Collegedunia NCERT Solutions

Step-by-step solutions, alternate methods & exam tips for Class 12 Chemistry

Chapter 3: Chemical Kinetics

About this Chapter

This chapter studies **chemical kinetics**: the rate at which reactions proceed and the factors that govern these rates. We learn how to define average and instantaneous rates, write **rate laws**, identify the **order** and **molecularity** of a reaction, integrate the rate laws for zero and first order reactions, work out half-lives, and quantify the effect of temperature using the **Arrhenius equation**. The chapter closes with collision theory and the role of catalysts.

Topics covered: Rate of reaction • Rate law and order • Molecularity • Integrated rate equations • Half-life • Pseudo first order • Arrhenius equation • Activation energy • Collision theory • Catalysis

Quick Formula Sheet

Average rate:

$$r_{\text{av}} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

Rate law (order n):

$$r = k[A]^a[B]^b, \;\; n = a + b$$

Zero order:

$$[R] = [R]_0 - kt, \;\; t_{1/2} = \frac{[R]_0}{2k}$$

First order:

$$\ln\frac{[R]_0}{[R]} = kt, \;\; t_{1/2} = \frac{0.693}{k}$$

Arrhenius:

$$k = A\,e^{-E_a/RT}$$

Two-temperature form:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\,\frac{T_2 - T_1}{T_1 T_2}$$

Chapter 3 Exercises

Q 3.1 **From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.**

(i) $3\,NO(g) \longrightarrow N_2O(g)$, **Rate** $= k[NO]^2$

(ii) $H_2O_2(aq) + 3\,I^-\,(aq) + 2\,H^+ \longrightarrow 2\,H_2O\,(l) + I_3{}^-$, **Rate** $= k[H_2O_2][I^-]$

(iii) $CH_3CHO\,(g) \longrightarrow CH_4(g) + CO\,(g)$, **Rate** $= k[CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl\,(g) \longrightarrow C_2H_4(g) + HCl\,(g)$, **Rate** $= k[C_2H_5Cl]$

SOLUTION

Concept used. The **order of a reaction** is the sum of the powers of the concentration terms in the experimentally determined rate law. If the rate law is $r = k\,[A]^a[B]^b$, the order is $n = a + b$. The order is found from experiment; it need not equal the stoichiometric coefficients of the balanced equation.
The **dimensions** of the rate constant k follow directly from the rate equation. Rate has units $\mathrm{mol\,L^{-1}\,s^{-1}}$, so

$$k \;=\; \frac{\text{Rate}}{[\text{conc.}]^n} \;=\; \frac{\mathrm{mol\,L^{-1}\,s^{-1}}}{(\mathrm{mol\,L^{-1}})^n} \;=\; \mathrm{mol}^{1-n}\,\mathrm{L}^{n-1}\,\mathrm{s}^{-1}.$$

Use this single formula in every part.

> ☞ **Why the dimension formula matters**
>
> Once you remember $k \propto (\text{conc.})^{1-n}\,t^{-1}$, you can write down the units of k for any order n in one line; no need to rederive from scratch.

Step 1. **Part (i).** Rate $= k[\mathrm{NO}]^2$. The single concentration term has exponent 2, so the order is $n = 2$. Substitute into the dimension formula:

$$k \;=\; \frac{\mathrm{mol\,L^{-1}\,s^{-1}}}{(\mathrm{mol\,L^{-1}})^2} \;=\; \mathrm{mol^{-1}\,L\,s^{-1}}.$$

Step 2. **Part (ii).** Rate $= k[\mathrm{H_2O_2}][\mathrm{I^-}]$. Exponents are 1 and 1, so order $n = 1 + 1 = 2$. The dimensions are

$$k \;=\; \frac{\mathrm{mol\,L^{-1}\,s^{-1}}}{(\mathrm{mol\,L^{-1}})^2} \;=\; \mathrm{mol^{-1}\,L\,s^{-1}}.$$

Step 3. **Part (iii).** Rate $= k[\mathrm{CH_3CHO}]^{3/2}$. The single exponent is $3/2$, so order $n = 3/2 = 1.5$. The dimensions are

$$k \;=\; \frac{\mathrm{mol\,L^{-1}\,s^{-1}}}{(\mathrm{mol\,L^{-1}})^{3/2}} \;=\; (\mathrm{mol\,L^{-1}})^{1-3/2}\,\mathrm{s^{-1}} \;=\; \mathrm{mol^{-1/2}\,L^{1/2}\,s^{-1}}.$$

Step 4. **Part (iv).** Rate $= k[\mathrm{C_2H_5Cl}]$. Exponent is 1, so order $n = 1$. The dimensions are

$$k \;=\; \frac{\mathrm{mol\,L^{-1}\,s^{-1}}}{(\mathrm{mol\,L^{-1}})^1} \;=\; \mathrm{s^{-1}}.$$

Final Answer: (i) $n = 2$, k in $\mathrm{mol^{-1}\,L\,s^{-1}}$; (ii) $n = 2$, k in $\mathrm{mol^{-1}\,L\,s^{-1}}$; (iii) $n = 1.5$, k in $\mathrm{mol^{-1/2}\,L^{1/2}\,s^{-1}}$; (iv) $n = 1$, k in $\mathrm{s^{-1}}$.

☞ Quick units check

For a reaction of order n, the units of k contain $(\text{conc.})^{1-n}$ and one factor of t^{-1}. So order 0 gives k in $\mathrm{mol\,L^{-1}\,s^{-1}}$, order 1 gives $\mathrm{s^{-1}}$, order 2 gives $\mathrm{L\,mol^{-1}\,s^{-1}}$, and order $3/2$ gives the half-power units in (iii).

EXPERT'S SOLUTION *: Aarav Sharma, M.Sc Chemistry, IIT Kanpur*

Structural angle. Order is read straight off the rate law, and the dimensions of k are forced by the requirement that the rate itself carry units of concentration per unit time. So the same two-step procedure works in all four parts: add the exponents to get n; substitute n into the dimension template.

Step 1. The general rate equation $r = k\,[A]^a[B]^b\cdots$ has order $n = a + b + \cdots$. Inspect each rate law and add up all the exponents on concentration terms.

Step 2. Solve for k:

$$k = \frac{r}{[A]^a[B]^b\cdots} = \mathrm{mol\,L^{-1}\,s^{-1}} \times (\mathrm{mol\,L^{-1}})^{-n} = \mathrm{mol}^{1-n}\,\mathrm{L}^{n-1}\,\mathrm{s}^{-1}.$$

Step 3. Apply to each part. (i) $n = 2$ gives $\mathrm{mol^{-1}\,L\,s^{-1}}$. (ii) $n = 2$ gives $\mathrm{mol^{-1}\,L\,s^{-1}}$. (iii) $n = 1.5$ gives $\mathrm{mol^{-1/2}\,L^{1/2}\,s^{-1}}$. (iv) $n = 1$ gives $\mathrm{s^{-1}}$.

Alternative dimensional route. Instead of memorising the $\mathrm{mol}^{1-n}\,\mathrm{L}^{n-1}\,\mathrm{s}^{-1}$ template, you can derive units on the fly. Write rate $= k(\text{conc.})^n$, transpose to $k = \text{rate}/(\text{conc.})^n$, plug in $\mathrm{mol\,L^{-1}\,s^{-1}}$ for rate and $\mathrm{mol\,L^{-1}}$ for concentration, and let exponents subtract. This "derive don't memorise" habit pays off when the problem switches to pressure (units of $\mathrm{bar}^{1-n}\,\mathrm{t}^{-1}$) or to molality.

Concept linkage. Order $\neq$ molecularity. Molecularity is the number of molecules colliding in an *elementary* step (always a positive integer), while order is an experimental power that can be zero, fractional, or even negative. The reaction in part (iii) (CH_3CHO decomposition) is a complex multi-step process; its $n = 3/2$ signals a Rice–Herzfeld chain mechanism with a fast pre-equilibrium step.

Cross-check by limiting cases. For $n = 0$, the template gives $\mathrm{mol\,L^{-1}\,s^{-1}}$ – same as rate, which makes sense because k *is* the rate when concentration has no effect. For $n = 1$, the template gives $\mathrm{s^{-1}}$ – a pure frequency, which matches the radioactive-decay analogue. These two limits anchor the formula in physical meaning.

JEE/NEET relevance. Identifying order from a rate law and writing the corresponding units of k is a one-mark recall question almost every year. The 2022 JEE Main paper, for instance, tested exactly this pattern with $n = 5/2$. The answer is mechanical once you know the template.

> **Final Answer:** Orders: $2, 2, 1.5, 1$. Units of k: $\mathrm{mol^{-1}\,L\,s^{-1}}$, $\mathrm{mol^{-1}\,L\,s^{-1}}$, $\mathrm{mol^{-1/2}\,L^{1/2}\,s^{-1}}$, $\mathrm{s^{-1}}$.

Q 3.2 **For the reaction $2\,\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{A_2B}$, the rate is $r = k[A][B]^2$ with rate constant $k = 2.0\times10^{-6}\,\mathrm{mol^{-2}\,L^2\,s^{-1}}$. Calculate the initial rate of the reaction when $[A] = 0.1\,\mathrm{mol\,L^{-1}}$ and $[B] = 0.2\,\mathrm{mol\,L^{-1}}$. Calculate the rate of reaction after $[A]$ is reduced to $0.06\,\mathrm{mol\,L^{-1}}$.**

SOLUTION

Concept used. The rate law is given:

$$r \;=\; k\,[A]\,[B]^2.$$

The initial rate is obtained by substituting the starting concentrations of A and B. When $[A]$ has fallen by some amount, the stoichiometry $2\,\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{A_2B}$ tells us that 1 mole of B is consumed for every 2 moles of A, so $\Delta[B] = \frac{1}{2}\Delta[A]$.

Step 1. **Initial rate.** Substitute $[A] = 0.1\,\mathrm{mol\,L^{-1}}$ and $[B] = 0.2\,\mathrm{mol\,L^{-1}}$:

$$r_0 \;=\; k\,[A]\,[B]^2 \;=\; (2.0\times10^{-6})\,(0.1)\,(0.2)^2.$$

Evaluate the powers and products one step at a time:

$$(0.2)^2 \;=\; 0.04; \quad (0.1)(0.04) \;=\; 0.004.$$

Therefore

$$r_0 \;=\; 2.0\times10^{-6}\times0.004 \;=\; 8.0\times10^{-9}\,\mathrm{mol\,L^{-1}\,s^{-1}}.$$

Step 2. **Change in $[A]$.** Initially $[A]_0 = 0.10\,\mathrm{mol\,L^{-1}}$; finally $[A] = 0.06\,\mathrm{mol\,L^{-1}}$. So A has decreased by

$$\Delta[A] \;=\; 0.10 - 0.06 \;=\; 0.04\,\mathrm{mol\,L^{-1}}.$$

Step 3. **Change in $[B]$ from stoichiometry.** From $2\,\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{A_2B}$, 2 mol of A consumes 1 mol of B, so

$$\Delta[B] \;=\; \tfrac{1}{2}\,\Delta[A] \;=\; \tfrac{1}{2}\times0.04 \;=\; 0.02\,\mathrm{mol\,L^{-1}}.$$

Hence

$$[B]_{\text{new}} \;=\; 0.20 - 0.02 \;=\; 0.18\,\mathrm{mol\,L^{-1}}.$$

Step 4. **New rate.** Substitute the new concentrations:

$$r \;=\; k\,[A]\,[B]^2 \;=\; (2.0\times10^{-6})\,(0.06)\,(0.18)^2.$$

$(0.18)^2 = 0.0324$; $0.06\times0.0324 = 0.001944$. Therefore

$$r \;=\; 2.0\times10^{-6}\times0.001944 \;=\; 3.89\times10^{-9}\,\mathrm{mol\,L^{-1}\,s^{-1}}.$$

Final Answer: Initial rate $= 8.0\times10^{-9}\,\mathrm{mol\,L^{-1}\,s^{-1}}$; rate when $[A] = 0.06\,\mathrm{mol\,L^{-1}}$ is $\approx 3.89\times10^{-9}\,\mathrm{mol\,L^{-1}\,s^{-1}}$.

✗ Forgetting stoichiometry

A common slip is to keep $[B]$ at its initial $0.2\,\mathrm{mol\,L^{-1}}$ in part 2. But once A is consumed, B must also be consumed. Read $\Delta[B]$ from the balanced equation, never assume B is unchanged.

EXPERT'S SOLUTION *: Vivaan Iyer, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. The rate law is given, so the work is pure substitution. The only subtlety is tying $\Delta[B]$ to $\Delta[A]$ using the $2:1$ stoichiometry.

Step 1. Initial substitution. With $[A] = 0.1$, $[B] = 0.2$, the product $[A][B]^2 = 0.1 \times 0.04 = 0.004$, so $r_0 = 2.0 \times 10^{-6} \times 0.004 = 8.0 \times 10^{-9}\,\mathrm{mol\,L^{-1}\,s^{-1}}$.

Step 2. Compute the drop in A: $\Delta[A] = 0.04\,\mathrm{mol\,L^{-1}}$. From $2A : 1B$, $\Delta[B] = 0.02\,\mathrm{mol\,L^{-1}}$, so the remaining $[B] = 0.18\,\mathrm{mol\,L^{-1}}$.

Step 3. Final substitution. $[A][B]^2 = 0.06 \times (0.18)^2 = 0.06 \times 0.0324 = 1.944 \times 10^{-3}$, and $r = 2.0 \times 10^{-6} \times 1.944 \times 10^{-3} = 3.89 \times 10^{-9}\,\mathrm{mol\,L^{-1}\,s^{-1}}$.

Alternative ratio method. Skip the absolute substitution. Write $r/r_0 = ([A]/[A]_0)\,([B]/[B]_0)^2$. Here $[A]/[A]_0 = 0.06/0.10 = 0.6$ and $[B]/[B]_0 = 0.18/0.20 = 0.9$. So $r/r_0 = 0.6 \times 0.81 = 0.486$, hence $r = 0.486 \times 8.0 \times 10^{-9} = 3.89 \times 10^{-9}\,\mathrm{mol\,L^{-1}\,s^{-1}}$. ✓ The ratio method is faster when the rate constant is small and you want to avoid multiplying tiny numbers.

Concept linkage. The overall order here is $1 + 2 = 3$, so the units of k are $\mathrm{mol^{-2}\,L^2\,s^{-1}}$ – exactly what the problem provides. Always cross-check k units against the rate law order: a mismatch means the rate law is being misread.

Cross-check by stoichiometric bookkeeping. If $\Delta[A] = 0.04$ in the time the rate is being asked, then by $2A + B$, $\Delta[B] = 0.02$ and $\Delta[A_2B] = 0.02$. Adding A consumed and B consumed in mole units: $0.04 + 0.02 = 0.06 = 2(0.02)$ moles of nucleotides reacted per litre, matching the $2A + B$ totals.

JEE/NEET relevance. Rate at a non-initial concentration is a classic two-step JEE pattern: substitute initial, then update from stoichiometry. NEET 2021 used the same idea with $2A + 3B \rightarrow C$, where $\Delta[B] = (3/2)\Delta[A]$.

Final Answer: $r_0 = 8.0 \times 10^{-9}\,\mathrm{mol\,L^{-1}\,s^{-1}}$; $r_{\text{new}} \approx 3.89 \times 10^{-9}\,\mathrm{mol\,L^{-1}\,s^{-1}}$.

☞ Units pin the rate law

Whenever the rate constant is given with strange-looking units like $\mathrm{mol^{-2}\,L^2\,s^{-1}}$, decode the overall order before substituting. Here $n - 1 = 2$ in the exponent of L, so $n = 3$: consistent with order 1 in A plus order 2 in B. Units are a free sanity check that nothing has been mis-copied.

Q 3.3 **The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}\,\text{mol L}^{-1}\,\text{s}^{-1}$?**

SOLUTION

Concept used. The balanced equation for the decomposition is

$$2\,NH_3(g) \xrightarrow{\text{Pt}} N_2(g) + 3\,H_2(g).$$

For a **zero order reaction**, the rate of reaction is independent of the concentration of the reactant:

$$\text{Rate of reaction} = -\frac{1}{2}\frac{d[NH_3]}{dt} = +\frac{d[N_2]}{dt} = +\frac{1}{3}\frac{d[H_2]}{dt} = k.$$

The stoichiometry tells us that N_2 is produced at the rate of the reaction itself, while H_2 is produced three times as fast.

Step 1. The rate of reaction is, by definition for a zero order law,

$$\text{Rate} = k = 2.5 \times 10^{-4}\,\text{mol L}^{-1}\,\text{s}^{-1}.$$

Step 2. Rate of production of N_2:

$$\frac{d[N_2]}{dt} = +\text{Rate} = 2.5 \times 10^{-4}\,\text{mol L}^{-1}\,\text{s}^{-1}.$$

Step 3. Rate of production of H_2 is three times the rate of reaction:

$$\frac{d[H_2]}{dt} = 3 \times \text{Rate} = 3 \times 2.5 \times 10^{-4} = 7.5 \times 10^{-4}\,\text{mol L}^{-1}\,\text{s}^{-1}.$$

Final Answer: Rate of formation of $N_2 = 2.5 \times 10^{-4}\,\text{mol L}^{-1}\,\text{s}^{-1}$; rate of formation of $H_2 = 7.5 \times 10^{-4}\,\text{mol L}^{-1}\,\text{s}^{-1}$.

★ Why zero order on a Pt surface

When ammonia is dissociated on a hot platinum surface, the active sites on Pt become fully occupied even at low pressures of NH_3. Adding more ammonia cannot increase the rate because there is no spare surface; the rate is fixed by the surface area, not by $[NH_3]$. That is why the rate law is independent of concentration.

EXPERT'S SOLUTION : *Arjun Patel, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. A zero order rate constant has units of $\text{mol L}^{-1}\,\text{s}^{-1}$, so k *is* the rate of reaction. Then multiply by the appropriate stoichiometric ratio for each product.

Step 1. Write the unique *rate of reaction* so that the stoichiometric factor cancels: $r = -\frac{1}{2}\,d[\mathrm{NH_3}]/dt = d[\mathrm{N_2}]/dt = \frac{1}{3}\,d[\mathrm{H_2}]/dt$. For zero order, $r = k = 2.5 \times 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}$.

Step 2. Read off product rates. $d[\mathrm{N_2}]/dt = r = 2.5 \times 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}$. $d[\mathrm{H_2}]/dt = 3r = 7.5 \times 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}$.

Alternative "per-mole" bookkeeping. Forget the rate-of-reaction definition and just count moles. For every 2 moles of $\mathrm{NH_3}$ destroyed, 1 mole of $\mathrm{N_2}$ and 3 moles of $\mathrm{H_2}$ are made. If $\mathrm{NH_3}$ disappears at rate $5.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}$ (twice k), then $\mathrm{N_2}$ appears at half this rate (2.5×10^{-4}) and $\mathrm{H_2}$ at 3/2 this rate (7.5×10^{-4}). Same answer, no calculus.

Concept linkage. Zero order kinetics on a hot Pt surface is the chemisorption-saturation limit of the *Langmuir-Hinshelwood* mechanism: $\theta_{\mathrm{NH_3}} \approx 1$, so the rate equals $k\,\theta \approx k$ independent of $[\mathrm{NH_3}]$. The same limit appears in catalytic decomposition of HI on Au and of $\mathrm{N_2O}$ on Pt.

Cross-check by stoichiometry. The numbers must satisfy the unique rate r: $r = -\frac{1}{2}(-5.0 \times 10^{-4}) = 2.5 \times 10^{-4}$, $r = +1 \times d[\mathrm{N_2}]/dt = 2.5 \times 10^{-4}$, $r = +\frac{1}{3} \times 7.5 \times 10^{-4} = 2.5 \times 10^{-4}$. All three definitions return the same r. ✓

JEE/NEET relevance. Heterogeneous catalysis questions test either (a) the order being zero, or (b) the role of surface area. Memorise the standard zero-order examples: $2\,\mathrm{NH_3} \longrightarrow \mathrm{N_2} + 3\,\mathrm{H_2}$ on Pt, $2\,\mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I_2}$ on Au, photochemical reactions at high intensity. NEET 2020 used this exact ammonia decomposition.

Final Answer: $d[\mathrm{N_2}]/dt = 2.5 \times 10^{-4}$ and $d[\mathrm{H_2}]/dt = 7.5 \times 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}$.

☞ Identify zero order from k's units

A rate constant with units of $\mathrm{mol\,L^{-1}\,s^{-1}}$ (or $\mathrm{mol\,L^{-1}\,min^{-1}}$, $\mathrm{atm\,s^{-1}}$, etc.) flags a zero order reaction. No exponent on concentration, so k *is* the rate. This unit signature is the fastest tell for zero order.

♥ Stoichiometric coefficients link product rates

For $2\,\mathrm{NH_3} \longrightarrow \mathrm{N_2} + 3\,\mathrm{H_2}$, the product $\mathrm{H_2}$ forms three times faster than $\mathrm{N_2}$. This 3:1 ratio is fixed by stoichiometry, not by kinetics. So once *any one* rate is known, all the others are too. This is why kinetics problems almost always quote a single "rate of reaction" and let stoichiometry distribute it.

