(c) independent of $[A]_0$** — $t_{½} = 0.693/k$.

Q03 **(d) 0** — At least one particle must take part.

Q04 **(b) decreasing Ea** — Lower-energy pathway.

Q05 **(a) [A] vs t** — $[A] = [A]_0 - kt$.

Q06 **(c) 0.1** — Half as fast as A disappears.

Q07 **(c) 1/8** — Three half-lives: $(1/2)^3$.

Q08 **(c) 2** — $2^x = 4$.

Q09 **(b) -Ea/2.303R** — $\log k = \log A - Ea/2.303RT$.

Q10 **(b) pseudo-first order** — Water is in large excess.

Q11 **(b) $[A]_0/2k$** — Half of $[A]_0$ used at constant rate k.

Q12 **(c) 40 min** — t(99%) = 2 × t(90%).

Q13 **(b) 1.5 p_0** — $p(A) = p_0/2$; $p(B) + p(C) = p_0$ → total $1.5p_0$.

Q14 **(c) is independent of T** — k = A when Ea = 0.

Q15 **(c) 2** — 0.5 + 1.5 = 2.

SECTION K

Advanced problems

K

Each needs two ideas from the chapter.

SOLVED EXAMPLE 07 — K AT A NEW TEMPERATURE

For a reaction Ea = 60 kJ mol^{-1} and k = 2.0 × 10^{-3} s^{-1} at 300 K. Estimate k at 310 K. (R = 8.314; antilog 0.337 ≈ 2.17)

SOLUTION

1. $\log(k_2/k_1) = [60000 / (2.303 \times 8.314)] \times [10 / (300 \times 310)]$.
2. $= 3133.6 \times 1.075 \times 10^{-4} \approx 0.337$.
3. $k_2/k_1 \approx 2.17$.

ANSWER $k \approx 4.3 \times 10^{-3}$ s^{-1}.

SOLVED EXAMPLE 08 — RADIOACTIVE DECAY

The half-life of ^{14}C is 5730 years. How old is a wooden sample with 25% of the ^{14}C of living wood?

SOLUTION

1. Radioactive decay is first order.
2. 25% left = $(1/2)^2$ → two half-lives.

ANSWER About 11 460 years.

Check-yourself answers

C1 First order (units s^{-1}).

C2 Three half-lives → 1/8 remains.

C3 No — it speeds both directions equally; K is unchanged.

C4 Because the fraction of collisions with energy ≥ Ea roughly doubles; collision frequency barely changes.

QUICK REVISION

One-page revision

Read this page the night before the exam.

Rate and rate law

- Rate = $-\frac{1}{a}\frac{d[A]}{dt} = +\frac{1}{c}\frac{d[C]}{dt}$
- Rate = $k[A]^x[B]^y$; order = x + y
- Order from experiment only
- k units: $(\text{mol L}^{-1})^{(1-n)}\ \text{s}^{-1}$

Order vs molecularity

- Order: 0, fraction, any; overall
- Molecularity: 1, 2, 3; elementary step
- Pseudo-1st: ester hydrolysis, sucrose
- Slowest step decides the rate law

Zero order

- $[A] = [A]_0 - kt$
- $t_{1/2} = [A]_0/2k \propto [A]_0$
- NH_3 on hot Pt
- [A] vs t: slope −k

First order

- $k = (2.303/t)\log([A]_0/[A])$
- $t_{1/2} = 0.693/k$, independent of $[A]_0$
- t99 = 2 t90; t99.9 ≈ 10 $t_{1/2}$
- Gas: $k = (2.303/t)\log[p_0/(2p_0 - p_t)]$

Arrhenius

- $k = A\cdot\exp(-Ea/RT)$
- $\log(k_2/k_1) = Ea/2.303R \times (T_2-T_1)/T_1T_2$
- log k vs 1/T: slope $-Ea/2.303R$
- 10 K rise → k × 2 to 3

Collisions and catalysts

- Need E ≥ Ea and right orientation
- Rate = $PZ\cdot\exp(-Ea/RT)$
- Catalyst lowers Ea both ways
- No change in ΔH, ΔG or K

END OF NOTES · RAMGOVINDYADAV.COM