RG

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RESOURCE · PDF

PHYSICAL CHEMISTRY

Kinetics & Thermodynamics Formula Book

All key equations, derivation outlines and MCQ patterns for rate laws, activation energy and Gibbs energy.

WHAT YOU WILL BE ABLE TO DO

- Pick the right formula for any rate-law, half-life or Arrhenius numerical
- Read the four graphs examiners love: rate plots, energy profile, Boltzmann curve, PV curves
- Handle work, ΔH, ΔU, ΔS and ΔG with correct signs every time
- Solve the most common MCQ patterns with a worked method for each

INSIDE

A Rate, order & rate law

B Integrated rate laws

C First-order toolkit

D Arrhenius & activation energy

E First law & work

F Enthalpy & thermochemistry

G Entropy, Gibbs energy & K

H Traps · MCQs · revision

USEFUL FOR CLASS 12 NEET JEE TGT / PGT

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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

Rate of reaction, order and rate law

A

Kinetics answers 'how fast?'; thermodynamics answers 'how far?' Keep them separate in your head — a reaction with a hugely negative ΔG can still be extremely slow (diamond ⟶ graphite).

IN ONE LINE Rate law $r = k[A]^x[B]^y$ is found by experiment, not from the balanced equation.

For $aA + bB \longrightarrow cC + dD$:

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

$$\text{Rate law: } r = k[A]^x[B]^y \qquad \text{Overall order} = x + y$$

Divide by the coefficient so every species gives the same rate. Minus sign for reactants (they decrease).

Order n	Units of k	Typical example
0	$\text{mol L}^{-1}\text{ s}^{-1}$	NH_3 decomposition on hot Pt (surface saturated)
1	s^{-1}	Radioactive decay; N_2O_5 decomposition
2	$\text{L mol}^{-1}\text{ s}^{-1}$	$2HI \longrightarrow H_2 + I_2$; saponification of ethyl acetate
3	$\text{L}^2\text{ mol}^{-2}\text{ s}^{-1}$	$2NO + O_2 \longrightarrow 2NO_2$
n	$(\text{mol L}^{-1})^{1-n}\text{ s}^{-1}$	General rule — memorise this one line

Order	Molecularity
Experimental, from the rate law	Theoretical, from an elementary step
Can be 0, fractional or negative	Always a whole number: 1, 2, (rarely) 3
Defined for the overall reaction	Defined only for elementary steps
Equals molecularity only for elementary reactions	The slow step often sets the observed order

KEY IDEA

Pseudo-first-order: one reactant is in huge excess, so its concentration hardly changes. Examples: acid hydrolysis of ethyl acetate and inversion of cane sugar (water in excess). Molecularity 2, order 1.

Rate-determining step: the slowest step of a mechanism controls the rate law.

SOLVED EXAMPLE 01 INITIAL-RATES METHOD

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

SOLUTION

1. Compare runs 1 and 2: [A] doubles, rate × 4 = 2^2 ⟹ order in A = 2.
2. Compare runs 1 and 3: [B] doubles, rate unchanged = 2^0 ⟹ order in B = 0.
3. Rate = $k[A]^2$. From run 1: $k = 2.0 \times 10^{-3} / (0.1)^2 = 0.20$.

ANSWER $r = k[A]^2$; overall order 2; $k = 0.20$ L mol^{-1} s^{-1}.

CHECK YOURSELF

C1 Units of k are L mol^{-1} s^{-1}. What is the order?

C2 Can a reaction have order 1.5? Can it have molecularity 1.5?

Answers at the end of the chapter.

SECTION B

Integrated rate laws

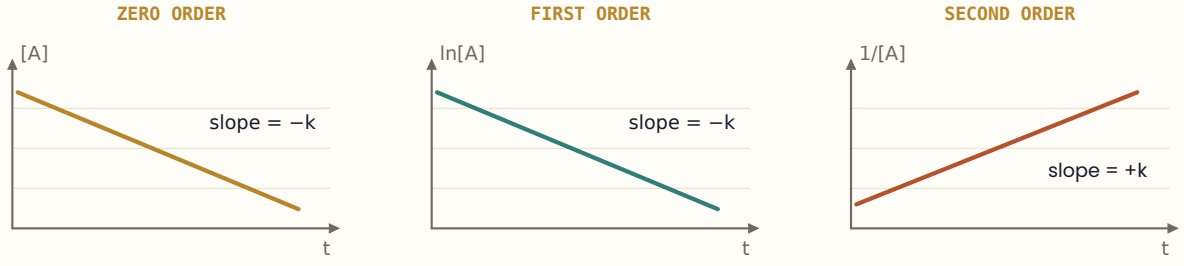
B

One table, four rows. The 'straight-line plot' column is exactly what graph-based questions test.

IN ONE LINE Zero: [A] vs t straight · First: ln[A] vs t straight · Second: 1/[A] vs t straight.