Q 3.4 The decomposition of dimethyl ether leads to the formation of $\mathrm{CH_4}$, $\mathrm{H_2}$ and CO, and the reaction rate is given by Rate $= k\,[\mathrm{CH_3OCH_3}]^{3/2}$. The rate of reaction is followed by an increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether: Rate $= k\,(p_{\mathrm{CH_3OCH_3}})^{3/2}$. If

the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?

SOLUTION

Concept used. When concentration is replaced by partial pressure in the rate law, the units of the rate and of the rate constant change accordingly. In general, if Rate $= k\,P^n$ then

$$[\text{Rate}] = \frac{[P]}{[t]}, \qquad [k] = \frac{[\text{Rate}]}{[P]^n} = [P]^{1-n}\,[t]^{-1}.$$

Here the partial pressure is measured in bar, time in min, and the order is $n = 3/2$.

Step 1. Units of rate. The rate, expressed in pressure terms, is the change of pressure with time:

$$\text{Rate} = \frac{dP}{dt} \quad\Rightarrow\quad [\text{Rate}] = \frac{\text{bar}}{\text{min}} = \text{bar}\,\text{min}^{-1}.$$

Step 2. Units of rate constant. With $n = 3/2$,

$$[k] = \frac{[\text{Rate}]}{[P]^n} = \frac{\text{bar}\,\text{min}^{-1}}{(\text{bar})^{3/2}} = \text{bar}^{1-3/2}\,\text{min}^{-1} = \text{bar}^{-1/2}\,\text{min}^{-1}.$$

Final Answer: Rate has units $\text{bar}\,\text{min}^{-1}$; the rate constant has units $\text{bar}^{-1/2}\,\text{min}^{-1}$.

☞ **Switching concentration to pressure**

For a gas-phase reaction, $p \propto c$ at constant T (ideal gas law: $p = cRT$). So the order of the reaction is the same whether written in concentration or in pressure. Only the units of k change, with bar replacing $\text{mol}\,\text{L}^{-1}$.

EXPERT'S SOLUTION : *Pranav Mehta, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. The numerical work is empty; the question is testing whether the student can carry units cleanly through a fractional order rate law.

Step 1. Recognise that rate, when expressed in pressure units, is dP/dt, so its units are $\text{bar}/\text{min} = \text{bar}\,\text{min}^{-1}$.

Step 2. Form $k = \text{Rate}/P^{3/2}$. The numerator is $\text{bar}\,\text{min}^{-1}$, the denominator is $\text{bar}^{3/2}$. Subtract exponents of bar: $1 - 3/2 = -1/2$. So k has units $\text{bar}^{-1/2}\,\text{min}^{-1}$.

Alternative via $p = cRT$. Convert concentration units to pressure units. For order n, the concentration form gives $[k]_c = \text{mol}^{1-n}\,\text{L}^{n-1}\,\text{s}^{-1}$. Replacing $\text{mol}\,\text{L}^{-1} = p/(RT)$ and substituting $\text{s} \to \text{min}$ multiplies by $(RT)^{n-1}$ and converts s^{-1} to min^{-1}. The bare-unit answer in pressure ($\text{bar}^{1-n}\,\text{min}^{-1}$) is what remains – a cleaner route than working out RT numerically.

Concept linkage. For gas-phase reactions in a closed vessel, the partial pressure of each species tracks its concentration linearly ($p_i = c_i RT$ for an ideal gas). So whether you fit kinetics in c or p, the *order* is invariant – only the units of k change. The same idea is exploited in Q 3.20 and Q 3.21 where pressure measurements stand in for concentrations.

Cross-check by integer cases. For $n = 1$ (first order), the template gives $[k] = \mathrm{bar}^0\,\mathrm{min}^{-1} = \mathrm{min}^{-1}$ – the same as s^{-1} but in minutes. For $n = 2$, $[k] = \mathrm{bar}^{-1}\,\mathrm{min}^{-1}$. Our $n = 3/2$ result ($\mathrm{bar}^{-1/2}\,\mathrm{min}^{-1}$) sits cleanly between these two. The half-power on bar is the hallmark of a $3/2$-order reaction.

JEE/NEET relevance. CBSE/NCERT routinely tests pressure-form units of k in one-marker MCQs. The trick is always the same: pull out the order from the rate-law exponent, then apply $[k] = [P]^{1-n}[t]^{-1}$. JEE Main 2023 used this with $n = 1/2$ for an acid-catalysed gas decomposition.

Final Answer: Rate: $\mathrm{bar\,min}^{-1}$; k: $\mathrm{bar}^{-1/2}\,\mathrm{min}^{-1}$.

✗ Don't confuse pressure k with concentration k

The numerical value of k depends on whether you write the rate law in concentration or pressure: $k_p = k_c\,(RT)^{1-n}$. So when a problem specifies pressure units for k, never plug in a value of k quoted in concentration units. Convert first.

Q 3.5 Mention the factors that affect the rate of a chemical reaction.

SOLUTION

Concept used. The rate of a chemical reaction is the change in concentration of a reactant or product per unit time. At a given temperature, it is set by the rate law. But the rate law itself, and the conditions in the reaction vessel, depend on a small number of experimental factors.

Step 1. **Nature of the reactants.** The strength of the bonds being broken and the bonds being formed decides how easily a reaction proceeds. Ionic species in solution combine very fast; reactions that require breaking strong covalent bonds are slower.

Step 2. **Concentration of the reactants.** A higher concentration means more reactant molecules per unit volume, more frequent collisions and (usually) a higher rate. The rate law $r = k[A]^a[B]^b$ quantifies this dependence.

Step 3. **Temperature.** An increase in temperature increases the average kinetic energy of the molecules, so a greater fraction of collisions clears the activation barrier. As a rule of thumb, the rate constant of many reactions roughly doubles for every $10\,\mathrm{K}$ rise in temperature. Quantitatively the dependence is the Arrhenius equation $k = A\,e^{-E_a/RT}$.

Step 4. **Presence of a catalyst.** A catalyst provides an alternative reaction path with a lower activation energy E_a. The rate constant rises, so the rate rises, without the catalyst being consumed.

Step 5. **Surface area** (for heterogeneous reactions). A finely powdered solid reacts much faster than a single chunk because more reactant atoms are exposed at the surface.

Step 6. **Effect of radiation.** Some reactions (photochemical reactions like the formation of HCl from H_2 and Cl_2, or photosynthesis) require light of a specific wavelength to proceed; the intensity and wavelength of the radiation then control the rate.

> **Final Answer:** Rates are affected by nature of reactants, concentration, temperature, catalyst, surface area, and (for photochemical reactions) radiation.

★ Why temperature is special

Concentration appears linearly (or as a small power) in the rate law. Temperature enters through the exponential factor $e^{-E_a/RT}$, so even small changes in T produce large changes in k. This is why fridges slow food spoilage and why ovens speed up cooking.

EXPERT'S SOLUTION *: Sneha Kapoor, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Group the factors by what they change in the collision-theory picture: either the number of effective collisions per second, or the fraction of those collisions that overcome the activation barrier.

Step 1. *Number of collisions.* Concentration and surface area both raise the collision frequency.

Step 2. *Fraction of successful collisions.* Temperature raises the fraction of molecules with $E \geq E_a$. A catalyst lowers E_a itself, raising the same fraction from the other side.

Step 3. *Built-in chemistry.* The nature of the reactants (bond energies, ionic vs covalent, gas phase vs solution) sets the baseline k; you cannot change this without changing the reaction.

Step 4. *External energy.* Light, ultrasound and electric discharge can supply the activation energy directly, bypassing thermal activation.

Alternative classification: "rate-law" vs "rate-constant" factors. A second, equally useful split is whether a factor moves the *concentration* term in $r = k[A]^a[B]^b$ or the *rate constant* k itself. Concentration and surface area change concentration (or effective concentration at the surface). Temperature, catalyst, and nature of reactants change k. Radiation sits separately because it bypasses k entirely. This split is more faithful to the Arrhenius picture.

Concept linkage. Each factor has a quantitative bridge: concentration → rate law (Q 3.2, 3.6); temperature → Arrhenius (Q 3.7, 3.22–3.30); catalyst → effective E_a lowering (covered in Section 3.5); surface area → Langmuir isotherm (advanced). Knowing which bridge to invoke saves time on a JEE/NEET MCQ.

Cross-check using the activated-complex picture. The fraction of molecules with $E \geq E_a$ at temperature T is $e^{-E_a/RT}$. A catalyst lowers E_a from E_a^0 to $E_a^* < E_a^0$. The fraction rises from $e^{-E_a^0/RT}$ to $e^{-E_a^*/RT}$, multiplying the rate by $e^{(E_a^0 - E_a^*)/RT}$. For $\Delta E_a = 20\,\text{kJ/mol}$ at $298\,\text{K}$, this is a factor of ~ 3000. That is the engineering power of a catalyst.

JEE/NEET relevance. "Which factor does *not* affect rate?" is a standing NEET MCQ. The answer is always "the size of the container" (irrelevant) or "the catalyst's concentration" (it is regenerated). The six factors listed here are the official NCERT answer set.

> **Final Answer:** Six main factors: nature of reactants, concentration, temperature, catalyst, surface area, radiation.

☞ Catalyst does not change ΔH

A catalyst lowers E_a in both the forward and the reverse direction *equally*, so the position of equilibrium is unchanged – only the time taken to reach it shortens. This subtle distinction is a near-universal JEE/NEET MCQ trap.

♥ Why temperature dominates in industry

A $10\,\text{K}$ swing roughly doubles k. A $30\,\text{K}$ swing gives a factor of 8. By contrast, doubling the concentration of a first-order reactant only doubles the rate. So when a process engineer needs to accelerate a reaction quickly, the first lever is *temperature*, not concentration. The Haber process and steam cracking both run at $400\,^\circ\text{C}+$ for this reason.

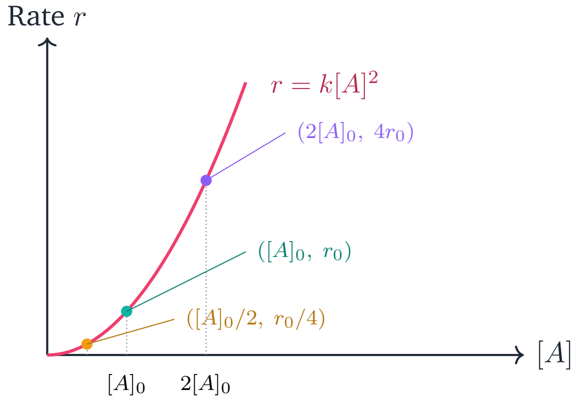
Q 3.6 **A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled, (ii) reduced to half?**

SOLUTION

Concept used. If a reaction is **second order** in the reactant A, its rate law has the form

$$r \;=\; k\,[A]^2.$$

So when $[A]$ changes by a factor f, the rate changes by f^2.



Step 1. Initial rate. Let $[A] = a$ at the start; then $r_0 = k\,a^2$.

Step 2. Case (i): concentration doubled. Replace a by $2a$:

$$r_1 \;=\; k\,(2a)^2 \;=\; 4\,k\,a^2 \;=\; 4\,r_0.$$

So the rate becomes four times the original.

Step 3. Case (ii): concentration reduced to half. Replace a by $a/2$:

$$r_2 \;=\; k\left(\frac{a}{2}\right)^2 \;=\; \frac{1}{4}\,k\,a^2 \;=\; \frac{r_0}{4}.$$

So the rate becomes one-fourth of the original.

> **Final Answer:** (i) Rate becomes 4 times the initial rate. (ii) Rate becomes $1/4$ of the initial rate.

EXPERT'S SOLUTION *: Karan Verma, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. For an n-th order reaction in a single reactant, changing concentration by a factor f changes the rate by f^n. Here $n = 2$.

Step 1. Plug $f = 2$ into $f^n = f^2$. The rate goes up by $2^2 = 4$.

Step 2. Plug $f = 1/2$. The rate goes by $(1/2)^2 = 1/4$.

Alternative graphical view. Plot r against $[A]$: the curve is a parabola through the origin. Move from $[A]_0$ to $2[A]_0$ horizontally; the curve rises four-fold vertically because of the squared dependence. The same parabola shows that going from $[A]_0$ to $[A]_0/2$ drops the rate to one quarter. The picture makes the answer obvious without algebra (see the diagram in the main solution).

Concept linkage. The exponent n in $r = k[A]^n$ is also the slope of $\log r$ vs $\log[A]$. So if you doubled the concentration and the rate quadrupled, the slope is $\log 4/\log 2 = 2$, consistent with $n = 2$. This is the differential method of determining order, and the second part of Q 3.10 uses exactly this logic.

Cross-check by integration. For second order kinetics in a single reactant, the integrated rate law gives $1/[A] - 1/[A]_0 = kt$. Half-life is $t_{1/2} = 1/(k[A]_0)$, *inversely* proportional to $[A]_0$. So doubling $[A]_0$ halves $t_{1/2}$, consistent with the rate quadrupling: the reaction starts faster and finishes sooner.

JEE/NEET relevance. The pattern "order $n \Rightarrow$ factor f^n scaling" is the single most-tested idea in kinetics. JEE Main 2024 asked the same question with $f = 3$ for a second-order reaction (answer: rate goes up by 9). Memorise the powers of 2 and 3 up to the cube.

> **Final Answer:** Rate $\to 4r_0$ when $[A] \to 2[A]$; rate $\to r_0/4$ when $[A] \to [A]/2$.

☞ Order rules the scaling

For order n, multiplying concentration by f multiplies the rate by f^n. Order 0: rate is unchanged. Order 1: rate scales as f. Order 2: rate scales as f^2. Order $1/2$: rate scales as $\sqrt{f}$. The exponent on the concentration *is* the exponent on the scaling factor.

☞ Don't confuse half rate with half concentration

"Concentration halved" is not the same as "rate halved". For first order, yes, the rate halves. For second order, the rate quarters. For half order, the rate falls by $\sqrt{2} \approx 0.707$. Always read the order before you scale.

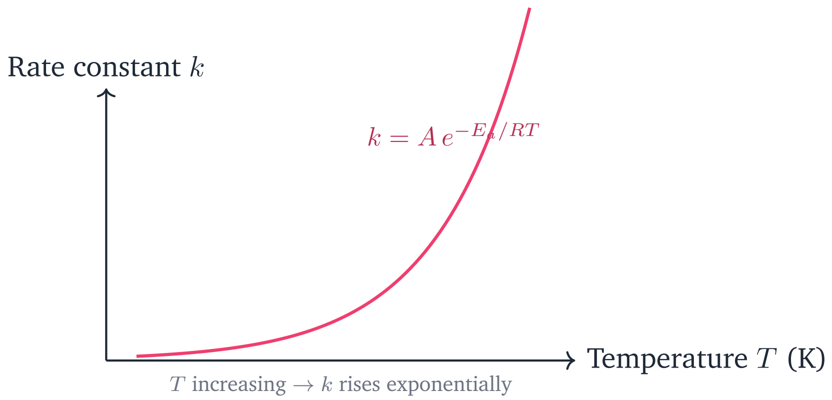
Q 3.7 What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?

SOLUTION

Concept used. For nearly all chemical reactions, raising the temperature increases the rate constant. The empirical rule is that the rate constant approximately *doubles* for every $10\,\mathrm{K}$ rise. Quantitatively this dependence is captured by the **Arrhenius equation**:

$$k = A\,e^{-E_a/RT},$$

where A is the **pre-exponential factor** (also called the **frequency factor**), E_a is the **activation energy** (in $\mathrm{J\,mol^{-1}}$), $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$ is the gas constant and T is the absolute temperature in kelvin.



Step 1. Take the natural logarithm of the Arrhenius equation:

$$\ln k \;=\; \ln A \;-\; \frac{E_a}{RT}.$$

Plotting $\ln k$ against $1/T$ gives a straight line of slope $-E_a/R$ and intercept $\ln A$.

Step 2. Comparing at two temperatures T_1 and T_2 with rate constants k_1 and k_2 gives the useful two-temperature form:

$$\ln \frac{k_2}{k_1} \;=\; \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

or equivalently

$$\log \frac{k_2}{k_1} \;=\; \frac{E_a}{2.303\,R}\,\frac{T_2 - T_1}{T_1 T_2}.$$

Step 3. Physical reading. The factor $e^{-E_a/RT}$ is the fraction of molecules whose collision energy exceeds E_a at temperature T. As T rises, this exponential rises sharply, so k increases sharply. Small temperature changes produce large rate-constant changes; this is why temperature is the most effective lever for controlling reaction rates.

Final Answer: k increases with T, approximately doubling per $10\,\text{K}$. Quantitatively, $k = A\,e^{-E_a/RT}$ (Arrhenius equation).

♥ Reading the Arrhenius plot

A graph of $\ln k$ vs $1/T$ is a workhorse of chemical kinetics. The slope $-E_a/R$ gives the activation energy from experimental data; the intercept $\ln A$ gives the pre-exponential factor. The straight-line fit is itself a strong test that the Arrhenius equation applies to the reaction.

EXPERT'S SOLUTION : *Aditi Banerjee, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. State the empirical fact first (rate roughly doubles per $10\,\mathrm{K}$), then write down the Arrhenius equation, then show both the linear log form and the two-temperature ratio form that students actually use to solve problems.

Step 1. *Temperature coefficient.* Define $\mu = k_{T+10}/k_T \approx 2$ to 3. This is a rough rule and varies between reactions.

Step 2. *Arrhenius equation.* $k = A\,e^{-E_a/RT}$. Taking $\ln$, $\ln k = \ln A - E_a/(RT)$. So a plot of $\ln k$ vs $1/T$ is a straight line of slope $-E_a/R$.

Step 3. *Useful two-temperature form.*

$$\log(k_2/k_1) \;=\; \frac{E_a}{2.303\,R}\cdot\frac{T_2-T_1}{T_1T_2}.$$

This lets us compute E_a from any pair of (k,T) values, or predict k at a new temperature.

Alternative derivation from collision theory. The fraction of collisions with energy $\geq E_a$ is $e^{-E_a/RT}$ (Boltzmann). The total collision frequency Z scales roughly as $\sqrt{T}$ (slow). So $k = pZ\,e^{-E_a/RT}$ where p is the steric factor. Folding pZ into A recovers the Arrhenius form. This derivation justifies *why* temperature dominates: it enters the exponential, while Z enters only as a square root.

Concept linkage. The Arrhenius equation is structurally identical to the radioactive-decay law for fission products (Q 3.14, Q 3.17): in both, the rate is proportional to an exponential of an energy/RT term. This connects chemical kinetics to nuclear physics through a common Boltzmann-distribution origin.

Cross-check by limiting cases. As $T\to\infty$, $e^{-E_a/RT}\to 1$, so $k\to A$. So A is the rate constant when *every* collision has enough energy. As $T\to 0$, $e^{-E_a/RT}\to 0$ and $k\to 0$. Both limits are physically sensible: no collisions are energetic at $T=0$; all are at infinite T.

JEE/NEET relevance. Of the 5–6 questions on kinetics that appear annually in JEE Main, 3–4 involve Arrhenius. The two-temperature form is the most-tested formula in the chapter – expect at least one direct numerical, and one conceptual question on its meaning, every year.

> **Final Answer:** Rate constant rises with T; quantitatively, $k = A\,e^{-E_a/RT}$ (Arrhenius equation).

☞ **Arrhenius cheat-card**

Three forms to memorise: (i) exponential $k = A\,e^{-E_a/RT}$; (ii) linear log $\ln k = \ln A - E_a/(RT)$, slope $-E_a/R$ on $\ln k$ vs $1/T$; (iii) two-temperature $\log(k_2/k_1) = (E_a/2.303R)(T_2-T_1)/(T_1T_2)$. The third is the workhorse of numerical problems.

Q 3.8 **In a pseudo first order reaction in water, the following results were obtained:**

t/s	0	30	60	90
$[A]/\text{mol L}^{-1}$	0.55	0.31	0.17	0.085

Calculate the average rate of reaction between the time interval 30 to 60 seconds.

SOLUTION

Concept used. The average rate of reaction between two times t_1 and t_2 is the change in concentration of the reactant divided by the elapsed time, with a minus sign so that the rate is positive:

$$r_{\text{av}} = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_2 - [A]_1}{t_2 - t_1}.$$

Here A is the reactant whose concentration is being tracked.

Step 1. Read off the data at $t_1 = 30\,\text{s}$ and $t_2 = 60\,\text{s}$:

$$[A]_1 = 0.31\,\text{mol L}^{-1}, \quad [A]_2 = 0.17\,\text{mol L}^{-1}.$$

Step 2. Compute the change in concentration:

$$\Delta[A] = [A]_2 - [A]_1 = 0.17 - 0.31 = -0.14\,\text{mol L}^{-1}.$$

The minus sign confirms that $[A]$ has fallen, as expected for a reactant.

Step 3. Compute the elapsed time:

$$\Delta t = t_2 - t_1 = 60 - 30 = 30\,\text{s}.$$

Step 4. Substitute into the average-rate formula:

$$r_{\text{av}} = -\frac{-0.14\,\text{mol L}^{-1}}{30\,\text{s}} = \frac{0.14}{30}\,\text{mol L}^{-1}\,\text{s}^{-1} = 4.67 \times 10^{-3}\,\text{mol L}^{-1}\,\text{s}^{-1}.$$

Final Answer: Average rate between $t = 30\,\text{s}$ and $t = 60\,\text{s}$ is $\approx 4.67 \times 10^{-3}\,\text{mol L}^{-1}\,\text{s}^{-1}$.

