NCERT Exemplar Solutions

Solved NCERT Exemplar Problems for Class 12th Chemistry, Chapter 3

Chapter 3: Chemical Kinetics

About this Chapter

Chemical Kinetics is the branch of chemistry that studies the rate of a reaction, the factors that change it (concentration, temperature, surface area, catalyst), and the mechanism by which reactants turn into products. This Exemplar set drills the core ideas: rate law, order vs molecularity, integrated rate equations for zero and first order, half-life, the **Arrhenius equation**, the role of activation energy and the collision theory.

Topics covered: Rate of reaction • Rate law • Order & molecularity • Integrated rate equations • Half-life • Arrhenius equation • Activation energy • Collision theory • Catalysis

Quick Formula Sheet

Rate law:

$r = k\,[A]^x\,[B]^y$, order $= x + y$

Zero order integrated:

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

First order integrated:

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

Arrhenius:

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

Two-point Arrhenius:

$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

I. Multiple Choice Questions (Type-I)

Q 3.1 **The role of a catalyst is to change __________.**

(i) gibbs energy of reaction.

(ii) enthalpy of reaction.

(iii) activation energy of reaction.

(iv) equilibrium constant.

SOLUTION

Correct option: (iii) activation energy of reaction.

Concept used. A **catalyst** is a substance that increases the rate of a chemical reaction without itself being consumed. It works by providing an *alternative reaction pathway* of lower **activation energy** E_a: the energy barrier between reactants and the transition state (activated complex). A catalyst does not change the energies of the reactants or the products themselves, so it cannot change any state function of the reaction.

Step 1. Recall the thermodynamic identities for a reaction at constant T and p:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}, \quad \Delta H = H_{\text{products}} - H_{\text{reactants}}.$$

Both are differences between the products' and the reactants' state functions. A catalyst does not alter either state.

Step 2. The equilibrium constant is fixed by ΔG°:

$$\Delta G^\circ = -RT \ln K_{\text{eq}}.$$

Since ΔG° is unchanged, K_{eq} is unchanged. So options (i), (ii) and (iv) are eliminated.

Step 3. Only the activation energy can be lowered. With E_a smaller, the Arrhenius rate constant $k = A\,e^{-E_a/RT}$ grows because the exponent becomes less negative.

> ☞ **Mental picture**
>
> Picture the energy profile as a hill between reactants and products. A catalyst carves a lower pass through the same hill, leaving the two valleys (reactants, products) at exactly the same height.

> **Final Answer:** Option **(iii)**: a catalyst changes the activation energy of the reaction.

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

Energy-profile angle. A clean way to remember this is to sketch the reaction-energy diagram and ask: "which segment does the catalyst touch?".

Concept used. Activation energy E_a is the vertical height from the reactant level to the peak of the activated complex. Thermodynamic quantities (ΔH, ΔG, K_{eq}) depend only on the reactant and product levels; the path between them is kinetic, not thermodynamic.

Step 1. Look at the four options as three thermodynamic quantities (i, ii, iv) and one kinetic quantity (iii). A catalyst is a *kinetic* object; it changes only how fast the reaction goes, not how far.

Step 2. Confirm with the Arrhenius equation $k = A\,e^{-E_a/RT}$: drop E_a by, say, $20\,\text{kJ/mol}$ at $T = 300\,\text{K}$ and

$$\frac{k_{\text{cat}}}{k} = e^{20000/(8.314\times 300)} = e^{8.02} \approx 3.0\times 10^3,$$

a ~ 3000-fold rate enhancement with the same ΔH and same K_{eq}.

Step 3. Cross-check: the IUPAC definition of a catalyst explicitly says it provides a lower-E_a pathway and is regenerated. Options (i), (ii), (iv) would all violate the "regenerated/unchanged thermodynamics" clause.

✗ Common Pitfall

Common pitfall. Students sometimes claim a catalyst "reduces ΔH". It does not; it only reduces the height of the activation barrier above the reactants.

♥ Concept Linkage

Concept linkage. This is the kinetic counterpart of the thermodynamic statement that K_{eq} depends only on T: K is set by ΔG°, k is set by E_a, and a catalyst affects only the second.

Final Answer: Option **(iii)**: only the activation energy is lowered by a catalyst.

Q 3.2 In the presence of a catalyst, the heat evolved or absorbed during the reaction __________.

(i) increases.
(ii) decreases.
(iii) remains unchanged.
(iv) may increase or decrease.