Order	Integrated form	Half-life $t_{½}$	Straight-line plot (slope)
0	$[A] = [A]_0 - kt$	$[A]_0 / 2k$	[A] vs t (−k)
1	$\ln([A]_0/[A]) = kt$	$0.693 / k$	ln[A] vs t (−k); log[A] vs t (−k/2.303)
2 ($r = k[A]^2$)	$1/[A] - 1/[A]_0 = kt$	$1 / (k[A]_0)$	1/[A] vs t (+k)
n ($n \neq 1$)	—	$\propto [A]_0^{1-n}$	log $t_{½}$ vs log$[A]_0$ (1 − n)

WHICH PLOT IS A STRAIGHT LINE?



If the question shows a straight line, read the y-axis label — it tells you the order.

$$\text{First order:}\quad k = (2.303 / t) \cdot \log([A]_0 / [A])$$

$$\text{Zero order:}\quad \text{reaction is complete at } t = [A]_0 / k = 2\, t_{½}$$

ORDER FROM HALF-LIFE

Use how $t_{½}$ responds when $[A]_0$ is doubled:

- $t_{½}$ unchanged ⟶ **first order**
- $t_{½}$ doubles ⟶ **zero order**
- $t_{½}$ halves ⟶ **second order**

Derivation outline — first order

$$-d[A]/dt = k[A] \implies \int d[A]/[A] = -k \int dt$$

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

$$\text{At } t_{½},\ [A] = [A]_0/2 \implies t_{½} = \ln 2 / k = 0.693 / k$$

SECTION C

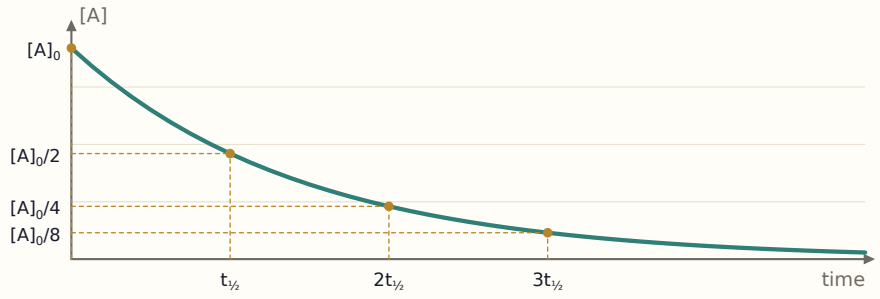
First-order toolkit

C

Most kinetics numericals are first order. These shortcuts remove the log-table step entirely.

IN ONE LINE First-order $t_{½}$ does not depend on how much you start with.

HALF-LIVES AT A GLANCE



Every half-life halves what is left — whatever the starting amount.

after n half-lives:
$[A] = [A]_0 / 2^n$

First-order decay: 1 ⟶ 1/2 ⟶ 1/4 ⟶ 1/8 at equal time steps.

Fraction reacted	Time needed	Shortcut
50%	0.693/k	$t_{½}$
75%	1.386/k	$2\,t_{½}$
87.5%	2.079/k	$3\,t_{½}$
90%	2.303/k	$\approx 3.32\,t_{½}$
99%	4.606/k	$t_{99\%} = 2\,t_{90\%}$
99.9%	6.909/k	$\approx 10\,t_{½}$

SOLVED EXAMPLE 02 FIRST-ORDER NUMERICAL

A first-order reaction is 20% complete in 10 min. Find k and $t_{½}$.

SOLUTION

1. 20% complete $\Longrightarrow [A]_0/[A] = 100/80 = 1.25$.
2. $k = (2.303/10) \times \log 1.25 = 0.2303 \times 0.0969 = 0.0223\ \text{min}^{-1}$.
3. $t_{½} = 0.693 / 0.0223 = 31.0$ min.

ANSWER $k \approx 2.23 \times 10^{-2}\ \text{min}^{-1}$; $t_{½} \approx 31$ min.

First order with other measurable quantities

Measured	Expression for k	Note
Gas pressure, A(g) ⟶ B(g) + C(g)	$k = (2.303/t)\log[P_0 / (2P_0 - P_t)]$	$P_A = 2P_0 - P_t$
Optical rotation (sucrose inversion)	$k = (2.303/t)\log[(r_0 - r_\infty)/(r_t - r_\infty)]$	r_∞ is negative
Titre (ester hydrolysis)	$k = (2.303/t)\log[(V_\infty - V_0)/(V_\infty - V_t)]$	Volume of NaOH used
Radioactivity	$\lambda = (2.303/t)\log(N_0/N)$; mean life $\tau = 1/\lambda = 1.44\,t_{½}$	Always first order

Parallel (competing) first-order reactions

$$A \longrightarrow B\ (k_1),\quad A \longrightarrow C\ (k_2):\qquad k_{\text{overall}} = k_1 + k_2 \qquad [B]/[C] = k_1/k_2$$

$$E_a(\text{overall}) = (k_1E_{a1} + k_2E_{a2}) / (k_1 + k_2)$$

CHECK YOURSELF

C3 A first-order reaction has $t_{½}$ = 15 min. About how long for 99.9% completion?