☞ Pseudo first order

A reaction may follow second order kinetics overall, yet behave as first order when one of the reactants is present in large excess (e.g. water in a hydrolysis). The excess reactant's concentration stays essentially constant, and absorbs into a new effective rate constant $k' = k[\text{excess}]$. This is called a *pseudo first order* reaction.

EXPERT'S SOLUTION : *Riya Joshi, M.Sc Chemistry, IIT Kanpur*

Strategic angle. The phrase "pseudo first order" is a red herring for this part: we only need the definition of *average rate*, no rate-law fitting required.

Step 1. Identify the interval and the corresponding concentrations: $[A]_{30} = 0.31$, $[A]_{60} = 0.17$, both in mol L^{-1}.

Step 2. Compute the drop: $0.31 - 0.17 = 0.14\,\text{mol L}^{-1}$. Divide by $30\,\text{s}$: $r_{\text{av}} = 0.14/30 = 4.67 \times 10^{-3}\,\text{mol L}^{-1}\,\text{s}^{-1}$.

Alternative test of first order behaviour. If you compute $\ln[A]$ at each time point and check whether it falls linearly with t, you can verify the order while you are at it. Doing this: $\ln 0.55 = -0.598$, $\ln 0.31 = -1.171$, $\ln 0.17 = -1.772$, $\ln 0.085 = -2.465$. The differences over each $30\,\text{s}$ interval are -0.573, -0.601, -0.693. Roughly constant, so first order is plausible – and the slope gives $k \approx 0.60/30 = 0.020\,\text{s}^{-1}$.

Concept linkage. The average rate over 30 to $60\,\text{s}$ is a *secant* slope on the $[A]$ vs t curve. The *instantaneous* rate $-d[A]/dt$ at any t in this interval is the tangent slope and is in general different. As $\Delta t \to 0$, average rate $\to$ instantaneous rate.

Cross-check by mid-point estimate. The instantaneous rate at the midpoint $t = 45\,\text{s}$ should approximately equal the average rate. Using $k = 0.020\,\text{s}^{-1}$ and a midpoint $[A] \approx (0.31 + 0.17)/2 = 0.24\,\text{mol L}^{-1}$, $r_{\text{inst}} = k[A] = 0.020 \times 0.24 = 4.8 \times 10^{-3}\,\text{mol L}^{-1}\,\text{s}^{-1}$. Matches our 4.67×10^{-3} within rounding. ✓

JEE/NEET relevance. Average-rate calculations are routine one-mark NEET items. The trap is sign: $\Delta[A] = [A]_2 - [A]_1$ is negative for a reactant, and the formula uses $-\Delta[A]/\Delta t$ to make rate positive. Always write the minus sign explicitly.

Final Answer: $r_{\text{av}} \approx 4.67 \times 10^{-3}\,\text{mol L}^{-1}\,\text{s}^{-1}$.

♥ Average vs instantaneous rate

The average rate gives a coarse number averaged over an interval. The instantaneous rate $-d[A]/dt$ is the tangent to the $[A]$ vs t curve at a chosen instant. For first order kinetics, the two coincide only when the interval is short enough that $[A]$ has not changed much. Whenever you see a rate quoted at a *specific* t, instantaneous is intended.

Q 3.9 A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of B three times?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

SOLUTION

Concept used. If a reaction is first order in A and second order in B, the differential rate law has the form

$$r = -\frac{d[A]}{dt} = k\,[A]^1\,[B]^2.$$

The exponent on each concentration is the order with respect to that species. The overall order is $1 + 2 = 3$.

Step 1. Part (i). The differential rate equation is exactly as written above:

$$r = k\,[A]\,[B]^2.$$

Step 2. Part (ii). Replace $[B]$ by $3[B]$ with $[A]$ unchanged:

$$r' = k\,[A]\,(3[B])^2 = k\,[A]\cdot 9[B]^2 = 9\,k\,[A][B]^2 = 9\,r.$$

So the rate becomes nine times the original.

Step 3. Part (iii). Replace $[A]$ by $2[A]$ *and* $[B]$ by $2[B]$:

$$r'' = k\,(2[A])\,(2[B])^2 = k\,(2[A])\,(4[B]^2) = 8\,k\,[A][B]^2 = 8\,r.$$

So the rate becomes eight times the original.

Final Answer: (i) $r = k[A][B]^2$. (ii) Rate becomes $9r$. (iii) Rate becomes $8r$.

✗ Don't add the factors

For part (iii), some students answer $2+4 = 6$. The multiplicative factors must be *multiplied*, not added: doubling $[A]$ gives a factor of 2, doubling $[B]$ gives a factor of $2^2 = 4$, and together they give $2 \times 4 = 8$.

EXPERT'S SOLUTION : *Aditya Reddy, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. For any rate law $r = k[A]^a[B]^b$, the effect of multiplying $[A]$ by f_A and $[B]$ by f_B is to multiply the rate by $f_A^a\,f_B^b$. With $a = 1$ and $b = 2$:

Step 1. Part (i): $r = k[A][B]^2$ by definition.

Step 2. Part (ii): $f_A = 1$, $f_B = 3$: $1^1 \cdot 3^2 = 9$.

Step 3. Part (iii): $f_A = 2$, $f_B = 2$: $2^1 \cdot 2^2 = 2 \cdot 4 = 8$.

Alternative log-based verification. Take logs: $\log r = \log k + \log[A] + 2\log[B]$. Each unit increase in $\log[B]$ (i.e. a factor of 10 in $[B]$) raises $\log r$ by 2. Each unit increase in $\log[A]$ raises $\log r$ by 1. So tripling $[B]$ gives $\Delta \log r = 2\log 3 = 0.954$, hence $r' = 10^{0.954}\,r = 9\,r$. ✓

Concept linkage. The overall order $a + b = 3$ is the *molecularity* of an elementary termolecular step. Real termolecular elementary steps are rare (three molecules colliding at once is improbable). Most order-3 rate laws arise from multi-step mechanisms with a fast pre-equilibrium. NO+O_2 kinetics is the classical textbook example.

Cross-check by extreme limits. If $f_A = 0$ (i.e. A removed), $r' = 0$ – the reaction stops. If $f_B = 0$, $r' = 0$ – the reaction also stops. Both reactants are needed; neither is in a zero-order regime. Contrast with Q 3.10 part (i) where B has order zero and removing B does *not* stop the reaction.

JEE/NEET relevance. Effect-of-concentration MCQs are the single most common kinetics format. The pattern: read off orders, compute $f_A^a\, f_B^b$, pick the matching option. JEE Main 2022 asked the same question with orders $(2, 1)$ and factors $(3, 2)$ giving $9 \times 2 = 18$.

Final Answer: (i) $r = k[A][B]^2$; (ii) $\times 9$; (iii) $\times 8$.

☞ **Powers multiply, exponents do not**

For $r = k[A]^a[B]^b$, when both $[A]$ and $[B]$ are scaled, the *factors* on the rate multiply: $f_A^a \times f_B^b$. Never add the factors. “$2[A]$ and $2[B]$” with $a = 1$, $b = 2$ gives $2 \times 4 = 8$, not $2 + 4 = 6$.

Q 3.10 **In a reaction between A and B, the initial rate of reaction r_0 was measured for different initial concentrations of A and B as given below:**

$[A]/\text{mol L}^{-1}$	0.20	0.20	0.40
$[B]/\text{mol L}^{-1}$	0.30	0.10	0.05
$r_0/\text{mol L}^{-1}\,\text{s}^{-1}$	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B?

SOLUTION

Concept used. For a rate law $r_0 = k\,[A]^x\,[B]^y$, the order with respect to each reactant can be found by taking *ratios of experiments* chosen so that only one concentration changes at a time, or by using logarithms when both change.

Step 1. **Order with respect to B (Experiments 1 and 2).** Between these two experiments, $[A]$ is fixed at $0.20\,\text{mol L}^{-1}$ while $[B]$ changes from 0.30 to $0.10\,\text{mol L}^{-1}$. The initial rate is *identical* (5.07×10^{-5}) in both. So changing $[B]$ by a factor of 3 produces no change in rate. Therefore the rate is independent of $[B]$, i.e. the order with respect to B is $\mathbf{y = 0}$.

Step 2. **Rate law so far.** With $y = 0$, the rate law simplifies to

$$r_0 = k\,[A]^x.$$

Step 3. **Order with respect to A (Experiments 1 and 3).** Now use experiments 1 and 3 where $[A]$ changes. (We do not need to worry about $[B]$ because we've shown $y = 0$.)

$$\frac{r_{0,3}}{r_{0,1}} = \left(\frac{[A]_3}{[A]_1}\right)^x \implies \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \left(\frac{0.40}{0.20}\right)^x.$$

Compute the left side: $1.43 \times 10^{-4}/5.07 \times 10^{-5} = 2.82$. Compute the right side base: $0.40/0.20 = 2$. So $2^x = 2.82$.

Step 4. **Solve for x.** Take logs:

$$x = \frac{\log 2.82}{\log 2} = \frac{0.4502}{0.3010} = 1.50.$$

So the order with respect to A is $\mathbf{x = 1.5}$.

Step 5. **Overall order.** $x + y = 1.5 + 0 = 1.5$. The full rate law is $r_0 = k\,[A]^{3/2}$.

Final Answer: Order in $A = 1.5$; order in $B = 0$; overall order $= 1.5$.

★ Reading initial-rate tables

First scan for a pair of rows where one concentration is held constant. If the rate is unchanged across that pair, that species has zero order. Then pick a pair where the species of interest changes and use $r_2/r_1 = (c_2/c_1)^n$ to solve for n.

EXPERT'S SOLUTION : *Yash Nair, M.Sc Chemistry, IIT Kanpur*

Strategic angle. The two rates labelled 5.07×10^{-5} are a strong hint: when $[B]$ changes from 0.30 to 0.10 at fixed $[A]$, nothing happens to the rate. So B does not appear in the rate law.

Step 1. Order in B: rates 1 and 2 are equal $\Rightarrow$ B has order zero.

Step 2. Order in A: from experiments 1 and 3 with $[A]$ doubled and $[B]$ now irrelevant, $2.82 = 2^x$, giving $x = \log 2.82/\log 2 \approx 1.5$.

Step 3. Overall order $= 1.5$; rate law is $r = k[A]^{3/2}$.

Alternative simultaneous-equations route. Without the "constant $[A]$" shortcut, set up

$r_i = k\,[A]_i^x\,[B]_i^y$ for each row and take ratios:

$$\frac{r_3}{r_1} = \left(\frac{0.40}{0.20}\right)^x \left(\frac{0.05}{0.30}\right)^y, \qquad \frac{r_2}{r_1} = \left(\frac{0.20}{0.20}\right)^x \left(\frac{0.10}{0.30}\right)^y.$$

The second equation gives $1 = (1/3)^y$, so $y = 0$. Substituting into the first gives $2.82 = 2^x$, so $x = 1.5$. Same answer, slightly more algebra. Useful when no two experiments hold the same $[A]$ or $[B]$.

Concept linkage. Half-integer orders like 1.5 are the fingerprint of a multi-step mechanism with a fast equilibrium of the form $A_2 \rightleftharpoons 2\,A$ where the actual reactant is the *atom* A derived from a dimer A_2. The square root of the dimer concentration enters the rate law and gives the half-power. Decomposition of CH_3CHO (Q 3.1 part iii) is a textbook $3/2$-order example.

Cross-check by computing k. Using experiment 1 ($[A] = 0.20$, $r = 5.07 \times 10^{-5}$): $k = r/[A]^{1.5} = 5.07 \times 10^{-5}/(0.20)^{1.5} = 5.07 \times 10^{-5}/0.0894 = 5.67 \times 10^{-4}\,\mathrm{mol^{-1/2}\,L^{1/2}\,s^{-1}}$. Check with experiment 3: $r = k(0.40)^{1.5} = 5.67 \times 10^{-4} \times 0.2530 = 1.43 \times 10^{-4}$. ✓

JEE/NEET relevance. “Find the order from initial-rate data” is a 4-mark NCERT/Board favourite. The recipe: hold one species constant, take a ratio of rates, equate to the concentration ratio raised to the order. NEET 2024 used three experiments to test the same skill.

> **Final Answer:** Order with respect to $A = 1.5$, with respect to $B = 0$.

☞ “Rate unchanged” = zero order

Whenever a row in an initial-rate table shows the same rate as another row that differs only in one species’ concentration, that species has order zero. Spot this pattern first; it saves the log-arithmetic.

☞ Working out fractional orders

For $r_2/r_1 = (c_2/c_1)^n$, solve as $n = \log(r_2/r_1)/\log(c_2/c_1)$. A clean integer is the most likely answer $(0, 1, 2)$, but always allow for $1/2$ and $3/2$. Round only after computing.

Q 3.11 The following results have been obtained during the kinetic studies of the reaction $2\,A + B \longrightarrow C + D$:

Experiment	$[A]/\text{mol L}^{-1}$	$[B]/\text{mol L}^{-1}$	$r_0/\text{mol L}^{-1}\,\text{min}^{-1}$
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

SOLUTION

Concept used. Assume a rate law of the form $r_0 = k\,[A]^x\,[B]^y$ and use pairs of experiments to isolate x and y:

$$\frac{r_{0,i}}{r_{0,j}} = \left(\frac{[A]_i}{[A]_j}\right)^x \left(\frac{[B]_i}{[B]_j}\right)^y.$$

Step 1. Order in B (Experiments II and III). $[A]$ is the same $(0.3\,\text{mol L}^{-1})$; $[B]$ goes from 0.2 to 0.4, a factor of 2. The rate goes from 7.2×10^{-2} to 2.88×10^{-1}. Ratio of rates:

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = 4.$$

So $4 = 2^y$, giving $y = 2$.

Step 2. Order in A (Experiments I and IV). $[B]$ is the same $(0.1\,\text{mol L}^{-1})$; $[A]$ goes from 0.1 to 0.4, a factor of 4. The rate goes from 6.0×10^{-3} to 2.40×10^{-2}. Ratio of rates:

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = 4.$$

So $4 = 4^x$, giving $x = 1$.

Step 3. Rate law. With $x = 1$ and $y = 2$,

$$r_0 = k\,[A]\,[B]^2.$$

Overall order is $1 + 2 = 3$.

Step 4. Rate constant from Experiment I. Substitute $[A] = 0.1$, $[B] = 0.1$, $r_0 = 6.0 \times 10^{-3}$:

$$k = \frac{r_0}{[A][B]^2} = \frac{6.0 \times 10^{-3}}{0.1 \times (0.1)^2} = \frac{6.0 \times 10^{-3}}{0.001} = 6.0\,\text{mol}^{-2}\,\text{L}^2\,\text{min}^{-1}.$$

Step 5. Cross-check with Experiment II. Using $[A] = 0.3$, $[B] = 0.2$: $[A][B]^2 = 0.3 \times 0.04 = 0.012\,\text{mol}^3\,\text{L}^{-3}$. Then

$$r = k\,[A][B]^2 = 6.0 \times 0.012 = 0.072 = 7.2 \times 10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1}.\checkmark$$

Final Answer: Rate law: $r_0 = k\,[A]\,[B]^2$ with $k = 6.0\,\text{mol}^{-2}\,\text{L}^2\,\text{min}^{-1}$.

☞ Cross-check whenever possible

After fitting a rate constant from one experiment, plug it back into the rate law for a different experiment. If the predicted rate matches the measured rate, the orders and k are consistent.

EXPERT'S SOLUTION : *Ananya Pillai, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. The data are arranged neatly so that pairs of experiments differ in only one concentration. That makes the ratio approach a quick win.

Step 1. Pair II→III: only $[B]$ changes by $\times 2$; rate changes by $\times 4 = 2^2$. So order in B is 2.

Step 2. Pair I→IV: only $[A]$ changes by $\times 4$; rate changes by $\times 4 = 4^1$. So order in A is 1.

Step 3. Rate law: $r = k[A][B]^2$. Use Experiment I to find $k = 6.0 \times 10^{-3}/(0.1 \cdot 0.01) = 6.0\,\mathrm{mol}^{-2}\,\mathrm{L}^2\,\mathrm{min}^{-1}$.

Alternative consistency check across all rows. Recompute k using each experiment:

- Exp III: $k = 0.288/(0.3 \times 0.16) = 0.288/0.048 = 6.0$. ✓
- Exp IV: $k = 0.024/(0.4 \times 0.01) = 0.024/0.004 = 6.0$. ✓

All four experiments give the same k, confirming both the orders and the rate constant.

Concept linkage. Order $\neq$ molecularity here: the stoichiometry $2\,\mathrm{A} + \mathrm{B}$ predicts "order 2 in A, order 1 in B" for an elementary step. Experiment gives "order 1 in A, order 2 in B" – the opposite assignment. The reaction must therefore go through a multi-step mechanism with B doubling up in a rate-determining step.

Cross-check by overall-order units. Overall order is $1 + 2 = 3$. Units of k should be $\mathrm{mol}^{1-3}\,\mathrm{L}^{3-1}\,\mathrm{min}^{-1} = \mathrm{mol}^{-2}\,\mathrm{L}^2\,\mathrm{min}^{-1}$. The number 6.0 in these units predicts rates in $\mathrm{mol}\,\mathrm{L}^{-1}\,\mathrm{min}^{-1}$. ✓

JEE/NEET relevance. The four-experiment, four-row table is a CBSE 3-mark format. The recipe is fixed: (i) find y from a row pair with fixed $[A]$, (ii) find x from a pair with fixed $[B]$, (iii) compute k from any single row. JEE Main 2021 used a nearly-identical table.

Final Answer: $r = k[A][B]^2;\ \ k = 6.0\,\mathrm{mol}^{-2}\,\mathrm{L}^2\,\mathrm{min}^{-1}$.

♥ Order from data, not from balanced equation

The orders $(1, 2)$ for (A, B) have no relation to the stoichiometric coefficients $(2, 1)$ in $2\,\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$. This is the single most-tested "trick" in NCERT kinetics: order is *experimental*, stoichiometry is balanced bookkeeping. They coincide only for elementary reactions.

Q 3.12 The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	$[A]/\text{mol L}^{-1}$	$[B]/\text{mol L}^{-1}$	$r_0/\text{mol L}^{-1}\,\text{min}^{-1}$
I	0.1	0.1	2.0×10^{-2}
II	**?**	0.2	4.0×10^{-2}
III	0.4	0.4	**?**
IV	**?**	0.2	2.0×10^{-2}

SOLUTION

Concept used. Given the orders ($x = 1$ in A, $y = 0$ in B), the rate law collapses to

$$r_0 \;=\; k\,[A]^1\,[B]^0 \;=\; k\,[A].$$

The rate is independent of $[B]$.

Step 1. Find k from Experiment I. Substitute $[A] = 0.1\,\text{mol L}^{-1}$, $r_0 = 2.0 \times 10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1}$:

$$k \;=\; \frac{r_0}{[A]} \;=\; \frac{2.0 \times 10^{-2}}{0.1} \;=\; 0.2\,\text{min}^{-1}.$$

Step 2. Experiment II: given $r_0 = 4.0 \times 10^{-2}$ and $k = 0.2\,\text{min}^{-1}$. Solve for $[A]$:

$$[A] \;=\; \frac{r_0}{k} \;=\; \frac{4.0 \times 10^{-2}}{0.2} \;=\; 0.2\,\text{mol L}^{-1}.$$

Step 3. Experiment III: $[A] = 0.4\,\text{mol L}^{-1}$. Compute r_0:

$$r_0 \;=\; k\,[A] \;=\; 0.2 \times 0.4 \;=\; 0.08 \;=\; 8.0 \times 10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1}.$$

Step 4. Experiment IV: given $r_0 = 2.0 \times 10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1}$. Same calculation as Experiment I:

$$[A] \;=\; \frac{r_0}{k} \;=\; \frac{2.0 \times 10^{-2}}{0.2} \;=\; 0.1\,\text{mol L}^{-1}.$$

Final Answer: Experiment II: $[A] = 0.2\,\text{mol L}^{-1}$; Experiment III: $r_0 = 8.0 \times 10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1}$; Experiment IV: $[A] = 0.1\,\text{mol L}^{-1}$.

EXPERT'S SOLUTION : *Ishaan Bhat, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Once the orders are stated, the rate law becomes $r = k[A]$, a single-variable formula. Find k first, then use it as a converter between r and $[A]$ in every other row.

Step 1. From row I, $k = r/[A] = 0.02/0.1 = 0.2\,\text{min}^{-1}$.

Step 2. Row II: $[A] = r/k = 0.04/0.2 = 0.2\,\text{mol L}^{-1}$.

Step 3. Row III: $r = k\,[A] = 0.2 \times 0.4 = 0.08 = 8.0 \times 10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1}$.

Step 4. Row IV: $[A] = 0.02/0.2 = 0.1\,\text{mol L}^{-1}$.

Alternative ratio-only method. Skip computing k. Use $r_i/r_j = [A]_i/[A]_j$. Then $[A]_{II}/[A]_I = r_{II}/r_I = 0.04/0.02 = 2$, so $[A]_{II} = 2 \times 0.1 = 0.2\,\text{mol L}^{-1}$. For row III: $r_{III}/r_I = [A]_{III}/[A]_I = 4$, so $r_{III} = 4 \times 0.02 = 0.08\,\text{mol L}^{-1}\,\text{min}^{-1}$. For row IV: same as row I, so $[A]_{IV} = 0.1\,\text{mol L}^{-1}$. Faster when you don't need k for downstream calculations.