SOLUTION

Correct option: (iii) remains unchanged.

Concept used. The "heat evolved or absorbed" at constant pressure is the enthalpy change of the reaction, $\Delta H_{\text{rxn}} = H_{\text{products}} - H_{\text{reactants}}$. Enthalpy is a **state function**: its value depends only on the initial (reactants) and final (products) states, not on the path between them. A catalyst changes only the path, never the endpoints.

Step 1. Write the energy profile with and without catalyst. Both start at $H_{\text{reactants}}$ and both end at H_{products}. So the vertical gap $\Delta H = H_{\text{products}} - H_{\text{reactants}}$ is the same in both pictures.

Step 2. Hess's law confirms this: any sequence of steps that takes the same reactants to the same products gives the same ΔH. The catalysed pathway is just a different sequence of elementary steps, so its overall ΔH matches the uncatalysed one.

Step 3. Eliminate (i), (ii), (iv): all three claim a change in ΔH, which violates Hess's law.

> **Final Answer:** Option **(iii)**: the heat exchanged is unchanged because ΔH is a state function.

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

State-function angle. The fastest way to settle questions about whether "X is changed by a catalyst" is to ask: is X a state function or a path quantity?
Concept used. State functions (U, H, G, S, K_{eq}) depend only on the start and end states. Path quantities like E_a depend on the route.

Step 1. Tabulate the options. (i) and (ii) make heat exchanged a non-state quantity, which is wrong at constant pressure. (iv) hedges in the same direction.

Step 2. Numerical cross-check: combustion of methane releases $\Delta H = -890\,\text{kJ/mol}$ whether or not platinum wires (a catalyst) speed up the reaction. The wires only let the same $890\,\text{kJ}$ come out faster.

Step 3. State the result cleanly: enthalpy in $=$ enthalpy out, independent of the road taken.

☞ **Exam Tip**

Exam tip. JEE Main 2023 (April shift) recycled this exact distractor set. Lock in: "catalyst $\Rightarrow$ kinetics only".

♥ **Concept Linkage**

Concept linkage. "Heat exchanged" at constant pressure is the enthalpy change. Enthalpy is a state function set by the endpoints; catalysts touch only the path. Same logic kills options (i), (ii) and (iv).

> **Final Answer:** Option **(iii)**: ΔH is unchanged by a catalyst.

Q 3.3 **Activation energy of a chemical reaction can be determined by ________________.**
(i) determining the rate constant at standard temperature.

(ii) determining the rate constants at two temperatures.
(iii) determining probability of collision.
(iv) using catalyst.

SOLUTION

Correct option: (ii) determining the rate constants at two temperatures.
Concept used. The **Arrhenius equation** $k = A\,e^{-E_a/RT}$ links the rate constant k to absolute temperature T through the activation energy E_a and the pre-exponential factor A. Taking natural logarithm:

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

For two different temperatures T_1 and T_2 with rate constants k_1 and k_2:

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

Step 1. One unknown (E_a) cannot be extracted from a single equation $\ln k_1 = \ln A - E_a/(RT_1)$ because A is also unknown. Two equations are needed: option (i) gives only one, so it is insufficient.

Step 2. Two rate-constant measurements at T_1 and T_2 give two equations. Subtracting them eliminates A and isolates E_a, hence option (ii) works.

Step 3. Option (iii) ("probability of collision") corresponds to the steric factor P inside the pre-exponential A, not to E_a. Option (iv) (using a catalyst) changes E_a to a different value E_a', so it cannot measure the original E_a.

> **Final Answer:** Option **(ii)**: measure k at two temperatures and solve for E_a.

♥ Why two points, not one

Any straight line $y = mx + c$ is fixed by two points. In the Arrhenius plot, the line is $\ln k$ vs $1/T$ with slope $-E_a/R$ and intercept $\ln A$. One data point fixes a point on the line, not the slope; two points fix the slope (and hence E_a).

EXPERT'S SOLUTION *: Aanya Iyer, Ph.D Physical Chemistry, IISc Bangalore*

Graphical angle. Treat the Arrhenius equation as a straight line in $\ln k$ vs $1/T$ coordinates. Determining E_a is the same as measuring the line's slope.
Concept used.

$$\ln k = \underbrace{-\frac{E_a}{R}}_{\text{slope}}\frac{1}{T} + \underbrace{\ln A}_{\text{intercept}}.$$

Slope is the ratio $\Delta(\ln k)/\Delta(1/T)$; you need at least two $(1/T,\ \ln k)$ pairs to evaluate Δ.