C4 What fraction remains after 4 half-lives?

Answers at the end of the chapter.

SECTION D

Arrhenius equation and activation energy

D

Rate constants climb steeply with temperature because the fraction of collisions carrying at least E_a grows exponentially.

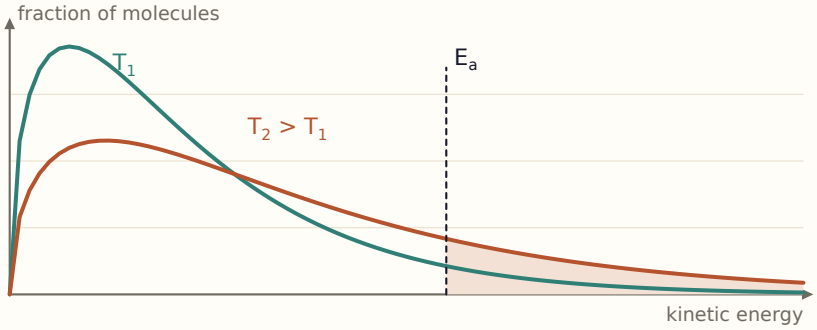
IN ONE LINE $k = A \cdot e^{-Ea/RT}$: higher T or lower $E_a \Longrightarrow$ larger k.

$$k = A \cdot e^{-Ea/RT}$$

$$\ln k = \ln A - E_a/RT \qquad \log k = \log A - E_a / 2.303RT$$

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

WHY TEMPERATURE MATTERS SO MUCH



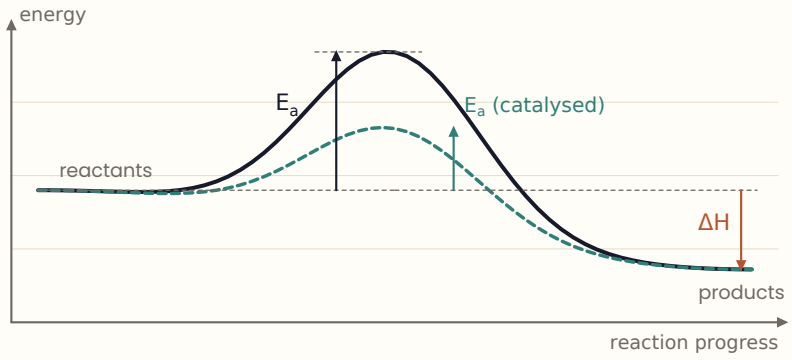
Shaded area = molecules with enough energy.

A 10 K rise roughly doubles this area, so rate ≈ doubles.

fraction ≈ $e^{-Ea/RT}$

Raising T flattens the distribution and pushes more molecules past Ea — the shaded tail grows sharply.

ENERGY PROFILE AND CATALYSTS



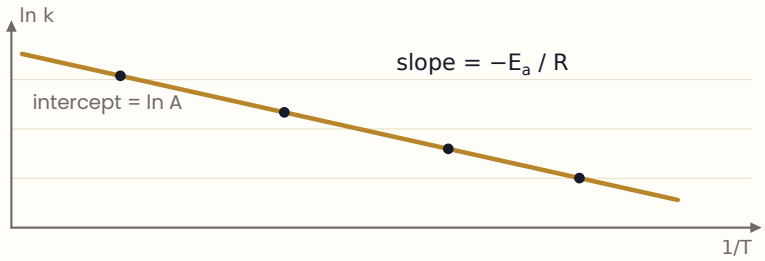
Catalyst lowers E_a for both directions.

ΔH (start and end levels) is unchanged, so K is unchanged.

$E_a(f) - E_a(b) = \Delta H$

Exothermic reaction shown. The catalysed path (dashed) has a lower hump but the same start and end.

ARRHENIUS PLOT



Steeper line = larger E_a = rate more sensitive to temperature.

Using log k (base 10): slope = $-E_a / 2.303R$

Plot ln k against 1/T: a straight line whose slope gives Ea.

Quantity	Formula / fact
Fraction of molecules with $E \geq E_a$	$e^{-Ea/RT}$
Temperature coefficient	$k_{T+10} / k_T \approx 2$ to 3 near room temperature
Effect of catalyst	Lowers E_a both ways; ΔH, ΔG and K unchanged
Rate ratio with catalyst	$k_{cat}/k = e^{(Ea - Ea,cat)/RT}$ (same A)
Link to ΔH	E_a(forward) - E_a(backward) = ΔH
Threshold energy	$E_{threshold} = E_a$ + average energy of reactants

SOLVED EXAMPLE 03 — TWO-TEMPERATURE ARRHENIUS

For N_2O_5 decomposition, $k = 3.46 \times 10^{-5}$ s^{-1} at 298 K and 4.87×10^{-3} s^{-1} at 338 K. Find E_a.