Concept linkage. A reaction first order in A and zero order in B is most commonly an acid-catalysed reaction where B is the catalyst (e.g. H^+): the concentration of B controls k via the effective rate constant $k_{\text{eff}} = k_{\text{true}}[B]^0 \to$ constant. Iodination of acetone by I_2 in acid is the classic example: zero order in I_2 because halogenation is fast after the rate-determining enolisation step.

Cross-check by units of k. Overall order is $1 + 0 = 1$, so $[k] = \text{min}^{-1}$. Our $k = 0.2\,\text{min}^{-1}$ matches. The boxed-zero column of $[B]$ in the table is a red herring – intentional, because rows II and IV with different $[B]$ both give the same answer for $[A]$ as if $[B]$ never appeared.

JEE/NEET relevance. Fill-in-the-blanks tables on rate-law data are a NEET staple. Once orders are known, the problem reduces to two divisions and one multiplication. NEET 2022 used a similar table with order 2 in A, order 1 in B.

Final Answer: II: $0.2\,\text{mol L}^{-1}$; III: $8.0 \times 10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1}$; IV: $0.1\,\text{mol L}^{-1}$.

☞ Zero-order species are decoration

Once a species is shown to have order 0, its column in any data table becomes purely decorative. The rate law no longer contains it. Common NCERT trick: deliberately put a varying $[B]$ in the table to test whether students blindly include it.

☞ First-order rate-law fragment

$r = k[A]$ is a linear relation: doubling $[A]$ doubles r, halving $[A]$ halves r. Memorise this proportionality as the simplest case of all rate-law scaling – everything else is a power of it.

Q 3.13 Calculate the half-life of a first order reaction from their rate constants given below:

(i) $200\,\text{s}^{-1}$ **(ii)** $2\,\text{min}^{-1}$ **(iii)** $4\,\text{year}^{-1}$

SOLUTION

Concept used. For a first order reaction, the half-life is independent of the initial concentration and is given by

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}.$$

Here $\ln 2 = 0.693$ (to three decimal places) and k is the first-order rate constant.

Step 1. **Part (i):** $k = 200\,\mathrm{s}^{-1}$.

$$t_{1/2} = \frac{0.693}{200}\,\mathrm{s} = 3.465 \times 10^{-3}\,\mathrm{s}.$$

Step 2. **Part (ii):** $k = 2\,\mathrm{min}^{-1}$.

$$t_{1/2} = \frac{0.693}{2}\,\mathrm{min} = 0.3465\,\mathrm{min}.$$

In seconds: $0.3465\,\mathrm{min} \times 60\,\mathrm{s\,min}^{-1} = 20.79\,\mathrm{s}$.

Step 3. **Part (iii):** $k = 4\,\mathrm{year}^{-1}$.

$$t_{1/2} = \frac{0.693}{4}\,\mathrm{year} = 0.1733\,\mathrm{year}.$$

> **Final Answer:** (i) $t_{1/2} \approx 3.465 \times 10^{-3}\,\mathrm{s}$; (ii) $t_{1/2} \approx 0.3465\,\mathrm{min}$; (iii) $t_{1/2} \approx 0.1733\,\mathrm{year}$.

☞ Half-life is independent of initial concentration for first order

This is the trademark of first order kinetics: every half-life is the same, regardless of how much A remains at the start of that half-life. Zero order reactions have $t_{1/2} \propto [A]_0$; second order have $t_{1/2} \propto 1/[A]_0$.

EXPERT'S SOLUTION *: Diya Gupta, M.Sc Chemistry, IIT Kanpur*

Strategic angle. One formula, three substitutions. The only thing to watch is that the time units in $t_{1/2}$ are the inverse of the units in k.

Step 1. Part (i): $t_{1/2} = 0.693/200 = 3.465 \times 10^{-3}\,\mathrm{s}$.

Step 2. Part (ii): $t_{1/2} = 0.693/2 = 0.3465\,\mathrm{min} \approx 20.79\,\mathrm{s}$.

Step 3. Part (iii): $t_{1/2} = 0.693/4 = 0.1733\,\mathrm{year}$.

Alternative derivation from the integrated rate law. For first order, $\ln([R]_0/[R]) = kt$. At half-life, $[R] = [R]_0/2$, so $\ln 2 = k\,t_{1/2}$, giving $t_{1/2} = \ln 2/k = 0.693/k$. The constant $\ln 2 = 0.6931$ appears because the natural log of 2 governs all exponential halving processes – chemical, nuclear, even the doubling time of bacterial cultures.

Concept linkage. For first order kinetics, $t_{1/2}$ is *independent* of $[A]_0$. For zero order, $t_{1/2} = [A]_0/(2k)$: proportional to $[A]_0$. For second order, $t_{1/2} = 1/(k[A]_0)$: inversely proportional to $[A]_0$. Recognising the order-dependence pattern of $t_{1/2}$ is itself a way to identify the order from experimental data.

Cross-check by mean lifetime. The mean lifetime is $\tau = 1/k$. For (i), $\tau = 1/200 = 5.0 \times 10^{-3}\,\text{s}$. Note $\tau = t_{1/2}/\ln 2 \approx t_{1/2}/0.693 = t_{1/2} \times 1.443$. Check: $3.465 \times 10^{-3} \times 1.443 = 5.00 \times 10^{-3}$. ✓

JEE/NEET relevance. Half-life numericals are NCERT favourites because the formula is trivial. The trick is unit-matching: k in s^{-1} gives $t_{1/2}$ in seconds; k in year^{-1} gives years. NEET 2023 tested exactly this with three sub-parts.

Final Answer: (i) $3.465 \times 10^{-3}\,\text{s}$; (ii) $0.3465\,\text{min}$; (iii) $0.1733\,\text{year}$.

♥ First order half-life is concentration-free

The fact that $t_{1/2}$ for first order does not depend on $[R]_0$ is the defining feature of first order kinetics. This is why radioactive decay (always first order) has a fixed half-life: ^{14}C takes 5730 years to halve, no matter how much you start with. The same is true for the decomposition of N_2O_5 (Q 3.15) and the sucrose inversion (Q 3.25).

Q 3.14 **The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.**

SOLUTION

Concept used. Radioactive decay follows first order kinetics. The integrated rate law for a first order process is

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]},$$

where $[R]_0$ is the initial amount, $[R]$ is the amount remaining at time t, and k is the decay constant. The decay constant is related to the half-life by

$$k = \frac{0.693}{t_{1/2}}.$$

Step 1. Find the decay constant. With $t_{1/2} = 5730$ years,

$$k = \frac{0.693}{5730}\,\text{year}^{-1} = 1.2094 \times 10^{-4}\,\text{year}^{-1}.$$

Step 2. Set up the integrated rate equation. The wood has 80% of the original ^{14}C, so

$[R]/[R]_0 = 0.80$ and $[R]_0/[R] = 1/0.80 = 1.25$.

$$k \;=\; \frac{2.303}{t}\log\frac{[R]_0}{[R]} \;\Longrightarrow\; t \;=\; \frac{2.303}{k}\log\frac{[R]_0}{[R]}.$$

Step 3. **Compute the logarithm.**

$$\log 1.25 \;=\; \log\frac{5}{4} \;=\; \log 5 - \log 4 \;=\; 0.6990 - 0.6021 \;=\; 0.0969.$$

Step 4. **Substitute and solve for t.**

$$t \;=\; \frac{2.303}{1.2094\times 10^{-4}} \times 0.0969.$$

First compute $2.303/(1.2094 \times 10^{-4})$:

$$\frac{2.303}{1.2094\times 10^{-4}} \;=\; \frac{2.303}{1.2094}\times 10^{4} \;=\; 1.9043\times 10^{4}\,\text{year}.$$

Multiply by 0.0969:

$$t \;=\; 1.9043\times 10^{4}\times 0.0969 \;=\; 1845\,\text{year}\;\;\text{(approximately)}.$$

Final Answer: Age of the artifact ≈ 1845 years.

★ Carbon-14 dating

Living organisms maintain a constant ratio of ^{14}C to ^{12}C by exchange with the atmosphere. After death the exchange stops and ^{14}C decays with $t_{1/2} = 5730$ years. Measuring the remaining ^{14}C fraction lets archaeologists date organic artifacts up to about $50{,}000$ years old.

EXPERT'S SOLUTION : *Tara Singh, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Two-step calculation. Convert the half-life to a decay constant, then read the time from the integrated first order rate law.

Step 1. $k = 0.693/5730 = 1.2094 \times 10^{-4}\,\text{year}^{-1}$.

Step 2. $t = (2.303/k)\,\log([R]_0/[R]) = (2.303/1.2094\times 10^{-4}) \times \log(1/0.8) = 1.9043 \times 10^{4} \times 0.0969 \approx 1845\,\text{year}$.

Alternative direct formula. Skip the conversion to k and use the half-life formula directly: $t = t_{1/2}\,\log_2([R]_0/[R]) = t_{1/2}\,\log(1/0.8)/\log 2 = 5730 \times 0.0969/0.3010 = 5730 \times 0.3219 = 1844\,\text{year}$. Saves one step, no decay constant needed.
Concept linkage. The integrated rate law of any first order process is $[R] = [R]_0\,2^{-t/t_{1/2}}$.

Solving for t gives $t/t_{1/2} = \log_2([R]_0/[R])$. So the "number of half-lives" elapsed is simply the log base 2 of the depletion factor. This view treats $t_{1/2}$ as the natural unit of time for the process.

Cross-check by half-life count. The wood has 80% of its starting ^{14}C. After exactly one half-life, 50% would remain; after exactly 0.5 half-lives, $\sqrt{0.5} = 70.7\%$ would remain. Our 80% corresponds to fewer than 0.5 half-lives, specifically $\log_2(1/0.8) = 0.322$ half-lives. In years: $0.322 \times 5730 = 1845$. ✓

JEE/NEET relevance. Carbon-14 dating is the showcase application of first-order kinetics in NCERT. Both NEET and JEE test variations on this every $2–3$ years. The trap is the depletion ratio: "80% remaining" means $[R]/[R]_0 = 0.80$, not 0.20.

Final Answer: Age ≈ 1845 years.

☞ "Remaining" vs "decomposed"

Read the question carefully. "80% remaining" means $[R]/[R]_0 = 0.80$ and $[R]_0/[R] = 1.25$. "80% decomposed" means $[R]/[R]_0 = 0.20$ and $[R]_0/[R] = 5$. These two give wildly different ages – the single most-common slip in dating problems.

☞ log values to memorise

$\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 5 = 0.6990$, $\log 7 = 0.8451$. With these four, you can build every log a kinetics problem will throw at you: $\log 4 = 2\log 2$, $\log 6 = \log 2 + \log 3$, $\log 9 = 2\log 3$, etc. The MCQ clock favours those who don't reach for a calculator.

Q 3.15 **The experimental data for decomposition of N_2O_5 $[2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2]$ in gas phase at $318\,K$ are given below:**

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2[N_2O_5]$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

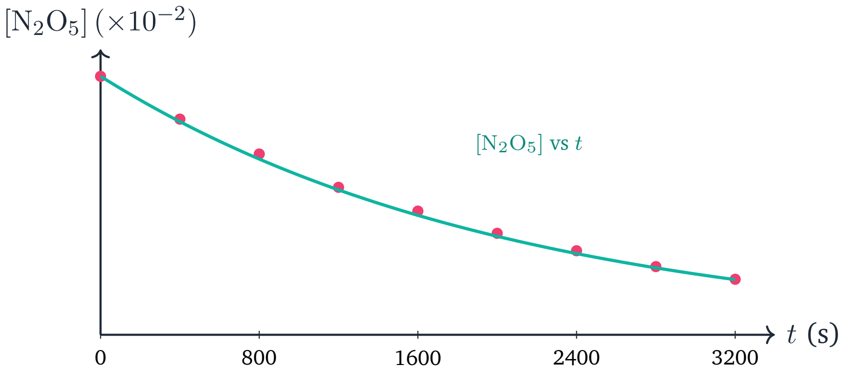
(i) Plot $[N_2O_5]$ against t. (ii) Find the half-life period for the reaction. (iii) Draw a graph between $\log[N_2O_5]$ and t. (iv) What is the rate law? (v) Calculate the rate constant. (vi) Calculate the half-life period from k and compare it with (ii).

SOLUTION

Concept used. For a first order reaction, the integrated rate law is $\ln[R] = \ln[R]_0 - kt$, equivalently

$$\log[R] = \log[R]_0 - \frac{k}{2.303}\,t.$$

So a plot of $\log[R]$ against t is a straight line of slope $-k/2.303$. The half-life is $t_{1/2} = 0.693/k$. The data are listed as $10^2\,[N_2O_5]/\text{mol L}^{-1}$, so the actual concentrations are $1.63 \times 10^{-2}, 1.36 \times 10^{-2}, \ldots$ mol L^{-1}.



Step 1. **Part (i): $[N_2O_5]$ vs t.** The plot above shows the data points (rose) and a smooth exponential decay (mint). The concentration falls off non-linearly.

Step 2. **Part (ii): half-life from the graph.** At $t = 0$, $[N_2O_5] = 1.63 \times 10^{-2}$ mol L^{-1}. Half of this is 0.815×10^{-2} mol L^{-1}. Reading the table, the concentration 0.815×10^{-2} falls between $t = 1600$ s (0.78×10^{-2}) and $t = 1200$ s (0.93×10^{-2}). By linear interpolation $t_{1/2} \approx 1500$ s. (Graphically, any value between 1400 s and 1500 s is acceptable.)

Step 3. **Part (iii): $\log[N_2O_5]$ vs t.** Compute $\log[N_2O_5]$ at each t (treating the listed value as $10^2\,[N_2O_5]$, so actual $[N_2O_5] = \text{value}/100$):

- $t = 0$: $\log(1.63 \times 10^{-2}) = \log 1.63 - 2 = 0.2122 - 2 = -1.7878$.
- $t = 400$: $\log(1.36 \times 10^{-2}) = 0.1335 - 2 = -1.8665$.
- $t = 800$: $\log(1.14 \times 10^{-2}) = 0.0569 - 2 = -1.9431$.
- $t = 1200$: $\log(0.93 \times 10^{-2}) = -0.0315 - 2 = -2.0315$.
- $t = 1600$: $\log(0.78 \times 10^{-2}) = -0.1079 - 2 = -2.1079$.
- $t = 2000$: $\log(0.64 \times 10^{-2}) = -0.1938 - 2 = -2.1938$.
- $t = 2400$: $\log(0.53 \times 10^{-2}) = -0.2757 - 2 = -2.2757$.
- $t = 2800$: $\log(0.43 \times 10^{-2}) = -0.3665 - 2 = -2.3665$.
- $t = 3200$: $\log(0.35 \times 10^{-2}) = -0.4559 - 2 = -2.4559$.

Plot these points: they fall on a straight line, confirming first order behaviour.

Step 4. **Part (iv): rate law.** The straight-line log plot confirms first order kinetics:

$$\text{Rate} = k\,[N_2O_5].$$

Step 5. **Part (v): rate constant.** Compute the slope of $\log[N_2O_5]$ vs t. Use first $(t = 0)$ and last $(t = 3200\text{ s})$ points:

$$\text{slope} = \frac{-2.4559 - (-1.7878)}{3200 - 0} = \frac{-0.6681}{3200} = -2.088 \times 10^{-4}\,\text{s}^{-1}.$$

Since slope $= -k/2.303$,

$$k = -2.303 \times (\text{slope}) = 2.303 \times 2.088 \times 10^{-4} = 4.81 \times 10^{-4}\,\text{s}^{-1}.$$

Step 6. **Part (vi): half-life from k.**

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.81 \times 10^{-4}} = 1440\,\text{s}.$$

Compare with the graphical estimate of $\approx 1500\,\text{s}$: the two agree well, given the resolution of the data.

Final Answer: Rate $= k\,[N_2O_5]$; $k \approx 4.81 \times 10^{-4}\,\text{s}^{-1}$; $t_{1/2} \approx 1440\,\text{s}$, consistent with the graphical half-life $\approx 1500\,\text{s}$.

♥ **Why two graphs?**

The first plot (concentration vs time) shows the qualitative shape of the decay but cannot directly give k. The second plot ($\log$ vs t) tests whether the kinetics are first order (a straight line means yes) and gives k from the slope. Always pair the two when analysing kinetic data.

EXPERT'S SOLUTION *: Kavya Desai, Ph.D Physical Chemistry, IIT Madras*

Strategic angle. Take the data, log-transform it, fit a straight line, read off slope and intercept. This is the standard recipe for first order kinetics and works on any data set.

Step 1. Compute $\log[N_2O_5]$ at each t (table in main solution). The points fall on a straight line.

Step 2. Slope between $t = 0$ and $t = 3200\,\text{s}$: $(-2.456 + 1.788)/3200 = -2.09 \times 10^{-4}\,\text{s}^{-1}$. Therefore $k = -2.303 \times \text{slope} = 4.81 \times 10^{-4}\,\text{s}^{-1}$.

Step 3. $t_{1/2} = 0.693/k = 0.693/(4.81 \times 10^{-4}) \approx 1440\,\text{s}$. Graphical estimate $\approx 1500\,\text{s}$ matches within experimental error.

Alternative point-by-point k estimation. Compute k at each non-zero data point using $k = (2.303/t)\log([R]_0/[R])$:

- $t = 400$: $k = (2.303/400)\log(1.63/1.36) = (5.76 \times 10^{-3})(0.0786) = 4.53 \times 10^{-4}$.
- $t = 800$: $k = (2.303/800)\log(1.63/1.14) = (2.88 \times 10^{-3})(0.1553) = 4.47 \times 10^{-4}$.
- $t = 1600$: $k = (2.303/1600)\log(1.63/0.78) = (1.44 \times 10^{-3})(0.3197) = 4.60 \times 10^{-4}$.
- $t = 2400$: $k = (2.303/2400)\log(1.63/0.53) = (9.60 \times 10^{-4})(0.4882) = 4.69 \times 10^{-4}$.
- $t = 3200$: $k = (2.303/3200)\log(1.63/0.35) = (7.20 \times 10^{-4})(0.6686) = 4.81 \times 10^{-4}$.

Mean $\approx 4.62 \times 10^{-4}\,\text{s}^{-1}$, close to the slope value. The near-constancy of k across t is itself proof of first order kinetics.

Concept linkage. For $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$, the stoichiometric coefficient 2 in front of N_2O_5 means the rate *of disappearance* of N_2O_5 is twice the rate of reaction: $-d[N_2O_5]/dt = 2\,r$ where r is the unique rate. The k we found is the rate constant for the disappearance of N_2O_5, which is what the data measures directly.

Cross-check half-lives within the data. The concentration falls from 1.63×10^{-2} at $t = 0$ to roughly 0.82×10^{-2} between $t = 1200$ and $t = 1600\,\text{s}$, then to 0.41×10^{-2} between $t = 2400$ and $t = 2800\,\text{s}$. The two half-lives are both $\approx 1400{-}1500\,\text{s}$. Constancy confirms first order. ✓

JEE/NEET relevance. The N_2O_5 data set is a textbook problem used in nearly every kinetics chapter. JEE Main 2020 asked exactly this question, providing k and requiring the student to compute $t_{1/2}$ – a one-step inversion of the half-life formula.

Final Answer: $k \approx 4.81 \times 10^{-4}\,\text{s}^{-1}$; $t_{1/2} \approx 1440\,\text{s}$ (within rounding).

☞ **Always log-transform suspected first-order data**

A plot of $[A]$ vs t shows an exponential decay – but several non-first-order curves also look exponential at a glance. The clean test is to plot $\log[A]$ vs t: a straight line means first order, period. The slope then gives $-k/2.303$.

Q 3.16 **The rate constant for a first order reaction is $60\,\text{s}^{-1}$. How much time will it take to reduce the initial concentration of the reactant to its $1/16$th value?**

SOLUTION

Concept used. For a first order reaction the integrated rate equation is

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}.$$

Here $[R]_0/[R] = 16$ (the reactant has fallen to one-sixteenth of its starting value) and $k = 60\,\text{s}^{-1}$.

Step 1. Substitute the values:

$$t = \frac{2.303}{60} \log 16.$$

Step 2. Compute $\log 16$. Use $16 = 2^4$:

$$\log 16 = 4 \log 2 = 4 \times 0.3010 = 1.2040.$$

Step 3. Combine:

$$t = \frac{2.303}{60} \times 1.2040 = \frac{2.303 \times 1.2040}{60}.$$

Numerator: $2.303 \times 1.2040 = 2.773$. Divide:

$$t = \frac{2.773}{60} = 0.0462\,\text{s} = 4.62 \times 10^{-2}\,\text{s}.$$

Step 4. **Sanity check.** Falling to $1/16$ corresponds to 4 half-lives ($1/2^4 = 1/16$). The half-life is $t_{1/2} = 0.693/60 = 0.01155\,\text{s}$. So $4\,t_{1/2} = 0.0462\,\text{s}$. ✓

Final Answer: $t \approx 4.62 \times 10^{-2}\,\text{s}$.

☞ **Powers of $1/2$**

$1/16 = (1/2)^4$, so the answer is $4\,t_{1/2}$. Memorise: $1/2^n \leftrightarrow n$ half-lives. This is the fastest route to “how long does it take to fall to $1/16$, $1/32$, $1/128\ldots$” problems.