SOLUTION

1. $\log(k_2/k_1) = \log(4.87 \times 10^{-3} / 3.46 \times 10^{-5}) = \log 140.8 = 2.149$.
2. $(T_2 - T_1)/(T_1T_2) = 40 / (298 \times 338) = 3.97 \times 10^{-4}$ K^{-1}.
3. $E_a = 2.149 \times 2.303 \times 8.314 / (3.97 \times 10^{-4}) = 1.036 \times 10^5$ J mol^{-1}.

ANSWER $E_a \approx 104$ kJ mol^{-1}.

SOLVED EXAMPLE 04 — CATALYST EFFECT

A catalyst lowers E_a by 20 kJ mol^{-1} at 298 K. By what factor does the rate rise (A unchanged)?

SOLUTION

1. $k_{cat}/k = e^{\Delta Ea/RT}$, with $\Delta E_a = 20\,000$ J mol^{-1}.
2. $\Delta E_a/RT = 20\,000 / (8.314 \times 298) = 8.07$.
3. $e^{8.07} \approx 3.2 \times 10^3$.

ANSWER About 3200 times faster.

WHY IT HAPPENS

Collision theory: rate = $Z_{AB} \cdot e^{-Ea/RT} \cdot P$, where Z_{AB} is the collision frequency and P the steric (orientation) factor. A in the Arrhenius equation bundles Z_{AB} and P.

Endothermic: $E_a(f) > E_a(b)$. Exothermic: $E_a(b) > E_a(f)$.

SECTION E

First law, heat and work

E

Sign convention (IUPAC / NCERT): heat absorbed by the system and work done on the system are positive.

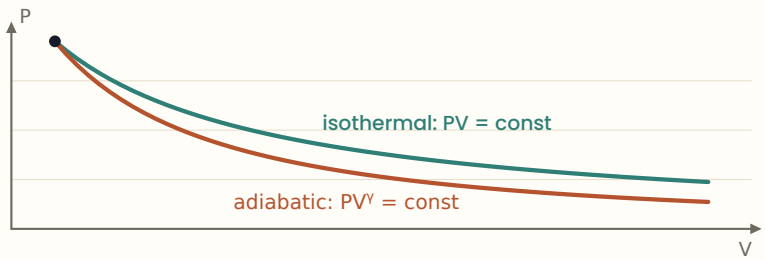
IN ONE LINE $\Delta U = q + w$. Expansion means the system does work, so w is negative.

$$\Delta U = q + w \qquad w = -P_{ext}\,\Delta V$$

Constant volume: $\Delta U = q_v$. Constant pressure: $\Delta H = q_p$. Expansion into vacuum: w = 0.

Process (ideal gas)	w	q	ΔU
Isothermal reversible	$-2.303\ nRT \log(V_2/V_1) = -2.303\ nRT \log(P_1/P_2)$	$= -w$	0
Isothermal irreversible	$-P_{ext}(V_2 - V_1)$	$= -w$	0
Adiabatic reversible	$nC_v(T_2 - T_1) = (P_2V_2 - P_1V_1)/(\gamma - 1)$	0	$= w$
Isochoric	0	$nC_v\Delta T$	$nC_v\Delta T$
Isobaric	$-P\Delta V = -nR\Delta T$	$nC_p\Delta T$	$nC_v\Delta T$

ISOTHERMAL VS ADIABATIC



Same start point: the adiabat falls faster ($\gamma > 1$). Area under the curve = work done.

Isothermal expansion does more work than adiabatic.

From the same starting state, an adiabatic expansion ends at lower pressure (the gas also cools).

Reversible adiabatic: $PV^{\gamma} = \text{const}$ $TV^{\gamma-1} = \text{const}$ $T^{\gamma}P^{1-\gamma} = \text{const}$

$C_p - C_v = R$ $\gamma = C_p/C_v$: monatomic 5/3, diatomic 7/5, non-linear polyatomic 4/3

SOLVED EXAMPLE 05 WORK DONE

1 mol of an ideal gas expands at 300 K from 10 L to 20 L (a) reversibly, (b) against a constant 1 atm. Find w.

SOLUTION

1. (a) $w = -2.303\ nRT \log(V_2/V_1) = -2.303 \times 1 \times 8.314 \times 300 \times \log 2 = -5744 \times 0.301$.
2. So $w_{rev} = -1729\ J \approx -1.73\ kJ$.
3. (b) $w = -P_{ext}\Delta V = -1\ atm \times 10\ L = -10\ L\ atm = -10 \times 101.3\ J = -1013\ J$.

ANSWER (a) −1.73 kJ; (b) −1.01 kJ. Reversible expansion gets more work out.

SECTION F

Enthalpy and thermochemistry

F

ΔH is the heat at constant pressure. Hess's law lets you add reactions like equations.

IN ONE LINE $\Delta H = \Delta U + \Delta n_g RT$ — only gas moles count.

$$H = U + PV \qquad \Delta H = \Delta U + \Delta n_g RT$$

$$\text{Kirchhoff: } \Delta H_2 - \Delta H_1 = \Delta C_p\,(T_2 - T_1)$$

Δn_g = gaseous product moles − gaseous reactant moles. Ignore liquids and solids.

Route	Formula
From enthalpies of formation	$\Delta_r H^\circ = \Sigma \Delta_f H^\circ(\text{products}) - \Sigma \Delta_f H^\circ(\text{reactants})$
From enthalpies of combustion	$\Delta_r H^\circ = \Sigma \Delta_c H^\circ(\text{reactants}) - \Sigma \Delta_c H^\circ(\text{products})$
From bond enthalpies (gases)	$\Delta_r H^\circ = \Sigma BE(\text{bonds broken}) - \Sigma BE(\text{bonds formed})$
Hess's law	ΔH of the overall reaction = sum of ΔH of the steps (path-independent)
Born–Haber (lattice energy)	$\Delta_f H = \Delta H_{sub} + IE + \tfrac{1}{2}BE + EA + U_{lattice}$ (EA, U as negative enthalpies)

SOLVED EXAMPLE 06 ΔH VS ΔU

For $C_6H_6(l) + 15/2\ O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$ at 298 K, find $\Delta H - \Delta U$.

SOLUTION

1. Gas moles: products 6 (CO_2), reactants 7.5 (O_2). Liquids ignored.
2. $\Delta n_g = 6 - 7.5 = -1.5$.
3. $\Delta H - \Delta U = \Delta n_g RT = -1.5 \times 2.478\ kJ = -3.72\ kJ\ mol^{-1}$.

ANSWER $\Delta H - \Delta U = -3.72\ kJ\ mol^{-1}$ (ΔH is more negative than ΔU).

NOTE

$\Delta_f H^\circ$ of an element in its standard state is zero (graphite, $O_2(g)$, $Br_2(l)$).

Strong acid + strong base: $\Delta H_{neut} \approx -57.1\ kJ\ mol^{-1}$. A weak acid or base gives a less negative value — some energy is spent ionising it.

SECTION G

Entropy, Gibbs energy and equilibrium

G

Spontaneity is decided by total entropy. At constant T and P, that reduces to one test: the sign of ΔG.

IN ONE LINE $\Delta G = \Delta H - T\Delta S < 0 \Longrightarrow$ spontaneous. $\Delta G^\circ = -RT \ln K$ links thermodynamics to equilibrium.

$$\Delta S = q_{rev} / T \qquad \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \geq 0 \qquad \Delta S_{surr} = -\Delta H_{sys}/T$$

$$\text{Ideal gas: } \Delta S = nC_v \ln(T_2/T_1) + nR \ln(V_2/V_1)$$

$$\text{Phase change: } \Delta S = \Delta H_{trans}/T_{trans} \qquad \text{Trouton: } \Delta H_{vap}/T_b \approx 88\ J\ K^{-1}\ mol^{-1}$$

$$G = H - TS \qquad \Delta G = \Delta H - T\Delta S$$

$$\Delta G^\circ = -RT \ln K = -2.303\ RT \log K \qquad \Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = -nFE^\circ_{cell} \qquad -\Delta G = \text{maximum useful (non-expansion) work}$$

ΔH	ΔS	ΔG = ΔH − TΔS	Spontaneous?
−	+	Always −	At all temperatures
+	−	Always +	Never (the reverse is spontaneous)
−	−	− at low T	Below T = ΔH/ΔS
+	+	− at high T	Above T = ΔH/ΔS

SOLVED EXAMPLE 07 — SPONTANEITY TEMPERATURE

For $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$, $\Delta H^\circ = +178$ kJ mol^{-1} and $\Delta S^\circ = +160$ J K^{-1} mol^{-1}. Above what temperature is it spontaneous?

SOLUTION

1. Both ΔH and ΔS are positive $\Longrightarrow$ spontaneous at high T.
2. At the switch-over, $\Delta G = 0 \Longrightarrow T = \Delta H/\Delta S$.
3. T = 178 000 J / 160 J K^{-1} = 1112.5 K. (Convert kJ to J!)

ANSWER Above about 1113 K (≈ 840 °C).

SOLVED EXAMPLE 08 — K FROM ΔG°

ΔG° for a reaction at 298 K is −11.42 kJ mol^{-1}. Find K.

SOLUTION

1. $\Delta G^\circ = -2.303RT \log K$, and 2.303RT at 298 K = 5.71 kJ mol^{-1}.
2. log K = 11.42 / 5.71 = 2.00.

ANSWER $K = 10^2 = 100$.

Van't Hoff: $\log(K_2/K_1) = (\Delta H^\circ / 2.303R) \cdot [(T_2 - T_1) / (T_1T_2)]$

Same shape as the two-temperature Arrhenius equation — with ΔH° in place of Ea.