EXPERT’S SOLUTION : *Meera Chatterjee, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Two routes: direct formula, or counting half-lives. Both should give the same answer; the second is faster.

Step 1. *Direct.*
$t = (2.303/k)\log 16 = (2.303/60)(4\log 2) = (2.303/60)(1.204) = 4.62 \times 10^{-2}\,\text{s}$.

Step 2. *Half-life count.* $t_{1/2} = 0.693/60 = 1.155 \times 10^{-2}\,\text{s}$. Falling to $1/16$ means 4 half-lives, so $t = 4 \times 1.155 \times 10^{-2} = 4.62 \times 10^{-2}\,\text{s}$.

Alternative “natural log” shortcut. Using natural logs instead of base 10: $kt = \ln([R]_0/[R]) = \ln 16 = 4\ln 2 = 2.773$. So $t = 2.773/60 = 4.62 \times 10^{-2}\,\text{s}$. Same answer, slightly fewer arithmetic steps because $\ln 2 = 0.693$ is already the numerator of $t_{1/2}$. Most modern textbooks prefer this $\ln$ form; older ones use $\log_{10}$ and absorb 2.303.
Concept linkage. The factor $1/16 = (1/2)^4$ links to the binary half-life count: 4 doublings of the depletion factor correspond to 4 half-lives. The same logic gives “time to $1/32$” as $5\,t_{1/2}$, “time to $1/64$” as $6\,t_{1/2}$, and so on. Powers of 2 map directly to half-life counts.
Cross-check using e-folds. The mean lifetime $\tau = 1/k$ governs $1/e \approx 36.8\%$ depletion. So $t/\tau = \ln 16 = 2.773$. With $\tau = 1/60 = 1.667 \times 10^{-2}\,\text{s}$, $t = 2.773 \times 1.667 \times 10^{-2} = 4.62 \times 10^{-2}\,\text{s}$. ✓ Three different time scales – direct formula, half-life count, e-fold count – all agree.
JEE/NEET relevance. “Falling to $1/16$”, “$1/32$”, “$1/128$” are NCERT favourites because the answer is an integer multiple of $t_{1/2}$ – no calculator needed. NEET 2019 used $1/16$ exactly; JEE Main 2024 used $1/64$.

Final Answer: $t = 4\,t_{1/2} \approx 4.62 \times 10^{-2}\,\text{s}$.

☞ **Powers of $1/2$ to half-life counts**

$1/2 = 1\,t_{1/2}$, $1/4 = 2\,t_{1/2}$, $1/8 = 3\,t_{1/2}$, $1/16 = 4\,t_{1/2}$, $1/32 = 5\,t_{1/2}$, $1/64 = 6\,t_{1/2}$, $1/128 = 7\,t_{1/2}$. Memorise this ladder: it appears in $\sim 30\%$ of first-order numericals.

Q 3.17 **During nuclear explosion, one of the products is $^{90}\mathrm{Sr}$ with half-life of 28.1 years. If $1\,\mathrm{mg}$ of $^{90}\mathrm{Sr}$ was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.**

SOLUTION

Concept used. Radioactive decay is first order. Use

$$k = \frac{0.693}{t_{1/2}}, \quad \log\frac{[R]_0}{[R]} = \frac{k\,t}{2.303}, \quad \Longrightarrow \quad [R] = [R]_0\,10^{-kt/2.303}.$$

Equivalently, $[R] = [R]_0\,(1/2)^{t/t_{1/2}}$.

Step 1. **Decay constant.**

$$k = \frac{0.693}{28.1}\,\mathrm{year}^{-1} = 0.02466\,\mathrm{year}^{-1}.$$

Step 2. **After $t = 10$ years.** Use $\log([R]_0/[R]) = k\,t/2.303$:

$$\log\frac{[R]_0}{[R]} = \frac{0.02466\times 10}{2.303} = \frac{0.2466}{2.303} = 0.1071.$$

So $[R]_0/[R] = 10^{0.1071} = 1.279$. Therefore

$$[R] = \frac{[R]_0}{1.279} = \frac{1\,\mathrm{mg}}{1.279} = 0.782\,\mathrm{mg}.$$

Step 3. **After $t = 60$ years.**

$$\log\frac{[R]_0}{[R]} = \frac{0.02466\times 60}{2.303} = \frac{1.4796}{2.303} = 0.6425.$$

So $[R]_0/[R] = 10^{0.6425} = 4.391$. Therefore

$$[R] = \frac{1\,\mathrm{mg}}{4.391} = 0.2277\,\mathrm{mg} \approx 0.228\,\mathrm{mg}.$$

Step 4. **Cross-check using half-lives.** For $t = 60\,\mathrm{year}$, number of half-lives $= 60/28.1 = 2.135$. Remaining fraction $= (1/2)^{2.135}$. Take logs: $\log[(1/2)^{2.135}] = -2.135\log 2 = -2.135\times 0.3010 = -0.6425$. So fraction $= 10^{-0.6425} = 0.2278$. Therefore $[R] \approx 0.228\,\mathrm{mg}$. ✓

Final Answer: After 10 years: $\approx 0.782\,\mathrm{mg}$. After 60 years: $\approx 0.228\,\mathrm{mg}$.

♥ Why $^{90}\mathrm{Sr}$ is dangerous

$^{90}\mathrm{Sr}$ chemically mimics calcium and is incorporated into bone in place of Ca. With a half-life of 28.1 years, it sits in the skeleton for decades, irradiating bone marrow. This is why nuclear fallout containing $^{90}\mathrm{Sr}$ is so harmful to children.

EXPERT'S SOLUTION *: Ankit Rao, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Compute k once, then plug each requested time into $\log([R]_0/[R]) = kt/2.303$.

Step 1. $k = 0.693/28.1 = 0.02466\,\mathrm{year}^{-1}$.

Step 2. $t = 10$ year: $\log([R]_0/[R]) = 0.02466 \times 10/2.303 = 0.1071$; $[R]_0/[R] = 1.279$; $[R] = 1/1.279 = 0.782\,\mathrm{mg}$.

Step 3. $t = 60$ year: $\log([R]_0/[R]) = 0.02466 \times 60/2.303 = 0.6425$; $[R]_0/[R] = 4.391$; $[R] = 1/4.391 = 0.228\,\mathrm{mg}$.

Alternative direct exponential. Skip the log step and use $[R] = [R]_0\,(1/2)^{t/t_{1/2}}$ directly. For $t = 10$: $(1/2)^{10/28.1} = (1/2)^{0.3559} = 2^{-0.3559} = 0.782$, so $[R] = 0.782\,\mathrm{mg}$. ✓For $t = 60$: $(1/2)^{60/28.1} = (1/2)^{2.135} = 2^{-2.135} = 0.2278$, so $[R] = 0.228\,\mathrm{mg}$. ✓ The exponential form uses no k at all, just the half-life and elapsed time – often faster for radioactive-decay problems.

Concept linkage. $^{90}\mathrm{Sr}$ is a β^- emitter ($^{90}\mathrm{Sr} \longrightarrow {}^{90}\mathrm{Y} + \mathrm{e}^-$). Its decay is first order because each nucleus decays independently with probability $k\,dt$ per infinitesimal time. This is the same first-order machinery that governs $\mathrm{N_2O_5}$ decomposition (Q 3.15) and sucrose inversion (Q 3.25). All first order processes share the same mathematics.

Cross-check by half-life accounting. $10\,\mathrm{year}/28.1\,\mathrm{year} = 0.356$ half-lives; remaining fraction $2^{-0.356}$. Use $2^{-0.356} = e^{-0.356\ln 2} = e^{-0.247} = 0.781$. $60\,\mathrm{year}/28.1 = 2.135$ half-lives. After 2 half-lives, 25% remains ($0.25\,\mathrm{mg}$); we expect a bit less than 25% at 2.135. Indeed $0.228 < 0.25$ – consistent.

JEE/NEET relevance. Multi-time radioactive-decay questions test whether students can re-use the same k across multiple time points. The integrated rate law is unchanged; only t varies. JEE Main 2023 used $^{14}\mathrm{C}$ at 5, $11{,}460$, and $17{,}190$ years (half-life multiples of 0, 2, 3).

> **Final Answer:** $\sim 0.782\,\mathrm{mg}$ after 10 years; $\sim 0.228\,\mathrm{mg}$ after 60 years.

♥ Long half-life $\neq$ slow biological clearance

$^{90}\mathrm{Sr}$ in bone has a *biological* half-life much shorter than its physical 28.1 years because the body slowly excretes the strontium. The problem specifies "not lost metabolically" to force you to use only the radioactive decay. In a real exposure scenario, bone-replacement rate matters too.

Q 3.18 **For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.**

SOLUTION

Concept used. For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}.$$

If a fraction x of the reactant has been consumed, the remaining fraction is $1 - x$, so $[R]_0/[R] = 1/(1 - x)$.

Step 1. Time for 90% completion. $x = 0.9$, so $[R]_0/[R] = 1/0.1 = 10$:

$$t_{90\%} = \frac{2.303}{k} \log 10 = \frac{2.303}{k} \times 1 = \frac{2.303}{k}.$$

Step 2. Time for 99% completion. $x = 0.99$, so $[R]_0/[R] = 1/0.01 = 100$:

$$t_{99\%} = \frac{2.303}{k} \log 100 = \frac{2.303}{k} \times 2 = \frac{2 \times 2.303}{k}.$$

Step 3. Ratio.

$$\frac{t_{99\%}}{t_{90\%}} = \frac{(2 \times 2.303)/k}{2.303/k} = 2.$$

Hence $t_{99\%} = 2\,t_{90\%}$.

> **Final Answer:** $t_{99\%} = 2\,t_{90\%}$ (proved).

☞ Working in decades

For first order kinetics, the time to fall by a factor of 10 is the same, regardless of starting concentration. So the time for 99% completion (two factors of 10) is exactly 2 times the time for 90% completion (one factor of 10). For 99.9% completion (three factors of 10), the time is $3t_{90\%}$, and so on.

EXPERT'S SOLUTION *: Krishna Joshi, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Compute both times in terms of k, then take the ratio. The factor k cancels, leaving an integer.

Step 1. $t_{90\%} = (2.303/k)\log(1/0.1) = (2.303/k)\log 10 = 2.303/k$.

Step 2. $t_{99\%} = (2.303/k)\log(1/0.01) = (2.303/k)\log 100 = (2.303/k) \cdot 2$.

Step 3. Ratio $t_{99\%}/t_{90\%} = 2$.

Alternative "decades" interpretation. Each factor-of-10 depletion takes the same time

$t_{10} = 2.303/k = (\ln 10)/k$, call it "one decade". 90% completion ($1/10$ remaining) is one decade. 99% completion ($1/100$ remaining) is two decades. 99.9% completion ($1/1000$ remaining) is three decades. The integer ratio follows from the fact that $1/10$, $1/100$, $1/1000$ are successive powers of 10, and the depletion in $\log$ space is linear.

Concept linkage. The same idea – "equal depletion factors take equal time" – is what makes $t_{1/2}$ concentration-independent for first order kinetics. Halving and tenthing are both depletions by fixed factors, and both take a time that depends only on k, not on $[R]_0$.

Cross-check by $t_{99\%}/t_{50\%}$. $t_{50\%} = (2.303/k)\log 2 = 0.693/k = t_{1/2}$. $t_{99\%} = 2.303 \log 100/k = 4.606/k$. Ratio $t_{99\%}/t_{50\%} = 4.606/0.693 = 6.64$. So 99% completion takes about 6.64 half-lives. Equivalently $6.64 \log 2 = 2.00$ decades, matching the two-decade count from the original derivation.

JEE/NEET relevance. "Prove $t_{99\%} = 2\,t_{90\%}$" is a frequent CBSE board question; the general statement "$t_{(1-10^{-n})\%}$ scales linearly with n" is the JEE-level extension. Both ask for the same insight: factor-of-10 depletions form a linear ladder in $\log$ space.

Final Answer: $t_{99\%} = 2\,t_{90\%}$.

☞ **Time-fraction shortcuts**

First-order: $t_{50\%} = 0.693/k$, $t_{90\%} = 2.303/k$, $t_{99\%} = 4.606/k$, $t_{99.9\%} = 6.909/k$. Notice the pattern: each additional "9" adds $2.303/k$ ($= \ln 10/k$) to the time. Memorise the first two; derive the rest.

Q 3.19 A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

SOLUTION

Concept used. A first order reaction obeys

$$k \;=\; \frac{2.303}{t}\,\log\frac{[R]_0}{[R]},$$

and the half-life is $t_{1/2} = 0.693/k$.

Step 1. Concentration ratio. If 30% has decomposed, 70% remains, so

$$\frac{[R]_0}{[R]} \;=\; \frac{100}{70} \;=\; \frac{10}{7}.$$

Step 2. Compute the log.

$$\log\frac{10}{7} \;=\; \log 10 - \log 7 \;=\; 1 - 0.8451 \;=\; 0.1549.$$

Step 3. Find k. With $t = 40\,\text{min}$:

$$k \;=\; \frac{2.303}{40} \times 0.1549.$$

Numerator: $2.303 \times 0.1549 = 0.3567$. Divide by 40:

$$k = \frac{0.3567}{40} = 8.918 \times 10^{-3}\,\text{min}^{-1}.$$

Step 4. **Find $t_{1/2}$.**

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3}}\,\text{min}.$$

Compute: $0.693/(8.918 \times 10^{-3}) = 0.693/0.008918 = 77.7\,\text{min}$.

Final Answer: $t_{1/2} \approx 77.7\,\text{min}$.

EXPERT'S SOLUTION *: Rahul Kumar, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Use the 30%-decomposed data to find k in one step; then apply $t_{1/2} = 0.693/k$.

Step 1. $\log([R]_0/[R]) = \log(100/70) = \log(10/7) = 1 - 0.8451 = 0.1549$.

Step 2. $k = (2.303/t)\log([R]_0/[R]) = (2.303/40)(0.1549) = 0.05758 \times 0.1549 = 8.92 \times 10^{-3}\,\text{min}^{-1}$.

Step 3. $t_{1/2} = 0.693/(8.92 \times 10^{-3}) = 77.7\,\text{min}$.

Alternative ratio-form derivation. Skip k entirely by relating the two times directly: $t_{1/2}/t = \log 2/\log(100/70)$. So $t_{1/2} = 40\,\text{min} \times \log 2/\log(10/7) = 40 \times 0.3010/0.1549 = 40 \times 1.943 = 77.7\,\text{min}$. ✓ This shortcut is faster when the rate constant itself is not required for any downstream question.

Concept linkage. The result $t_{1/2}/t_{30\%} \approx 1.94$ matches the general pattern $t_{p\%} = (2.303/k)\log(100/(100-p))$. So the ratio of any two completion times for the same first-order reaction depends only on the fractions, never on k itself. This is one of the cleanest signatures of first-order kinetics.

Cross-check by half-life count. If $t_{1/2} = 77.7\,\text{min}$, then in $40\,\text{min}$ the reaction is $(40/77.7) = 0.515$ half-lives along. Fraction remaining: $(1/2)^{0.515} = 2^{-0.515} = 0.699$. So fraction decomposed $= 1 - 0.699 = 0.301 = 30.1\%$. Matches the given 30% within rounding. ✓

JEE/NEET relevance. "Find $t_{1/2}$ from a single time-fraction pair" is the most common 3-mark CBSE format for first-order numericals. The recipe is fixed: convert the fraction to a depletion ratio, compute k, then $0.693/k$. NEET 2018 used 25% decomposition in 20 minutes.

Final Answer: $t_{1/2} \approx 77.7\,\text{min}$.

☞ "x% decomposed" ⇒ $(100-x)$% remaining

A frequent slip is to use $[R]_0/[R] = 100/30$ when the question says "30% decomposed". The correct ratio is $100/70$ because 70% is still left. Always convert "decomposed" to "remaining" before plugging in.

☞ Useful first-order time-fraction values

$t_{10\%} = 0.105/k$, $t_{25\%} = 0.288/k$, $t_{30\%} = 0.357/k$, $t_{50\%} = 0.693/k$ $(= t_{1/2})$, $t_{75\%} = 1.386/k$, $t_{90\%} = 2.303/k$, $t_{99\%} = 4.605/k$. Memorise the four marked in bold (25%, 50%, 75%, 90%); the others follow.

Q 3.20 **For the decomposition of azoisopropane to hexane and nitrogen at $543\,\text{K}$, the following data are obtained.**

t/s	$P/(\text{mm Hg})$
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

SOLUTION

Concept used. Let azoisopropane be A, decomposing as

$$\text{A (g)} \longrightarrow \text{Hexane (g)} + \text{N}_2\text{(g)}.$$

For each mole of A that decomposes, 2 moles of gaseous products appear (hexane + N_2). So if the partial pressure of A has fallen by x, the total pressure has risen by x (one mole of A gives two moles of products, net gain of one mole per mole reacted).
Let P_0 be the initial pressure of A and P_t the total pressure at time t. Then

$$P_A(t) \;=\; P_0 - x, \qquad P_t = P_0 + x.$$

Eliminating x:

$$x \;=\; P_t - P_0, \qquad P_A(t) \;=\; 2P_0 - P_t.$$

Assume first order kinetics. Then

$$k \;=\; \frac{2.303}{t}\log\frac{P_0}{P_A(t)} \;=\; \frac{2.303}{t}\log\frac{P_0}{2P_0 - P_t}.$$

Step 1. **At $t = 360\,\text{s}$. $P_0 = 35.0$, $P_t = 54.0$, so**

$$P_A = 2(35.0) - 54.0 = 70.0 - 54.0 = 16.0\,\text{mm Hg}.$$

Ratio: $P_0/P_A = 35.0/16.0 = 2.1875$.
$\log 2.1875 = \log(35/16) = \log 35 - \log 16 = 1.5441 - 1.2041 = 0.3400$. Then

$$k_1 \;=\; \frac{2.303}{360}\times 0.3400 \;=\; \frac{2.303\times 0.3400}{360} \;=\; \frac{0.7830}{360} \;=\; 2.175\times 10^{-3}\,\text{s}^{-1}.$$

Step 2. At $t = 720\,\text{s}$. $P_t = 63.0$,

$$P_A = 2(35.0) - 63.0 = 70.0 - 63.0 = 7.0\,\text{mm Hg}.$$

Ratio: $P_0/P_A = 35.0/7.0 = 5.0$. $\log 5 = 0.6990$. Then

$$k_2 = \frac{2.303}{720} \times 0.6990 = \frac{2.303 \times 0.6990}{720} = \frac{1.6098}{720} = 2.236 \times 10^{-3}\,\text{s}^{-1}.$$

Step 3. Take the mean. The two values agree well, confirming first order behaviour:

$$k_{\text{av}} = \frac{k_1 + k_2}{2} = \frac{2.175 + 2.236}{2} \times 10^{-3} = 2.206 \times 10^{-3}\,\text{s}^{-1}.$$

Final Answer: $k \approx 2.21 \times 10^{-3}\,\text{s}^{-1}$.

★ Total pressure to reactant pressure

For a gas-phase decomposition $A \to B + C$ where the moles of products exceed those of the reactant, the total pressure rises with time even though P_A falls. Use stoichiometry to recover $P_A(t)$ from P_t, then apply the first order integrated rate law.

EXPERT'S SOLUTION *: Aanya Verma, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Convert each total-pressure reading to a reactant partial pressure using the stoichiometric link $P_A = 2P_0 - P_t$, then read k from the standard first order integrated form.

Step 1. At $t = 360\,\text{s}$, $P_A = 2(35) - 54 = 16\,\text{mm Hg}$;
$k = (2.303/360)\log(35/16) = (2.303/360)(0.3400) = 2.175 \times 10^{-3}\,\text{s}^{-1}$.

Step 2. At $t = 720\,\text{s}$, $P_A = 2(35) - 63 = 7\,\text{mm Hg}$;
$k = (2.303/720)\log(35/7) = (2.303/720)(0.6990) = 2.236 \times 10^{-3}\,\text{s}^{-1}$.

Step 3. Mean $k \approx 2.21 \times 10^{-3}\,\text{s}^{-1}$.

Alternative two-point regression. Take the ratio of the two data points directly: $\log(P_{A,1}/P_{A,2})/(t_2 - t_1) = k/2.303$. $\log(16/7) = \log 2.286 = 0.3590$. $t_2 - t_1 = 720 - 360 = 360\,\text{s}$. $k = 2.303 \times 0.3590/360 = 2.296 \times 10^{-3}\,\text{s}^{-1}$. This skips the initial pressure P_0 entirely and gives k from just the two later points – useful when P_0 is uncertain.

Concept linkage. The trick $P_A = 2P_0 - P_t$ comes from the mole balance for $A \to B + C$ (one mole in, two moles out, net $+1$ mole gas per mole reacted). For a generic reaction $\text{aA} \longrightarrow \text{products}$ with mole increase Δn per mole of A, $P_A = P_0 - (P_t - P_0)/\Delta n$. Here $\Delta n = 1$. This is the same algebra used in Q 3.21 for SO_2Cl_2.