Constants you will need

Constant	Value
R	8.314 J K^{-1} mol^{-1} = 0.0821 L atm K^{-1} mol^{-1} = 1.987 cal K^{-1} mol^{-1}
RT at 298 K	2.478 kJ mol^{-1}
2.303 RT at 298 K	5.71 kJ mol^{-1} (so $\Delta G^\circ = -5.71 \log K$ kJ mol^{-1})
F	96 485 C mol^{-1}
1 L atm	101.3 J
ln 2; ln 10	0.693; 2.303
log 2; log 3; log 5	0.3010; 0.4771; 0.6990

SECTION H

Exam trap gallery

H

Cover the right column; check you would have caught each one.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Order is read from the balanced equation.	Order comes from **experiment** (the rate law).

WHY Coefficients give molecularity only for elementary steps.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Zero-order $t_{½}$ is constant.	Only **first-order** $t_{½}$ is constant; zero-order $t_{½} \propto [A]_0$.

WHY $t_{½} \propto [A]_0^{1-n}$; the exponent is zero only when n = 1.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Slope of log[A] vs t is -k.	Slope is **-k/2.303**; for ln[A] vs t it is -k.

WHY log x = ln x / 2.303.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
A catalyst shifts equilibrium towards products.	A catalyst changes **only the rate**; K, ΔH and ΔG are unchanged.

WHY It lowers E_a for forward and backward reactions equally.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Spontaneous means fast.	Spontaneous (ΔG < 0) says nothing about rate.

WHY Diamond ⟶ graphite is spontaneous but immeasurably slow — that is kinetics.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Expansion work is positive.	Work done **by** the gas in expansion is **negative** (IUPAC).

WHY $w = -P_{ext}\Delta V$ and ΔV > 0.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
T = ΔH/ΔS with ΔH in kJ and ΔS in J K^{-1}.	Convert to the **same unit** first (kJ ⟶ J).

WHY A factor-of-1000 slip is the most common numerical error.

✗ TRAP 08 · WHAT STUDENTS WRITE

Use ΔG° to decide spontaneity under any conditions.

✓ WHAT IS ACTUALLY CORRECT

Use $\Delta G = \Delta G^\circ + RT \ln Q$ for actual conditions.

WHY ΔG° refers only to standard states (1 bar, 1 M).

MEMORY HOOK

"Zero-line, One-log, Two-flip." Straight line: [A], ln[A], 1/[A] against t.

"A catalyst changes the road, not the destination." E_a down; ΔH and K unchanged.

"Same signs, temperature decides." When ΔH and ΔS share a sign, the switch-over is T = ΔH/ΔS.

SECTION I

Practice MCQs

I

Easy = recall · Moderate = one reasoning step · Tough = two ideas combined.

Q01 The rate constant of a reaction is 2.5×10^{-3} mol L^{-1} s^{-1}. The order is: [EASY]

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

Q02 For a first-order reaction, a plot of log[A] vs t has slope: [EASY]

(a) -k (b) -k/2.303
(c) +k (d) k/2.303

Q03 A catalyst changes which of these? [EASY]

(a) ΔH (b) K
(c) E_a (d) ΔG°

Q04 One mole of an ideal gas expands into a vacuum. Work done: [EASY]

(a) -nRT ln 2 (b) 0
(c) -PΔV (d) +nRT

Q05 A first-order reaction has $t_{½}$ = 20 min. Time for 75% completion: [MODERATE]

(a) 30 min (b) 40 min
(c) 60 min (d) 80 min

Q06 Doubling $[A]_0$ halves $t_{½}$. The order of reaction is: [MODERATE]

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

Q07 For $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, ΔH − ΔU equals: [MODERATE]

(a) +2RT (b) −2RT
(c) +RT (d) −4RT

Q08 $\Delta H = +30$ kJ mol^{-1}, $\Delta S = +100$ J K^{-1} mol^{-1}. Spontaneous above: [MODERATE]

(a) 30 K (b) 300 K
(c) 3000 K (d) 0.3 K

Q09 $\Delta G^\circ = 0$ for a reaction at 298 K. Then K equals: [MODERATE]

(a) 0 (b) 1
(c) 10 (d) Infinity

Q10 Rate doubles from 300 K to 310 K. E_a is approximately: [TOUGH]

(a) 26.8 kJ mol^{-1} (b) 53.6 kJ mol^{-1}
(c) 107 kJ mol^{-1} (d) 5.36 kJ mol^{-1}

Q11 For an exothermic reaction with E_a(forward) = 50 kJ and $\Delta H = -30$ kJ, E_a(backward) is: [TOUGH]

(a) 20 kJ (b) 30 kJ
(c) 50 kJ (d) 80 kJ

Q12 A first-order reaction is 90% complete in 46 min. Its $t_{½}$ is close to: [TOUGH]

(a) 6.9 min (b) 13.9 min
(c) 23 min (d) 46 min

Answer key with explanations

Q01 (a) **0** — units mol L^{-1} s^{-1} match (mol L^{-1})$^{1-n}$ s^{-1} with n = 0.

Q02 (b) **-k/2.303** — $\log[A] = \log[A]_0 - kt/2.303$.

Q03 (c) **E_a** — thermodynamic quantities (ΔH, K, ΔG°) are unchanged.

Q04 (b) **0** — $P_{ext} = 0$, so $w = -P_{ext}\Delta V = 0$.

Q05 (b) **40 min** — 75% = two half-lives.

Q06 (c) **2** — $t_{½} \propto 1/[A]_0$ for second order.

Q07 (b) **-2RT** — $\Delta n_g = 2 - 4 = -2$.

Q08 (b) **300 K** — $T = 30\,000$ J / 100 J K^{-1}.

Q09 (b) **1** — $\Delta G^\circ = -RT \ln K = 0 \Longrightarrow \ln K = 0$.

Q10 (b) **53.6 kJ mol^{-1}** — $\log 2 = (E_a/19.147) \times (10/93\,000) \Longrightarrow E_a \approx 53\,600$ J.

Q11 (d) **80 kJ** — $E_a(f) - E_a(b) = \Delta H \Longrightarrow 50 - E_a(b) = -30$.

Q12 (b) **13.9 min** — $t_{90\%} = 2.303/k \Longrightarrow k = 0.05$ min^{-1}; $t_{½} = 0.693/0.05 = 13.9$ min.

SECTION J

Previous-year questions

J

Real exam questions on this topic, tagged with the exam and session. Stems are lightly edited for clarity; the chemistry and the answer are unchanged.

ABOUT THESE TAGS

Sessions: NEET 2025; JEE Main 2017 (9 April, online, morning); JEE Main 2022 (27 June, shift 2 — a numerical-answer question; the options here are added by me); JEE Main 2025 (April, shift 1); NEET 2017; NEET 2016.

Sources: questions.examside.com, cracku.in, canvasclasses.in, satheeneet.iitk.ac.in.

Q01 For a first-order reaction $t_{½}$ = 1 min. The time for 99.9% completion is closest to: [NEET 2025]

(a) 5 min
(b) 10 min
(c) 2 min
(d) 4 min

Q02 The rate of a reaction quadruples when the temperature rises from 300 K to 310 K. E_a is: [JEE MAIN 2017]

(a) 107.2 kJ mol^{-1}
(b) 53.6 kJ mol^{-1}
(c) 26.8 kJ mol^{-1}
(d) 214.4 kJ mol^{-1}

Q03 A rate constant doubles when the temperature rises by 9 K from 300 K. E_a (nearest integer, kJ mol^{-1}) is (R = 8.3, log 2 = 0.30): [JEE MAIN 2022]

(a) 39
(b) 59
(c) 69
(d) 89

Q04 1 mol of an ideal gas expands isothermally and reversibly from 10 dm^3 to 20 dm^3 at 300 K. ΔU, q and w are: [JEE MAIN 2025]

(a) 0, 21.84 kJ, −1.26 kJ
(b) 0, −17.18 kJ, 1.718 J
(c) 0, 21.84 kJ, 21.84 kJ
(d) 0, +1.718 kJ, −1.718 kJ

Q05 ΔH = 35.5 kJ mol^{-1} and ΔS = 83.6 J K^{-1} mol^{-1}. The reaction is spontaneous at: [NEET 2017]

(a) T > 298 K
(b) T < 425 K
(c) T > 425 K
(d) All temperatures

Q06 The conditions for a reaction to be spontaneous at all temperatures are: [NEET 2016]

(a) ΔH < 0, ΔS = 0
(b) ΔH > 0, ΔS < 0
(c) ΔH < 0, ΔS > 0
(d) ΔH < 0, ΔS < 0

Previous-year answer key

Q01 (b) 10 min — 99.9% ≈ 10 half-lives (6.909/0.693).

Q02 (a) 107.2 kJ mol^{-1} — log 4 = 2 log 2; double the 'rate doubles' answer (53.6 × 2).

Q03 59 — log 2 = (E_a/2.303R)(9/(300 × 309)) ⟹ E_a ≈ 59 kJ mol^{-1}.

Q04 (d) — ΔU = 0; w = −2.303nRT log 2 ≈ −1.718 kJ; q = −w.

Q05 (c) T > 425 K — T = ΔH/ΔS = 35 500 / 83.6 ≈ 425 K; both positive ⟹ spontaneous above it.

Q06 (c) — ΔH − TΔS is negative at every T only when ΔH < 0 and ΔS > 0.

SECTION K

Advanced problems

K

Problems at JEE Advanced / PGT level. Each combines two formulas from this book.

IN ONE LINE	Each problem combines two ideas from this chapter. Try it before reading the solution.

SOLVED EXAMPLE 09 — PRESSURE DATA

A(g) ⟶ B(g) + C(g) is first order. Starting with pure A at 0.40 atm, the total pressure is 0.60 atm after 100 s. Find k.