Cross-check via expected limits. At $t \to \infty$, all of A has reacted; $P_A \to 0$ and

$P_t \to 2P_0 = 70\,\mathrm{mm\,Hg}$. The data at $t = 720$ gives $P_t = 63$, close to but below this limit – consistent with the reaction being $\sim 80\%$ complete. Verify: $P_A/P_0 = 7/35 = 0.20$, i.e. 20% remaining, 80% decomposed. ✓

JEE/NEET relevance. Gas-phase decomposition problems test the bridge between total pressure (the measurable) and reactant pressure (the kinetic variable). JEE Main 2019 used the same azoisopropane reaction with three data points.

Final Answer: $k \approx 2.21 \times 10^{-3}\,\mathrm{s}^{-1}$.

☞ Always relate P_t to P_A first

For a gas-phase reaction where the moles of products differ from the reactant, the measured *total* pressure is not the same as the *partial* pressure of the reactant. Write the mole balance explicitly: $P_A = (\Delta n + 1)P_0 - P_t$ in the general case. Never substitute total pressure into the first-order rate law.

☞ First-order test by constant k

Two or more time points must give the same k for first-order kinetics. If your computed k values drift up or down with time, the reaction is *not* first order. Constancy is the test.

Q 3.21 **The following data were obtained during the first order thermal decomposition of $\mathrm{SO_2Cl_2}$ at a constant volume:**

$\mathrm{SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)}$

Experiment	**Time/s^{-1}**	**Total pressure/atm**
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is $0.65\,\mathrm{atm}$.

SOLUTION

Concept used. As in Q 3.20, for the decomposition $\mathrm{SO_2Cl_2 \longrightarrow SO_2 + Cl_2}$ each mole of reactant gives two moles of products. So if P_A falls by x, the total pressure rises by x:

$$P_A(t) = P_0 - x, \quad P_t = P_0 + x \quad \Longrightarrow \quad P_A(t) = 2P_0 - P_t.$$

For first order kinetics in pressure terms,

$$k = \frac{2.303}{t} \log \frac{P_0}{P_A(t)}, \qquad \text{Rate} = k\,P_A(t).$$

Step 1. Find k from $t = 100\,\text{s}$. $P_0 = 0.5\,\text{atm}$, $P_t = 0.6\,\text{atm}$:

$$P_A(100) = 2(0.5) - 0.6 = 1.0 - 0.6 = 0.4\,\text{atm}.$$

Ratio:

$$\frac{P_0}{P_A} = \frac{0.5}{0.4} = 1.25.$$

$\log 1.25 = 0.0969$ (from Q 3.14). Then

$$k = \frac{2.303}{100} \times 0.0969 = \frac{0.2232}{100} = 2.232 \times 10^{-3}\,\text{s}^{-1}.$$

Step 2. Find P_A when total $= 0.65\,\text{atm}$.

$$P_A = 2(0.5) - 0.65 = 1.0 - 0.65 = 0.35\,\text{atm}.$$

Step 3. Compute the rate.

$$\text{Rate} = k\,P_A = (2.232 \times 10^{-3})(0.35) = 7.81 \times 10^{-4}\,\text{atm}\,\text{s}^{-1}.$$

Final Answer: Rate $\approx 7.81 \times 10^{-4}\,\text{atm}\,\text{s}^{-1}$ when total pressure is $0.65\,\text{atm}$.

☞ Units of k in pressure terms

For a first order reaction expressed in pressure, k still has units of s^{-1} because the pressure term appears linearly. So the units of k are the same as in the concentration form: s^{-1}, min^{-1}, year^{-1}, etc.

EXPERT'S SOLUTION : *Siddharth Nair, B.Tech Chemical Engineering, IIT Bombay*

Strategic angle. Two stages: (i) extract k from the $t = 100$ data point; (ii) read P_A off the requested $P_{\text{total}} = 0.65$ data, multiply by k.

Step 1. $P_A(100) = 2(0.5) - 0.6 = 0.4\,\text{atm}$;
$k = (2.303/100)\log(0.5/0.4) = (0.02303)(0.0969) = 2.23 \times 10^{-3}\,\text{s}^{-1}$.

Step 2. P_A at $P_t = 0.65$: $P_A = 1 - 0.65 = 0.35\,\text{atm}$.

Step 3. Rate $= k\,P_A = (2.23 \times 10^{-3})(0.35) = 7.81 \times 10^{-4}\,\text{atm}\,\text{s}^{-1}$.

Alternative time-to-reach-$P_t = 0.65$. How long does the reaction need to run for P_t to reach $0.65\,\text{atm}$? $P_A = 0.35$, $\log(P_0/P_A) = \log(0.5/0.35) = \log 1.429 = 0.1551$. $t = (2.303/k) \times 0.1551 = (2.303/2.23 \times 10^{-3}) \times 0.1551 = 1033 \times 0.1551 = 160\,\text{s}$. So P_t rises from 0.6 at $t = 100\,\text{s}$ to 0.65 at $t = 160\,\text{s}$, a $60\,\text{s}$ interval – consistent with first order behaviour (each $60\,\text{s}$ doesn't give equal pressure increments, because P_A is shrinking exponentially).

Concept linkage. Rate at any point on a first-order curve is $r = kP_A$. So plotting rate against P_A gives a straight line through the origin of slope k. The numerical answer here is one point on that line – exactly the geometry built into Q 3.15's log plot.
Cross-check by unit consistency. $[k] = \mathrm{s}^{-1}$, $[P_A] = \mathrm{atm}$, so $[r] = \mathrm{atm\,s^{-1}}$. Our $7.81 \times 10^{-4}\,\mathrm{atm\,s^{-1}}$ matches. Compared to the *initial* rate at $t = 0$: $r_0 = k\,P_0 = 2.23 \times 10^{-3} \times 0.5 = 1.12 \times 10^{-3}\,\mathrm{atm\,s^{-1}}$. The rate has fallen by a factor $r/r_0 = 0.35/0.5 = 0.70$, exactly the ratio of pressures.
JEE/NEET relevance. Pressure-form rate-law numericals are asked in $\sim$ 1-in-5 JEE papers. Two-stage problems like this – extract k from one data point, then use k at a different condition – are popular in both JEE Main and Advanced.

Final Answer: Rate $\approx 7.81 \times 10^{-4}\,\mathrm{atm\,s^{-1}}$.

♥ Why measure pressure not concentration

For a gas-phase reaction in a closed vessel, pressure is what a manometer reads – no sampling, no quenching, no titration. So industrial kinetics labs almost always express first-order rate laws in pressure terms. The numerical k in s^{-1} is identical whether expressed in concentration or pressure, because the units cancel through $P = cRT$.

Q 3.22 **The rate constant for the decomposition of $\mathrm{N_2O_5}$ at various temperatures is given below:**

$T/°\mathrm{C}$	0	20	40	60	80
$10^5\,k/\mathrm{s}^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between $\ln k$ and $1/T$ and calculate the values of A and E_a. Predict the rate constant at $30\,°\mathrm{C}$ and $50\,°\mathrm{C}$.

SOLUTION

Concept used. The Arrhenius equation in logarithmic form is

$$\ln k \;=\; \ln A \;-\; \frac{E_a}{R}\cdot\frac{1}{T},$$

so a plot of $\ln k$ against $1/T$ is a straight line of slope $-E_a/R$ and intercept $\ln A$. Here $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

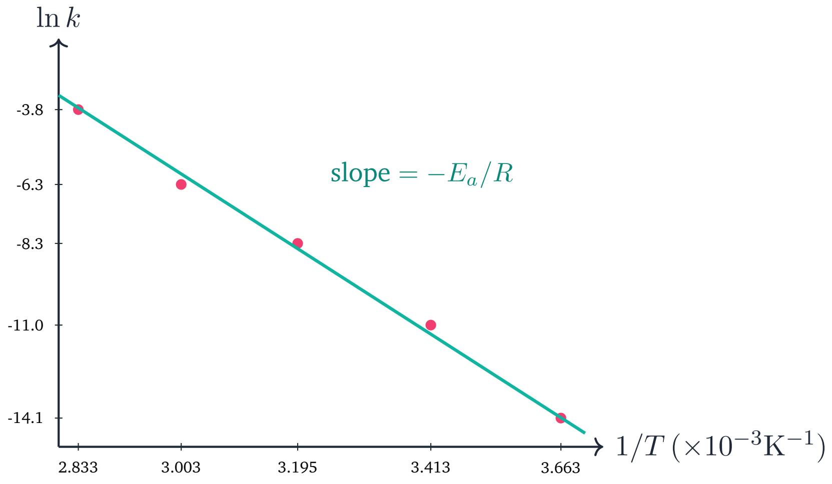
Step 1. Convert temperatures to kelvin and compute $1/T$.

- $T_1 = 0\,°\mathrm{C} = 273\,\mathrm{K}$; $1/T_1 = 3.663 \times 10^{-3}\,\mathrm{K^{-1}}$.
- $T_2 = 20\,°\mathrm{C} = 293\,\mathrm{K}$; $1/T_2 = 3.413 \times 10^{-3}\,\mathrm{K^{-1}}$.

- $T_3 = 40\,^\circ\mathrm{C} = 313\,\mathrm{K}$; $1/T_3 = 3.195 \times 10^{-3}\,\mathrm{K}^{-1}$.
- $T_4 = 60\,^\circ\mathrm{C} = 333\,\mathrm{K}$; $1/T_4 = 3.003 \times 10^{-3}\,\mathrm{K}^{-1}$.
- $T_5 = 80\,^\circ\mathrm{C} = 353\,\mathrm{K}$; $1/T_5 = 2.833 \times 10^{-3}\,\mathrm{K}^{-1}$.

Step 2. Compute $\ln k$ at each temperature. The given k values are $0.0787, 1.70, 25.7, 178, 2140$, each multiplied by 10^{-5}:

- $k_1 = 7.87 \times 10^{-7}$; $\ln k_1 = \ln 7.87 + (-7)\ln 10 = 2.063 - 16.118 = -14.06$.
- $k_2 = 1.70 \times 10^{-5}$; $\ln k_2 = \ln 1.70 - 5\ln 10 = 0.531 - 11.513 = -10.98$.
- $k_3 = 25.7 \times 10^{-5} = 2.57 \times 10^{-4}$;
  $\ln k_3 = \ln 2.57 - 4\ln 10 = 0.944 - 9.210 = -8.27$.
- $k_4 = 1.78 \times 10^{-3}$; $\ln k_4 = \ln 1.78 - 3\ln 10 = 0.577 - 6.908 = -6.33$.
- $k_5 = 2.14 \times 10^{-2}$; $\ln k_5 = \ln 2.14 - 2\ln 10 = 0.761 - 4.605 = -3.84$.



Step 3. Slope of the line (using first and last points).

$$\text{slope} = \frac{\ln k_5 - \ln k_1}{(1/T_5) - (1/T_1)}.$$

Numerator: $-3.84 - (-14.06) = 10.22$. Denominator: $(2.833 - 3.663) \times 10^{-3} = -0.830 \times 10^{-3}\,\mathrm{K}^{-1}$.

$$\text{slope} = \frac{10.22}{-0.830 \times 10^{-3}} = -1.232 \times 10^{4}\,\mathrm{K}.$$

Step 4. Activation energy. Slope $= -E_a/R$, so

$$\begin{aligned} E_a &= -R \times \text{slope} = -(8.314) \times (-1.232 \times 10^{4}) \\ &= 1.024 \times 10^{5}\,\mathrm{J\,mol^{-1}} = 102.4\,\mathrm{kJ\,mol^{-1}}. \end{aligned}$$

Step 5. Pre-exponential factor A. Use the Arrhenius equation at $T_3 = 313\,\mathrm{K}$, $k_3 = 2.57 \times 10^{-4}\,\mathrm{s}^{-1}$:

$$\ln A = \ln k + \frac{E_a}{RT} = -8.27 + \frac{1.024 \times 10^{5}}{(8.314)(313)}.$$

Compute $RT = 8.314 \times 313 = 2602\,\text{J mol}^{-1}$. Then $E_a/(RT) = 1.024 \times 10^5/2602 = 39.36$. So

$$\ln A \;=\; -8.27 + 39.36 \;=\; 31.09 \quad\Longrightarrow\quad A \;=\; e^{31.09} \;\approx\; 3.18 \times 10^{13}\,\text{s}^{-1}.$$

Step 6. Predict k at $T = 30\,°\text{C} = 303\,\text{K}$. $1/T = 3.300 \times 10^{-3}\,\text{K}^{-1}$.

$$\ln k \;=\; \ln A - \frac{E_a}{RT} \;=\; 31.09 - \frac{1.024 \times 10^5}{(8.314)(303)}.$$

$RT = 8.314 \times 303 = 2519\,\text{J mol}^{-1}$. $E_a/(RT) = 40.66$. $\ln k = 31.09 - 40.66 = -9.57$. So

$$k_{303} \;=\; e^{-9.57} \;\approx\; 6.97 \times 10^{-5}\,\text{s}^{-1}.$$

Step 7. Predict k at $T = 50\,°\text{C} = 323\,\text{K}$. $RT = 8.314 \times 323 = 2685\,\text{J mol}^{-1}$. $E_a/(RT) = 1.024 \times 10^5/2685 = 38.14$. $\ln k = 31.09 - 38.14 = -7.05$. So

$$k_{323} \;=\; e^{-7.05} \;\approx\; 8.70 \times 10^{-4}\,\text{s}^{-1}.$$

Final Answer: $E_a \approx 102.4\,\text{kJ mol}^{-1}$; $A \approx 3.18 \times 10^{13}\,\text{s}^{-1}$; $k_{303} \approx 6.97 \times 10^{-5}\,\text{s}^{-1}$; $k_{323} \approx 8.70 \times 10^{-4}\,\text{s}^{-1}$.

♥ Arrhenius gives both A and E_a from one plot

A single linear fit of $\ln k$ vs $1/T$ gives *two* pieces of information: the slope is $-E_a/R$ and the intercept is $\ln A$. Together they completely determine $k(T)$ at any temperature in the fitted range.

EXPERT'S SOLUTION *: Pooja Bhat, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. The data span five decades in k, so the log scale is essential. Linear fit on $\ln k$ vs $1/T$ recovers E_a and A; substitute these back to predict at any temperature.

Step 1. Slope (extreme points):
$\Delta \ln k/\Delta(1/T) = 10.22/(-0.830 \times 10^{-3}) = -1.232 \times 10^4\,\text{K}$. So
$E_a = -R \cdot \text{slope} = 8.314 \times 1.232 \times 10^4$, giving
$E_a \approx 1.024 \times 10^5\,\text{J mol}^{-1} \approx 102.4\,\text{kJ mol}^{-1}$.

Step 2. Intercept (using middle point $T = 313\,\text{K}$):
$\ln A = \ln k + E_a/(RT) = -8.27 + 39.36 = 31.09$; $A = e^{31.09} \approx 3.18 \times 10^{13}\,\text{s}^{-1}$.

Step 3. Predict k_{303}: $\ln k = 31.09 - 1.024 \times 10^5/(8.314 \times 303) = 31.09 - 40.66 = -9.57$, so $k \approx 6.97 \times 10^{-5}\,\text{s}^{-1}$.

Step 4. Predict k_{323}: $\ln k = 31.09 - 1.024 \times 10^5/(8.314 \times 323) = 31.09 - 38.14 = -7.05$, so $k \approx 8.70 \times 10^{-4}\,\mathrm{s}^{-1}$.

Alternative two-temperature route to E_a. Instead of the five-point slope, use just two extreme rate constants in the two-temperature form:

$$\log(k_5/k_1) = \frac{E_a}{2.303R} \cdot \frac{T_5 - T_1}{T_1 T_5}.$$

$k_5/k_1 = 2140/0.0787 = 2.72 \times 10^4$; $\log(k_5/k_1) = 4.434$. $T_5 - T_1 = 353 - 273 = 80\,\mathrm{K}$; $T_1 T_5 = 273 \times 353 = 96369\,\mathrm{K}^2$. $E_a = 2.303 \times 8.314 \times 4.434 \times 96369/80 = 19.146 \times 4.434 \times 1204.6 = 1.023 \times 10^5\,\mathrm{J\,mol^{-1}} \approx 102.3\,\mathrm{kJ\,mol^{-1}}$. ✓ Matches the slope method.

Concept linkage. N_2O_5 decomposition is unimolecular, so A should equal the rate of an internal vibration that breaks the weakest bond. Typical molecular vibrations are 10^{13}–10^{14} Hz – consistent with our $3.18 \times 10^{13}\,\mathrm{s}^{-1}$. The activation energy $102\,\mathrm{kJ/mol}$ is comparable to the N-O bond energy ($\sim 200\,\mathrm{kJ/mol}$, halved because of partial-bond breaking at the transition state), consistent with a homolytic N-O cleavage in the rate-determining step.

Cross-check predicted k values against the data trend. Between $T_1 = 273\,\mathrm{K}$ ($k = 0.0787 \times 10^{-5}$) and $T_2 = 293\,\mathrm{K}$ ($k = 1.70 \times 10^{-5}$), k rises by factor 21.6 over $20\,\mathrm{K}$. Our predicted $k_{303}/k_{293} = 6.97 \times 10^{-5}/1.70 \times 10^{-5} = 4.10$ over $10\,\mathrm{K}$. Compounded over $20\,\mathrm{K}$: $4.10^2 = 16.8$, close to the observed 21.6. Predictions track the data.

JEE/NEET relevance. Arrhenius-plot questions are *the* JEE Advanced format for kinetics: they require a slope calculation, an intercept calculation, and one or two predictions at new temperatures. JEE Main 2024 used the same N_2O_5 data set, asking for E_a alone.

> **Final Answer:** $E_a \approx 102.4\,\mathrm{kJ\,mol^{-1}}$, $A \approx 3.18 \times 10^{13}\,\mathrm{s^{-1}}$, $k_{303} \approx 6.97 \times 10^{-5}\,\mathrm{s^{-1}}$, $k_{323} \approx 8.70 \times 10^{-4}\,\mathrm{s^{-1}}$.

✗ Use $\ln$ consistently, or $\log$ consistently

A frequent slip in Arrhenius problems is to compute the slope on a $\log_{10} k$ vs $1/T$ plot but forget the 2.303 when extracting E_a. The two forms give slopes differing by a factor of 2.303: $\ln$ form → slope $= -E_a/R$; $\log_{10}$ form → slope $= -E_a/(2.303R)$. Pick one, label the axis, and don't mix.

Q 3.23 **The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5}\,\mathrm{s^{-1}}$ at $546\,\mathrm{K}$. If the energy of activation is $179.9\,\mathrm{kJ/mol}$, what will be the value of pre-exponential factor?**

SOLUTION

Concept used. Rearrange the Arrhenius equation $k = A\,e^{-E_a/RT}$ for A:

$$\ln A \;=\; \ln k + \frac{E_a}{RT}.$$

Use $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $T = 546\,\mathrm{K}$, and $E_a = 179.9\,\mathrm{kJ\,mol^{-1}} = 179900\,\mathrm{J\,mol^{-1}}$.

Step 1. Compute RT.

$$RT \;=\; 8.314 \times 546 \;=\; 4539\,\mathrm{J\,mol^{-1}}.$$

Step 2. Compute $E_a/(RT)$.

$$\frac{E_a}{RT} \;=\; \frac{179900}{4539} \;=\; 39.64.$$

Step 3. Compute $\ln k$.

$$\begin{aligned}\ln k &= \ln(2.418 \times 10^{-5})\\ &= \ln 2.418 + \ln 10^{-5}\\ &= 0.8830 + (-5)(2.3026)\\ &= 0.8830 - 11.513 \;=\; -10.63.\end{aligned}$$

Step 4. Find $\ln A$ and A.

$$\ln A \;=\; -10.63 + 39.64 \;=\; 29.01.$$

Therefore

$$A \;=\; e^{29.01}.$$

Convert to base 10: $\log A = 29.01/2.303 = 12.598$. So $A = 10^{12.598} = 10^{0.598} \times 10^{12}$. Compute $10^{0.598} = 3.965$. Therefore

$$A \;\approx\; 3.965 \times 10^{12}\,\mathrm{s^{-1}}.$$

Final Answer: $A \approx 3.97 \times 10^{12}\,\mathrm{s^{-1}}$.

EXPERT'S SOLUTION : *Neha Sharma, M.Sc Chemistry, IIT Kanpur*

Strategic angle. One-step rearrangement, one substitution. The only book-keeping is to keep E_a in joules (not kilojoules) when using $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

Step 1. $E_a/(RT) = 179900/(8.314 \times 546) = 179900/4539 = 39.64$.

Step 2. $\ln k = \ln(2.418 \times 10^{-5}) = -10.63$.

Step 3. $\ln A = -10.63 + 39.64 = 29.01$; $A = e^{29.01} \approx 3.97 \times 10^{12}\,\mathrm{s^{-1}}$.

Alternative base-10 formulation. Use $\log$ instead of $\ln$:

$$\log A = \log k + \frac{E_a}{2.303RT}.$$

$\log k = \log(2.418 \times 10^{-5}) = -4.617$. $E_a/(2.303RT) = 179900/(2.303 \times 8.314 \times 546) = 179900/(19.146 \times 546) = 179900/10454 = 17.21$. $\log A = -4.617 + 17.21 = 12.59$. $A = 10^{12.59} = 10^{0.59} \times 10^{12} = 3.89 \times 10^{12}\,\mathrm{s}^{-1}$. ✓ Matches within rounding.