SOLUTION

1. Let A fall by p: total = (0.40 − p) + p + p = 0.40 + p = 0.60 ⟹ p = 0.20 atm.
2. P_A = 0.40 − 0.20 = 0.20 atm (check: $2P_0 - P_t$ = 0.80 − 0.60 = 0.20).
3. k = (2.303/100) log(0.40/0.20) = 0.02303 × 0.301 = 6.93 × 10^{-3} s^{-1}.

ANSWER k ≈ 6.93 × 10^{-3} s^{-1} ($t_{½}$ = 100 s).

SOLVED EXAMPLE 10 — PARALLEL REACTIONS

A decomposes by two parallel first-order paths: A ⟶ B (k_1 = 1 × 10^{-3} s^{-1}, E_{a1} = 40 kJ) and A ⟶ C (k_2 = 3 × 10^{-3} s^{-1}, E_{a2} = 60 kJ). Find the % of B and the overall E_a.

SOLUTION

1. [B]/[C] = k_1/k_2 = 1/3 ⟹ B is 1/4 = 25% of product.
2. E_a = ($k_1E_{a1} + k_2E_{a2}$)/($k_1 + k_2$) = (40 + 180)/4 = 55 kJ mol^{-1}.

ANSWER 25% B; overall E_a = 55 kJ mol^{-1}.

SOLVED EXAMPLE 11 VAN'T HOFF

K for a reaction doubles when T rises from 298 K to 308 K. Estimate ΔH°.

SOLUTION

1. Van't Hoff: $\log 2 = (\Delta H^\circ/2.303R) \times (10 / (298 \times 308))$.
2. $\Delta H^\circ = 0.301 \times 19.147 \times 9178 = 5.29 \times 10^4$ J mol^{-1}.
3. K rises with T, so the reaction is endothermic — consistent with a positive ΔH°.

ANSWER $\Delta H^\circ \approx +52.9$ kJ mol^{-1}.

SOLVED EXAMPLE 12 ADIABATIC

1 mol of a monatomic ideal gas at 300 K expands reversibly and adiabatically until its volume doubles. Find T_2 and w.

SOLUTION

1. Monatomic: $\gamma = 5/3$, so $\gamma - 1 = 2/3$. $TV^{\gamma-1} = \text{const} \Longrightarrow T_2 = 300 \times (1/2)^{2/3} = 300 / 1.587 = 189$ K.
2. $q = 0$, so $w = \Delta U = nC_v\Delta T = 1 \times (3/2)(8.314) \times (189 - 300)$.
3. $w = 12.47 \times (-111) = -1384$ J.

ANSWER $T_2 \approx 189$ K; $w \approx -1.38$ kJ (the gas cools because it does work with no heat input).

Check-yourself answers

C1 2.

C2 Order: yes. Molecularity: no — it must be a whole number.

C3 $\approx 10\ t_{½} = 150$ min (exactly 149.5 min).

C4 $(1/2)^4 = 1/16$.

QUICK REVISION

One-page revision

Read this page the night before the exam. Every line points back to a section in these notes.

Rate & order

- $r = k[A]^x[B]^y$; order by experiment
- Units of k: $(\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$
- Molecularity: whole number, elementary steps only
- Pseudo-first-order: one reactant in excess

Integrated laws

- 0: $[A] = [A]_0 - kt$; $t_{½} = [A]_0/2k$
- 1: $k = (2.303/t)\log([A]_0/[A])$; $t_{½} = 0.693/k$
- 2: $1/[A] - 1/[A]_0 = kt$; $t_{½} = 1/k[A]_0$
- Straight lines: [A], ln[A], 1/[A] vs t

First-order shortcuts

- 75% = $2t_{½}$; 87.5% = $3t_{½}$; 99.9% ≈ $10t_{½}$
- $t_{99\%} = 2t_{90\%}$
- Left after n half-lives: $1/2^n$
- Mean life $\tau = 1.44\ t_{½}$

Arrhenius

- $k = A\ e^{-Ea/RT}$; slope of ln k vs 1/T = $-E_a/R$
- $\log(k_2/k_1) = (E_a/2.303R)(T_2-T_1)/(T_1T_2)$
- Catalyst: lowers E_a; K, ΔH unchanged
- $E_a(f) - E_a(b) = \Delta H$

First law

- $\Delta U = q + w$; $w = -P_{ext}\Delta V$
- Rev. isothermal: $w = -2.303nRT\log(V_2/V_1)$
- Adiabatic: q = 0, ΔU = w; PV^γ = const
- $\Delta H = \Delta U + \Delta n_g RT$; $C_p - C_v = R$

Gibbs & K

- $\Delta G = \Delta H - T\Delta S$; spontaneous if $\Delta G < 0$
- $\Delta G^\circ = -2.303RT\log K = -nFE^\circ$
- Switch-over T = ΔH/ΔS (same units!)
- 2.303RT at 298 K = 5.71 kJ mol^{-1}