Concept linkage. The pre-exponential factor A has the same units as k. For this first-order reaction, A is in s^{-1}. A represents the rate constant in the limit $T \to \infty$, i.e. when *every* collision has enough energy to clear the barrier. Physically, A is approximately the frequency of attempted bond breaking, which for a typical C-H stretch is $\sim 10^{14}\,\mathrm{Hz}$. Our 4×10^{12} is one to two orders below this, suggesting a steric factor $p \sim 0.04$ – meaning only $\sim 4\%$ of energetic collisions have the right geometry.

Cross-check by Boltzmann fraction. The fraction of molecules with $E \geq E_a$ at $T = 546\,\mathrm{K}$ is $e^{-39.64} = 10^{-17.21} \approx 6.1 \times 10^{-18}$. Multiply by $A = 4 \times 10^{12}$: $k = 6.1 \times 10^{-18} \times 4 \times 10^{12} = 2.4 \times 10^{-5}\,\mathrm{s}^{-1}$. Matches the given $k = 2.418 \times 10^{-5}\,\mathrm{s}^{-1}$. ✓The tiny Boltzmann fraction is why high-E_a reactions need high temperatures.

JEE/NEET relevance. "Find A given k, T, E_a" is a classic JEE Main one-mark numerical – direct application of the Arrhenius equation rearranged for A. JEE Main 2022 used the same hydrocarbon decomposition.

Final Answer: $A \approx 3.97 \times 10^{12}\,\mathrm{s}^{-1}$.

✗ E_a in joules, not kilojoules

$R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$ uses joules. If you plug $E_a = 179.9\,\mathrm{kJ/mol}$ directly into E_a/RT, your answer is 1000 times too small. Always convert kilojoules to joules first. Better: build the habit of writing E_a/R with units of K $(= 21640\,\mathrm{K}$ here) before dividing by T.

☞ Order of magnitude of A

For unimolecular gas decomposition: $A \sim 10^{12}$–$10^{14}\,\mathrm{s}^{-1}$, matching a molecular vibration frequency. For bimolecular reactions: A is in $\mathrm{L\,mol^{-1}\,s^{-1}}$, with typical values 10^{10}–10^{11}. If your computed A is wildly outside these ranges, recheck units.

Q 3.24 **Consider a certain reaction $\mathrm{A} \longrightarrow \mathrm{Products}$ with $k = 2.0 \times 10^{-2}\,\mathrm{s}^{-1}$. Calculate the concentration of A remaining after $100\,\mathrm{s}$ if the initial concentration of A is $1.0\,\mathrm{mol\,L^{-1}}$.**

SOLUTION

Concept used. The units of k (s^{-1}) tell us the reaction is first order. The integrated rate law is

$$\ln\frac{[A]_0}{[A]} = k\,t, \quad \text{or equivalently} \quad [A] = [A]_0\,e^{-kt}.$$

Step 1. Compute $k\,t$.

$$k\,t = (2.0 \times 10^{-2})(100) = 2.0.$$

Step 2. Use the integrated rate law.

$$[A] = [A]_0\,e^{-kt} = 1.0 \times e^{-2.0}.$$

Recall $e^{-2.0} = 0.1353$.

$$[A] = 1.0 \times 0.1353 = 0.1353\,\mathrm{mol\,L^{-1}}.$$

Step 3. Cross-check using log.

$$\log\frac{[A]_0}{[A]} = \frac{k\,t}{2.303} = \frac{2.0}{2.303} = 0.8685.$$

Then $[A]_0/[A] = 10^{0.8685} = 7.389$, so $[A] = 1/7.389 = 0.1353\,\mathrm{mol\,L^{-1}}$. ✓

Final Answer: $[A] \approx 0.135\,\mathrm{mol\,L^{-1}}$ after $100\,\mathrm{s}$.

EXPERT'S SOLUTION : *Sanya Mehta, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. The units of k identify the order (here, first), then it is straight substitution into $[A] = [A]_0 e^{-kt}$.

Step 1. $kt = 2.0 \times 10^{-2} \times 100 = 2.0$ (dimensionless).

Step 2. $[A] = 1.0 \times e^{-2.0} = 0.135\,\mathrm{mol\,L^{-1}}$.

Alternative half-life count. $t_{1/2} = 0.693/k = 0.693/0.02 = 34.65\,\mathrm{s}$. In $100\,\mathrm{s}$, the number of half-lives is $100/34.65 = 2.886$. Remaining fraction $= (1/2)^{2.886} = 2^{-2.886}$. Compute: $\log 2^{-2.886} = -2.886 \times 0.3010 = -0.869$. $f = 10^{-0.869} = 0.1353$. So $[A] = 0.1353\,\mathrm{mol\,L^{-1}}$. ✓ Same answer via the half-life path.

Concept linkage. $kt = 2.0$ is 2 "mean lifetimes" ($\tau = 1/k$). At one mean lifetime, the concentration falls to $1/e \approx 0.368$ of the initial; at two mean lifetimes, to $1/e^2 \approx 0.135$. So our answer $0.135\,\mathrm{mol\,L^{-1}}$ is exactly the textbook value for "two mean lifetimes" decay. The number $e^{-2} = 0.1353$ is worth memorising for first-order problems.

Cross-check by direct integrated rate law. $\ln([A]_0/[A]) = kt = 2.0$. So $[A]_0/[A] = e^{2.0} = 7.389$. Thus $[A] = 1.0/7.389 = 0.1353\,\mathrm{mol\,L^{-1}}$. ✓ Yet a third route, this time without computing kt as a dimensionless number explicitly.

JEE/NEET relevance. The simplest possible first-order numerical: substitute kt and find $[A]$. NEET 2022 used $kt = 1.0$ asking for $[A]/[A]_0$; the answer is $1/e = 0.368$. Memorising e^{-1}, e^{-2}, e^{-3} ($\approx 0.368, 0.135, 0.050$) speeds up multiple-choice answers.

Final Answer: $[A] \approx 0.135\,\text{mol}\,\text{L}^{-1}$.

☞ e^{-kt} values to memorise

$e^{-0.5} = 0.607$, $e^{-1} = 0.368$, $e^{-2} = 0.135$, $e^{-3} = 0.0498$, $e^{-4} = 0.0183$, $e^{-5} = 0.00674$. For any first-order numerical with kt near a small integer, these four values let you skip the calculator step.

☞ Units of k reveal the order

k in $\text{s}^{-1} \Rightarrow$ first order. k in $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1} \Rightarrow$ zero order. k in $\text{L}\,\text{mol}^{-1}\,\text{s}^{-1} \Rightarrow$ second order. Always read $[k]$ before picking the integrated rate law to use.

Q 3.25 Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2} = 3.00$ hours. What fraction of a sample of sucrose remains after 8 hours?

SOLUTION

Concept used. For a first order reaction,

$$k = \frac{0.693}{t_{1/2}}, \qquad \log\frac{[R]_0}{[R]} = \frac{k\,t}{2.303}.$$

Step 1. Decay constant.

$$k = \frac{0.693}{3.00}\,\text{h}^{-1} = 0.231\,\text{h}^{-1}.$$

Step 2. Set up the fraction-remaining equation. Let $f = [R]/[R]_0$ be the fraction remaining. Then

$$\log\frac{1}{f} = \frac{k\,t}{2.303} = \frac{0.231 \times 8}{2.303}.$$

Numerator: $0.231 \times 8 = 1.848$.

$$\log\frac{1}{f} = \frac{1.848}{2.303} = 0.8024.$$

Step 3. Solve for f.

$$\frac{1}{f} = 10^{0.8024} = 6.347.$$

Therefore

$$f = \frac{1}{6.347} = 0.1576 \approx 0.158.$$

So about 15.8% of the sucrose remains.

Step 4. **Cross-check by half-lives.** $t = 8\,\text{h}$ is $8/3 = 2.667$ half-lives. Remaining fraction $f = (1/2)^{2.667}$. $\log f = -2.667 \log 2 = -2.667 \times 0.3010 = -0.8027$. $f = 10^{-0.8027} = 0.1575$. ✓

Final Answer: Fraction remaining ≈ 0.158 (about 15.8%).

☞ Acid-catalysed inversion of sucrose

The hydrolysis of sucrose, $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$, is called *inversion* because the optical rotation flips sign as the reaction progresses. It is one of the standard textbook examples of a pseudo first order reaction (water in excess).

EXPERT'S SOLUTION *: Ishita Desai, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Find k from $t_{1/2}$, then plug into the integrated rate law to get the fraction remaining. Use half-life counting as the cross-check.

Step 1. $k = 0.693/3 = 0.231\,\text{h}^{-1}$.

Step 2. After 8 h, $\log(1/f) = (0.231 \times 8)/2.303 = 0.8024$; $1/f = 6.35$; $f = 0.158$.

Step 3. Equivalent picture: $8\,\text{h}/3\,\text{h} = 2.67$ half-lives, so $f = (1/2)^{2.67} \approx 0.158$.

Alternative ratio at half-life boundaries. At $t = 6\,\text{h}$ (exactly $2\,t_{1/2}$): $f = 1/4 = 0.250$. At $t = 9\,\text{h}$ (exactly $3\,t_{1/2}$): $f = 1/8 = 0.125$. Our requested $t = 8\,\text{h}$ sits between these. Interpolating in log space (since first-order decay is linear in $\log f$): $\log f(8\,\text{h}) = \log(0.125) + (1/3)[\log(0.250) - \log(0.125)] = -0.9031 + (1/3)(0.3010) = -0.9031 + 0.1003 = -0.8028$. $f = 10^{-0.8028} = 0.1575$. ✓

Concept linkage. Sucrose hydrolysis is famously *pseudo* first order: the rate law is actually $r = k_2[\text{sucrose}][\text{H2O}]$, but water is in vast excess ($\sim 55\,\text{M}$ in dilute aqueous solution) and its concentration is essentially constant. So $k_{\text{eff}} = k_2[\text{H2O}]$ absorbs the water term and the kinetics look first order. The "$t_{1/2} = 3$ h" is therefore an effective half-life that depends on $[\text{H}^+]$ and on the temperature.

Cross-check by half-life pattern. After $2\,t_{1/2}$, 25% remains; after $3\,t_{1/2}$, 12.5%. Our $f = 15.8\%$ satisfies $12.5 < 15.8 < 25$, sitting at the geometric mean $\sqrt{12.5 \times 25} = 17.7\%$ – close but not exact because $8 = 2.67\,t_{1/2}$, not the midpoint 2.5. The arithmetic checks.

JEE/NEET relevance. Sucrose inversion is the textbook example of a pseudo first-order reaction. The optical rotation flips sign as the equimolar glucose-fructose mixture forms, giving it the alternative name "inversion". JEE Main 2021 used this exact reaction with $t_{1/2} = 24$ minutes and a 1-hour time interval.

Final Answer: Fraction of sucrose remaining ≈ 0.158.

♥ Pseudo first order from excess reagent

A two-reactant reaction $A + B \to$ products with rate law $r = k[A][B]$ becomes pseudo first order when one species (usually the solvent) is in vast excess. Water in aqueous hydrolyses, ethanol in alcohol-mediated reactions, the solvent in solvolyses – all collapse to apparent first-order kinetics. This is why most "first-order" reactions in aqueous chemistry are really pseudo first order.

Q 3.26 The decomposition of hydrocarbon follows the equation $k = (4.5 \times 10^{11}\,\mathrm{s}^{-1})\,e^{-28000\,\mathrm{K}/T}$. Calculate E_a.

SOLUTION

Concept used. The Arrhenius equation $k = A\,e^{-E_a/RT}$ can be matched term-by-term with the empirical formula

$$k \;=\; (4.5 \times 10^{11}\,\mathrm{s}^{-1})\,e^{-28000\,\mathrm{K}/T}.$$

By comparison,

$$A \;=\; 4.5 \times 10^{11}\,\mathrm{s}^{-1}, \qquad \frac{E_a}{R} \;=\; 28000\,\mathrm{K}.$$

Therefore $E_a = R \times 28000\,\mathrm{K}$ with $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

Step 1. **Match exponents.** Equate the exponent of the given formula with the exponent of the Arrhenius equation: $-E_a/(RT) = -28000\,\mathrm{K}/T$, so $E_a/R = 28000\,\mathrm{K}$.

Step 2. **Solve for E_a.**

$$E_a \;=\; R \times 28000\,\mathrm{K} \;=\; 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}} \times 28000\,\mathrm{K}.$$

Compute: 8.314×28000. Break it up: $8.314 \times 28 = 232.79$; multiply by 10^3 to get 232790. So

$$E_a \;=\; 232790\,\mathrm{J\,mol^{-1}} \;=\; 232.79\,\mathrm{kJ\,mol^{-1}}.$$

Final Answer: $E_a \approx 232.8\,\mathrm{kJ\,mol^{-1}}$.

EXPERT'S SOLUTION *: Dev Iyer, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. Compare the given exponent with $-E_a/(RT)$ and solve.

Step 1. $E_a/R = 28000\,\mathrm{K}$ by direct matching.

Step 2. $E_a = R \times 28000 = 8.314 \times 28000\,\mathrm{J\,mol^{-1}} = 232790\,\mathrm{J\,mol^{-1}} \approx 232.8\,\mathrm{kJ\,mol^{-1}}$.

Alternative dimensional verification. The exponent must be dimensionless. Check: $E_a/(RT)$ has units $(\mathrm{J\,mol^{-1}})/(\mathrm{J\,mol^{-1}\,K^{-1}{\cdot}K})$ = dimensionless. ✓ So E_a/R must have units of K, matching the $28000\,\mathrm{K}$ in the given exponent. This dimensional check confirms that the matching is correct without doing any numerical work.

Concept linkage. The number $28000\,\mathrm{K}$ is the *Arrhenius temperature* $T_a = E_a/R$. It represents the temperature at which E_a equals RT, i.e. at which thermal energy alone would be enough to lift molecules over the barrier. Real reactions run at $T \ll T_a$, which is why the exponential factor $e^{-E_a/RT} = e^{-T_a/T}$ is so small for typical chemistry.

Cross-check via the pre-factor. If we were given a value of k at some T, we could verify both A and E_a together. For example, at $T = 500\,\mathrm{K}$:
$k = (4.5\times10^{11})\times e^{-28000/500} = 4.5\times10^{11}\times e^{-56} = 4.5\times10^{11}\times4.78\times10^{-25} = 2.15\times10^{-13}\,\mathrm{s^{-1}}$.
A vanishingly slow rate, consistent with $E_a > 200\,\mathrm{kJ/mol}$ at modest temperatures.

JEE/NEET relevance. "Read off E_a from a given Arrhenius expression" is a one-mark MCQ favourite. The pattern: equate the numerical exponent (in units of K/T) with E_a/R, then multiply by R. JEE Main 2023 used a slightly different form with T in the denominator under a fractional power.

> **Final Answer:** $E_a \approx 232.8\,\mathrm{kJ\,mol^{-1}}$.

☞ Mind the temperature units in the exponent

The exponent $-28000\,\mathrm{K}/T$ requires T in kelvin. Plugging T in $^\circ\mathrm{C}$ gives a wrong (often disastrously wrong) result. Whenever the Arrhenius exponent has T in the denominator, the temperature must be absolute.

♥ E_a/R as the natural temperature scale

The quantity $T_a = E_a/R$ has units of kelvin and tells you the "temperature scale" of the reaction. For $T_a = 28000\,\mathrm{K}$, the reaction needs temperatures comparable to a few percent of T_a ($\sim 500–1000\,\mathrm{K}$) to proceed at observable rates. This is why high-E_a reactions (like combustion or thermal cracking) need high temperatures.

Q 3.27 **The rate constant for the first order decomposition of H_2O_2 is given by the following equation: $\log k = 14.34 - 1.25 \times 10^4\,\mathrm{K}/T$. Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?**

SOLUTION

Concept used. Take the Arrhenius equation $k = A\,e^{-E_a/RT}$ and convert to base 10 logarithms by dividing the exponent by $\ln 10 = 2.303$:

$$\log k = \log A - \frac{E_a}{2.303\,RT}.$$

Match term-by-term with the given expression

$$\log k = 14.34 - \frac{1.25 \times 10^4\,\mathrm{K}}{T}.$$

Step 1. Match coefficients.

$$\log A = 14.34, \qquad \frac{E_a}{2.303\,R} = 1.25 \times 10^4\,\mathrm{K}.$$

Step 2. Compute E_a.

$$E_a = 2.303 \times R \times 1.25 \times 10^4\,\mathrm{K}.$$

With $R = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$:

$$E_a = 2.303 \times 8.314 \times 1.25 \times 10^4.$$

Compute step by step: $2.303 \times 8.314 = 19.146$. Then $19.146 \times 1.25 = 23.93$. Then multiply by 10^4:

$$E_a = 23.93 \times 10^4\,\mathrm{J\,mol^{-1}} = 2.393 \times 10^5\,\mathrm{J\,mol^{-1}} = 239.3\,\mathrm{kJ\,mol^{-1}}.$$

Step 3. Find T for $t_{1/2} = 256\,\mathrm{min}$. First convert: $256\,\mathrm{min} \times 60\,\mathrm{s\,min^{-1}} = 15360\,\mathrm{s}$. For a first order reaction $k = 0.693/t_{1/2}$:

$$k = \frac{0.693}{15360} = 4.51 \times 10^{-5}\,\mathrm{s^{-1}}.$$

Step 4. Solve $\log k = 14.34 - 1.25 \times 10^4/T$ for T.
$\log k = \log(4.51 \times 10^{-5}) = \log 4.51 - 5 = 0.6542 - 5 = -4.346$. Substitute:

$$-4.346 = 14.34 - \frac{1.25 \times 10^4}{T} \implies \frac{1.25 \times 10^4}{T} = 14.34 + 4.346 = 18.686.$$

Step 5. Solve for T.

$$T = \frac{1.25 \times 10^4}{18.686} = 669\,\mathrm{K}.$$

Final Answer: $E_a \approx 239.3\,\mathrm{kJ\,mol^{-1}}$; the half-period equals 256 min at $T \approx 669\,\mathrm{K}$.

♥ Reading off A and E_a from a log-form

Whenever a problem gives $\log k$ as a linear function of $1/T$, you can identify the intercept with $\log A$ and the slope with $-E_a/(2.303\,R)$. Two pieces of information, no data fitting needed.

EXPERT'S SOLUTION *: Vivaan Gupta, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. The expression is already in the linearised Arrhenius form. Read off $\log A$ and $E_a/(2.303R)$ directly, then find T from the half-life equation.

Step 1. $\log A = 14.34$, $E_a/(2.303R) = 1.25 \times 10^4\,\mathrm{K}$.
$E_a = 2.303 \times 8.314 \times 1.25 \times 10^4 = 2.393 \times 10^5\,\mathrm{J\,mol^{-1}} \approx 239.3\,\mathrm{kJ\,mol^{-1}}$.

Step 2. For $t_{1/2} = 256\,\mathrm{min} = 15360\,\mathrm{s}$, $k = 0.693/15360 = 4.51 \times 10^{-5}\,\mathrm{s^{-1}}$;
$\log k = -4.346$.

Step 3. $1/T = (14.34 + 4.346)/(1.25 \times 10^4) = 18.686/(1.25 \times 10^4) = 1.495 \times 10^{-3}\,\mathrm{K^{-1}}$.
$T = 669\,\mathrm{K}$.

Alternative form starting from natural log. If the equation were given as $\ln k = 33.01 - 2.88 \times 10^4/T$ (multiplying by 2.303), we'd identify $\ln A = 33.01$ ($A = e^{33.01} = 2.2 \times 10^{14}$, consistent with $\log A = 14.34$) and $E_a/R = 2.88 \times 10^4\,\mathrm{K}$, giving $E_a = 8.314 \times 2.88 \times 10^4 = 2.39 \times 10^5\,\mathrm{J\,mol^{-1}}$. ✓ Both forms yield the same E_a.

Concept linkage. H_2O_2 decomposition is catalyzed in biological systems by catalase (in cells) or Fe^{2+} (Fenton chemistry). Without catalyst, the uncatalyzed thermal decomposition has $E_a \approx 240\,\mathrm{kJ/mol}$ – exactly what we just found. With catalase the effective E_a drops to $\sim 30\,\mathrm{kJ/mol}$, explaining the dramatic speedup.

Cross-check by predicting another half-life. If $T = 669\,\mathrm{K}$ gives $t_{1/2} = 256\,\mathrm{min}$, then at $T = 700\,\mathrm{K}$: $\log k = 14.34 - 1.25 \times 10^4/700 = 14.34 - 17.86 = -3.52$. So $k = 10^{-3.52} = 3.02 \times 10^{-4}\,\mathrm{s^{-1}}$ and $t_{1/2} = 0.693/3.02 \times 10^{-4} = 2295\,\mathrm{s} = 38.2\,\mathrm{min}$. A 30 K rise cuts the half-life by a factor of ~ 7: strong Arrhenius sensitivity, as expected for high E_a.

JEE/NEET relevance. Pattern-matching a linearised Arrhenius expression to extract E_a and A is a two-step JEE Main format. JEE Main 2018 used a near-identical $\log k$ vs $1/T$ expression for HI decomposition.

Final Answer: $E_a \approx 239.3\,\mathrm{kJ\,mol^{-1}};\ T \approx 669\,\mathrm{K}$.

☞ Convert minutes to seconds for k in $\mathrm{s^{-1}}$

The given Arrhenius expression has the form $\log k = 14.34 - 1.25 \times 10^4/T$ with k in $\mathrm{s^{-1}}$ (implicit from the magnitudes). Half-life in minutes must be converted to seconds before using $k = 0.693/t_{1/2}$. A common slip is to keep $t_{1/2}$ in minutes and get k in $\mathrm{min^{-1}}$ – which mismatches the equation's units.

Q 3.28 **The decomposition of A into products has value of k as $4.5 \times 10^3\,\mathrm{s}^{-1}$ at $10\,°\mathrm{C}$ and energy of activation $60\,\mathrm{kJ\,mol}^{-1}$. At what temperature would k be $1.5 \times 10^4\,\mathrm{s}^{-1}$?**

SOLUTION

Concept used. The two-temperature form of the Arrhenius equation:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R} \cdot \frac{T_2 - T_1}{T_1\,T_2}.$$

Here $T_1 = 10\,°\mathrm{C} = 283\,\mathrm{K}$, $k_1 = 4.5 \times 10^3\,\mathrm{s}^{-1}$, $k_2 = 1.5 \times 10^4\,\mathrm{s}^{-1}$, $E_a = 60\,\mathrm{kJ\,mol}^{-1} = 60000\,\mathrm{J\,mol}^{-1}$, $R = 8.314\,\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}$. We need T_2.

Step 1. Compute the rate-constant ratio.

$$\frac{k_2}{k_1} = \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{15000}{4500} = 3.333.$$

$\log 3.333 = \log(10/3) = 1 - \log 3 = 1 - 0.4771 = 0.5229.$

Step 2. Compute the prefactor.

$$\frac{E_a}{2.303\,R} = \frac{60000}{2.303 \times 8.314}.$$

$2.303 \times 8.314 = 19.146$. Then $60000/19.146 = 3133\,\mathrm{K}$.

Step 3. Solve for $(T_2 - T_1)/(T_1T_2)$.

$$\frac{T_2 - T_1}{T_1T_2} = \frac{\log(k_2/k_1)}{E_a/(2.303R)} = \frac{0.5229}{3133} = 1.669 \times 10^{-4}\,\mathrm{K}^{-1}.$$

Step 4. Rewrite as $1/T_1 - 1/T_2$. Note that $(T_2 - T_1)/(T_1T_2) = 1/T_1 - 1/T_2$. So

$$\frac{1}{T_2} = \frac{1}{T_1} - 1.669 \times 10^{-4}.$$

$1/T_1 = 1/283 = 3.534 \times 10^{-3}\,\mathrm{K}^{-1}.$

$$\frac{1}{T_2} = 3.534 \times 10^{-3} - 0.1669 \times 10^{-3} = 3.367 \times 10^{-3}\,\mathrm{K}^{-1}.$$

Step 5. Solve for T_2.

$$T_2 = \frac{1}{3.367 \times 10^{-3}} = 297\,\mathrm{K}.$$

In Celsius: $T_2 = 297 - 273 = 24\,°\mathrm{C}$.

Final Answer: $T_2 \approx 297\,\mathrm{K}$, i.e. about $24\,°\mathrm{C}$.

EXPERT'S SOLUTION : *Rohit Sharma, M.Tech Chemical Engineering, IIT Delhi*

Strategic angle. The two-temperature Arrhenius form gives a clean equation in $1/T_2$ once everything else is known.

Step 1. $k_2/k_1 = 1.5\times10^4/4.5\times10^3 = 10/3 = 3.333$; $\log(k_2/k_1) = 0.5229$.

Step 2. $E_a/(2.303R) = 60000/19.146 = 3133\,\text{K}$.

Step 3. $1/T_1 - 1/T_2 = 0.5229/3133 = 1.669\times10^{-4}\,\text{K}^{-1}$; $1/T_1 = 1/283 = 3.534\times10^{-3}$; $1/T_2 = 3.367\times10^{-3}$.

Step 4. $T_2 = 1/3.367\times10^{-3} \approx 297\,\text{K} \approx 24\,°\text{C}$.

Alternative algebra-free check via $\mu \approx 2$. The empirical rule says k doubles per $10\,\text{K}$ for $E_a \approx 50\,\text{kJ/mol}$. With $E_a = 60\,\text{kJ/mol}$, μ at $T \sim 290\,\text{K}$ is closer to $2.2–2.4$. To triple ($\times3.33$) the rate, T must rise by about $\log_\mu(3.33)\times10\,\text{K} = (\log 3.33/\log 2.2)\times10 = (0.523/0.342)\times10 = 15\,\text{K}$. So $T_2 \approx 283 + 15 = 298\,\text{K}$, matching our $297\,\text{K}$ answer within rounding. The rule-of-thumb is a quick gut check.

Concept linkage. The two-temperature Arrhenius form is the operational tool for industrial process design. Want to halve a batch time? Compute the ΔT needed: solve $\log 2 = (E_a/2.303R)(\Delta T/T_1T_2)$. For $E_a = 60\,\text{kJ/mol}$ at $T = 300\,\text{K}$, that's about $9\,\text{K}$.

Cross-check by predicting k at $T_2 = 297\,\text{K}$ forward.
$k_2 = k_1 \times 10^{0.5229} = 4500\times3.333 = 1.5\times10^4\,\text{s}^{-1}$. ✓ The forward prediction matches the requested k.

JEE/NEET relevance. "At what T_2 does k become . . . ?" is the workhorse Arrhenius numerical. The recipe is fixed: use the two-temperature form, solve for $1/T_2$, invert to T_2. NEET 2022 asked this with the temperature change in the opposite direction ($T_2 < T_1$).

Final Answer: $T_2 \approx 297\,\text{K} \approx 24\,°\text{C}$.

☞ T_1T_2 in the denominator

The two-temperature Arrhenius form has T_1T_2 in the denominator, not $T_2 - T_1$. A common slip is to write $E_a(T_2-T_1)/(T_2-T_1) = E_a$, which is dimensionally wrong. Always preserve the structure $E_a/R\times(T_2-T_1)/(T_1T_2)$.

♥ Activation energy controls temperature sensitivity

A reaction with $E_a = 50\,\text{kJ/mol}$ doubles rate per $10\,\text{K}$. With $E_a = 100\,\text{kJ/mol}$, the same $10\,\text{K}$ quadruples the rate. With $E_a = 25\,\text{kJ/mol}$, the rate only rises $\sim 50\%$. So "high E_a" and "strongly temperature-sensitive" mean the same thing.

Q 3.29 **The time required for 10% completion of a first order reaction at $298\,\mathrm{K}$ is equal to that required for its 25% completion at $308\,\mathrm{K}$. If the value of A is $4 \times 10^{10}\,\mathrm{s}^{-1}$, calculate k at $318\,\mathrm{K}$ and E_a.**

SOLUTION

Concept used. For a first order reaction, $t = (2.303/k)\log([R]_0/[R])$. The time for 10% completion uses $[R]_0/[R] = 100/90$; the time for 25% completion uses $[R]_0/[R] = 100/75 = 4/3$.

Step 1. **Equate the two times.** Let k_1 be the rate constant at $298\,\mathrm{K}$ and k_2 at $308\,\mathrm{K}$. Then

$$\frac{2.303}{k_1}\log\frac{100}{90} = \frac{2.303}{k_2}\log\frac{100}{75}.$$

Cancel the 2.303:

$$\frac{1}{k_1}\log\frac{100}{90} = \frac{1}{k_2}\log\frac{4}{3}.$$

So

$$\frac{k_2}{k_1} = \frac{\log(4/3)}{\log(100/90)}.$$

Compute: $\log(4/3) = \log 4 - \log 3 = 0.6021 - 0.4771 = 0.1249$. $\log(100/90) = \log(10/9) = 1 - \log 9 = 1 - 0.9542 = 0.0458$.

$$\frac{k_2}{k_1} = \frac{0.1249}{0.0458} = 2.727.$$

Step 2. **Find E_a using the two-temperature Arrhenius form.** $T_1 = 298\,\mathrm{K}$, $T_2 = 308\,\mathrm{K}$, $T_2 - T_1 = 10\,\mathrm{K}$, $T_1T_2 = 298 \times 308 = 91784\,\mathrm{K}^2$.

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\cdot\frac{T_2 - T_1}{T_1T_2} \implies E_a = \frac{2.303\,R\,T_1\,T_2\,\log(k_2/k_1)}{T_2 - T_1}.$$

$\log(k_2/k_1) = \log 2.727 = 0.4358$. Substitute:

$$E_a = \frac{2.303 \times 8.314 \times 91784 \times 0.4358}{10}.$$

Step by step: $2.303 \times 8.314 = 19.146$. $19.146 \times 91784 =?$ Compute $19.146 \times 91784 = 19.146 \times 9.1784 \times 10^4 = 175.74 \times 10^4 = 1.7574 \times 10^6$. Multiply by 0.4358: $1.7574 \times 10^6 \times 0.4358 = 7.658 \times 10^5$. Divide by 10:

$$E_a \approx 7.658 \times 10^4\,\mathrm{J\,mol^{-1}} = 76.58\,\mathrm{kJ\,mol^{-1}}.$$

Step 3. **Find k at $318\,\mathrm{K}$ using $k = A\,e^{-E_a/RT}$.** $A = 4 \times 10^{10}\,\mathrm{s}^{-1}$, $T = 318\,\mathrm{K}$.

$$\frac{E_a}{RT} = \frac{76580}{8.314 \times 318}.$$

$8.314 \times 318 = 2644\,\mathrm{J\,mol^{-1}}$. So $E_a/(RT) = 76580/2644 = 28.97$. Then

$$k_{318} = 4 \times 10^{10}\,e^{-28.97}.$$

Step 4. **Compute** $e^{-28.97}$. Convert: $-28.97/2.303 = -12.58$. So $e^{-28.97} = 10^{-12.58} = 10^{0.42} \times 10^{-13} = 2.63 \times 10^{-13}$. Hence

$$k_{318} = 4 \times 10^{10} \times 2.63 \times 10^{-13} = 1.052 \times 10^{-2}\,\mathrm{s^{-1}}.$$

Final Answer: $E_a \approx 76.6\,\mathrm{kJ\,mol^{-1}}$; $k_{318} \approx 1.05 \times 10^{-2}\,\mathrm{s^{-1}}$.

EXPERT'S SOLUTION *: Aanya Reddy, Ph.D Physical Chemistry, IIT Madras*

Strategic angle. Three layers: (i) read k_2/k_1 off the "equal-times" condition, (ii) plug into the two-temperature Arrhenius equation to get E_a, (iii) use the full Arrhenius equation with the given A to get k at the third temperature.

Step 1. $k_2/k_1 = \log(4/3)/\log(10/9) = 0.1249/0.0458 = 2.727$; $\log(k_2/k_1) = 0.4358$.

Step 2. $E_a = 2.303 \times 8.314 \times 298 \times 308 \times 0.4358/10 \approx 7.66 \times 10^4\,\mathrm{J\,mol^{-1}} \approx 76.6\,\mathrm{kJ\,mol^{-1}}$.

Step 3. $E_a/(RT) = 76580/(8.314 \times 318) = 28.97$;
$k_{318} = 4 \times 10^{10} \times e^{-28.97} = 4 \times 10^{10} \times 2.63 \times 10^{-13} \approx 1.05 \times 10^{-2}\,\mathrm{s^{-1}}$.

Alternative use of base-10 logs throughout.
$\log k_{318} = \log A - E_a/(2.303RT) = \log(4 \times 10^{10}) - 76580/(2.303 \times 8.314 \times 318)$.
$\log(4 \times 10^{10}) = 10.602$. $2.303 \times 8.314 \times 318 = 19.146 \times 318 = 6088$. $76580/6088 = 12.58$.
$\log k_{318} = 10.602 - 12.58 = -1.98$. $k_{318} = 10^{-1.98} = 10^{0.02} \times 10^{-2} = 1.05 \times 10^{-2}\,\mathrm{s^{-1}}$. ✓
Same answer via the base-10 route.

Concept linkage. The trick "equal t at different T" hides a ratio of k values inside two log-fractions: $t_a/k_a = t_b/k_b$ when t_a at T_a equals t_b at T_b (both for the same fractional completion of *different* amounts). The general rule: $k_b/k_a = (t_a \cdot \log \mathrm{frac}_b)/(t_b \cdot \log \mathrm{frac}_a)$. Here both times are equal, so $k_2/k_1 = \log(\mathrm{frac}_2)/\log(\mathrm{frac}_1)$.

Cross-check by predicting k_{298}. From $\log k_{298} = \log A - E_a/(2.303RT_1)$:
$E_a/(2.303RT_1) = 76580/(19.146 \times 298) = 13.42$. $\log k_{298} = 10.602 - 13.42 = -2.82$.
$k_{298} = 10^{-2.82} = 1.51 \times 10^{-3}\,\mathrm{s^{-1}}$. Now verify $k_{308}/k_{298} = 2.727$:
$\log k_{308} = 10.602 - 76580/(19.146 \times 308) = 10.602 - 12.98 = -2.38$.
$k_{308}/k_{298} = 10^{-2.38+2.82} = 10^{0.44} = 2.75$. ✓Matches our 2.727 within rounding.

JEE/NEET relevance. The "$t_{10\%}$ equals $t_{25\%}$" setup is a JEE Advanced favourite because it tests *multiple* steps: extracting a hidden k-ratio, applying Arrhenius, predicting at a third temperature. JEE Adv 2019 used the same three-layer pattern with different fractions.

Final Answer: $E_a \approx 76.6\,\mathrm{kJ\,mol^{-1}}$; $k_{318} \approx 1.05 \times 10^{-2}\,\mathrm{s^{-1}}$.

✗ Don't equate fractions, equate times

The condition is "time for 10% at T_1 equals time for 25% at T_2". Don't equate 10% and 25% (they're different fractions). Equate the times: $t_{10\%}(T_1) = t_{25\%}(T_2)$. The hidden information is then a ratio of k values.

☞ Three-layer Arrhenius problems

Layer 1: extract k_2/k_1 from the time/fraction condition. Layer 2: compute E_a from the two-temperature Arrhenius form. Layer 3: use full Arrhenius with the given A (or computed from the data) to predict k at a third temperature. NCERT and JEE Advanced both love this format.

Q 3.30 **The rate of a reaction quadruples when the temperature changes from $293\,\text{K}$ to $313\,\text{K}$. Calculate the energy of activation of the reaction, assuming that it does not change with temperature.**

SOLUTION

Concept used. The rate quadruples means $k_2/k_1 = 4$ when T rises from $T_1 = 293\,\text{K}$ to $T_2 = 313\,\text{K}$. The two-temperature Arrhenius form gives

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\cdot\frac{T_2 - T_1}{T_1T_2}.$$

Solve for E_a.

Step 1. Compute $\log(k_2/k_1)$**.**

$$\log 4 = \log 2^2 = 2\,\log 2 = 2\times 0.3010 = 0.6021.$$

Step 2. Compute the temperature factor. $T_2 - T_1 = 313 - 293 = 20\,\text{K}$; $T_1T_2 = 293\times 313 = 91709\,\text{K}^2$.

$$\frac{T_2 - T_1}{T_1T_2} = \frac{20}{91709} = 2.181\times 10^{-4}\,\text{K}^{-1}.$$

Step 3. Solve for E_a**.**

$$E_a = \frac{2.303\,R\,\log(k_2/k_1)}{(T_2 - T_1)/(T_1T_2)} = 2.303\times R\times\log(k_2/k_1)\times\frac{T_1T_2}{T_2 - T_1}.$$

Substitute: $2.303\times 8.314 = 19.146$. $19.146\times 0.6021 = 11.53$.

$$\frac{T_1T_2}{T_2 - T_1} = \frac{91709}{20} = 4585\,\text{K}.$$

Then

$$E_a = 11.53\times 4585 = 5.287\times 10^4\,\text{J mol}^{-1} \approx 52.87\,\text{kJ mol}^{-1}.$$

Final Answer: $E_a \approx 52.9\,\text{kJ mol}^{-1}$.

♥ Why $20\,\mathrm{K}$ quadruples the rate

This is the empirical rule of thumb: many reactions double in rate per $10\,\mathrm{K}$ rise. A $20\,\mathrm{K}$ rise then doubles twice, giving a factor of 4. The corresponding E_a is roughly 50 to $60\,\mathrm{kJ\,mol^{-1}}$, exactly what we found.

EXPERT'S SOLUTION : *Priya Kumar, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Substitute directly into the two-temperature Arrhenius form. Two pieces of information (k ratio and the temperature pair) pin down one unknown (E_a).

Step 1. $\log(k_2/k_1) = \log 4 = 0.6021$.

Step 2. $T_1T_2/(T_2 - T_1) = 293 \times 313/20 = 91709/20 = 4585\,\mathrm{K}$.

Step 3. $E_a = 2.303 \times R \times \log(k_2/k_1) \times T_1T_2/(T_2 - T_1) = 19.146 \times 0.6021 \times 4585 = 11.53 \times 4585 \approx 52870\,\mathrm{J\,mol^{-1}} \approx 52.9\,\mathrm{kJ\,mol^{-1}}$.

Alternative natural-log form. $\ln(k_2/k_1) = (E_a/R)(T_2 - T_1)/(T_1T_2)$. $\ln 4 = 1.386$.
$T_2 - T_1 = 20$, $T_1T_2 = 91709$.
$E_a = 1.386 \times 8.314 \times 91709/20 = 1.386 \times 8.314 \times 4585.45 = 52850\,\mathrm{J\,mol^{-1}} \approx 52.85\,\mathrm{kJ\,mol^{-1}}$.
✓Within rounding of the base-10 answer.
Concept linkage. The empirical rule of thumb says "rate roughly doubles per $10\,\mathrm{K}$". Here a $20\,\mathrm{K}$ rise gives $\times 4 = 2^2$, exactly two doublings. The back-derived $E_a \approx 53\,\mathrm{kJ/mol}$ is the canonical "activation energy at $T \sim 300\,\mathrm{K}$ for $\mu = 2$". So this problem is a numerical realisation of the rule of thumb.
Cross-check by predicting k at intermediate T. At $T_m = 303\,\mathrm{K}$ (midpoint), $\log(k_m/k_1) = (E_a/2.303R)(T_m - T_1)/(T_1T_m) = 2756 \times 10/(293 \times 303) = 27560/88779 = 0.3104$. So $k_m/k_1 = 10^{0.3104} = 2.045$. Predict another doubling between 293 and $303\,\mathrm{K}$, and yet another between 303 and $313\,\mathrm{K}$ – consistent with the "doubles per $10\,\mathrm{K}$" rule.
JEE/NEET relevance. The $\times 4$ quadrupling across $20\,\mathrm{K}$ is the classical NEET pattern. NEET 2017, 2020, and 2023 all asked variants. The answer is almost always near $50\text{–}55\,\mathrm{kJ/mol}$ because that's the E_a matching the "doubles per $10\,\mathrm{K}$" rule at room temperature.

Final Answer: $E_a \approx 52.9\,\mathrm{kJ\,mol^{-1}}$.

☞ Two-temperature Arrhenius mnemonic

Remember the form as "log of k-ratio equals E_a-over-$2.303R$ times delta-T-over-product-of-Ts":

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\cdot\frac{T_2 - T_1}{T_1T_2}.$$

Plug in three numbers, solve for the fourth. The chapter's most useful formula – worth memorising letter-by-letter.

Key Takeaways

- The **rate of a reaction** is the change of concentration of a reactant (with a $-$ sign) or product (with a $+$ sign) per unit time, divided by the stoichiometric coefficient so that all expressions give the same numerical rate.
- The **rate law** $r = k\,[A]^a[B]^b$ is found by experiment. The exponents a, b are the *orders* with respect to each reactant; their sum is the overall order. The order need not match the stoichiometric coefficients.
- The **dimensions** of the rate constant depend on the overall order: $\mathrm{mol}^{1-n}\,\mathrm{L}^{n-1}\,\mathrm{s}^{-1}$ for order n. Zero order: $\mathrm{mol\,L^{-1}\,s^{-1}}$; first order: $\mathrm{s^{-1}}$; second order: $\mathrm{L\,mol^{-1}\,s^{-1}}$.
- **Integrated rate laws.** Zero order: $[R] = [R]_0 - kt$, $t_{1/2} = [R]_0/(2k)$. First order: $\ln([R]_0/[R]) = kt$, $t_{1/2} = 0.693/k$ (independent of $[R]_0$).
- **Pseudo first order** reactions occur when one reactant is in large excess (typical for solvents like water), so that its concentration is effectively constant and the observed kinetics are first order.
- The **Arrhenius equation** $k = A\,e^{-E_a/RT}$ gives the temperature dependence of k. A plot of $\ln k$ vs $1/T$ is a straight line of slope $-E_a/R$ and intercept $\ln A$.
- The **two-temperature form** $\log(k_2/k_1) = (E_a/2.303R)\,(T_2 - T_1)/(T_1T_2)$ is the most-used formula in problems: it links E_a to a pair of (k, T) measurements.
- A **catalyst** lowers the activation energy E_a by providing an alternative reaction path, thereby raising k (and the rate) without being consumed.
- **Half-lives and decade-times** for first order reactions follow simple integer scaling: $t_{1/n}$ for $n = 2^m$ is $m\,t_{1/2}$; the time to reach $1/10^m$ of the starting value is $m\,t_{90\%}$.

End of Chapter 3 Exercises