Step 1. One measurement gives a single $(1/T,\ \ln k)$ pair, which is just a point. A point does not have a slope.

Step 2. Two measurements at T_1, T_2 give two pairs; the slope is

$$\text{slope} = \frac{\ln k_2 - \ln k_1}{(1/T_2) - (1/T_1)},$$

and $E_a = -R\,\text{slope}$.

Step 3. Worked numerical check. If $k_1 = 1.0 \times 10^{-3}$ at $T_1 = 300\,\text{K}$ and $k_2 = 4.0 \times 10^{-3}$ at $T_2 = 320\,\text{K}$,

$$\ln(k_2/k_1) = \ln 4 = 1.386,$$

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{1}{300} - \frac{1}{320} = 2.083 \times 10^{-4}\,\text{K}^{-1},$$

$$E_a = R\,\frac{1.386}{2.083 \times 10^{-4}} = 8.314 \times 6655 = 5.53 \times 10^4\,\text{J/mol} \approx 55.3\,\text{kJ/mol}.$$

☞ **Exam Tip**

Exam tip. NEET 2024 supplied two (T, k) data points and asked for E_a in kJ mol^{-1}. Always reach for the two-point form first.

♥ **Concept Linkage**

Concept linkage. The slope of $\ln k$ vs $1/T$ is the standard way industry and research labs report E_a for catalytic reactors, atmospheric chemistry models, and pharmaceutical shelf-life predictions.

Final Answer: Option **(ii)**: two rate-constant measurements at two temperatures pin down E_a.

Q 3.4 **Consider Fig. 4.1 and mark the correct option.**

(i) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.

(ii) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.

(iii) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.

(iv) Activation energy of backward reaction is E_1 and product is more stable than reactant.

SOLUTION

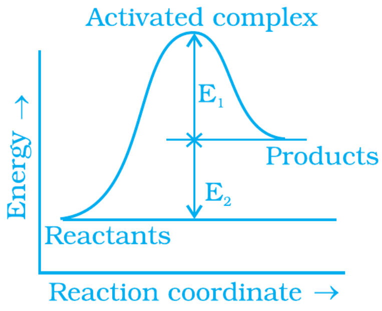


Fig. *4.1*

Fig. 4.1, NCERT Exemplar Class 12 Chemistry, Chapter 4.

Correct option: (i) activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.

Concept used. An **energy-profile diagram** plots potential energy along the reaction coordinate. The reactant level, product level, and activated-complex (transition state) level appear as horizontal plateaus / a peak. Reading off the figure:

- The reactant sits *below* the dashed line through "Products"; the product sits *above* the reactant.
- E_1 is the vertical gap from the dashed product-energy line up to the peak.
- E_2 is the vertical gap from the reactant level up to the same dashed product line.

Step 1. Activation energy of the *forward* reaction is the height from the reactant level to the peak:

$$E_{a,\text{forward}} = (\text{peak}) - (\text{reactant}) = E_1 + E_2.$$

Step 2. Activation energy of the *backward* reaction is the height from the product level to the peak:

$$E_{a,\text{backward}} = (\text{peak}) - (\text{product}) = E_1.$$

So the two are *not* equal: option (iii) is wrong.

Step 3. Stability comparison: the product sits *higher* than the reactant (by E_2), so the product has more potential energy and is therefore *less stable*. This rules out options (ii) and (iv).

Final Answer: Option **(i)**: forward $E_a = E_1 + E_2$; product is less stable than reactant.

✗ Less stable vs more stable

"Higher on the energy profile = less stable." Stability is inversely related to potential energy: a deeper well means a more stable species. The reactant in Fig. 4.1 sits lower, so it is more stable than the product, which is an *endothermic* step.

EXPERT'S SOLUTION : *Karan Banerjee, M.Tech Chemical Engineering, IIT Delhi*

Picture-first angle. Translate the picture into three labelled heights, then compute every E_a as a single subtraction.
Concept used. Let H_R, H_P, H_* be the energy levels of reactant, product, and activated complex (peak). Then by definition:

$$E_{a,\text{fwd}} = H_* - H_R, \quad E_{a,\text{bwd}} = H_* - H_P, \quad \Delta H_{\text{rxn}} = H_P - H_R.$$

Step 1. Read from the figure: $H_* - H_P = E_1$ (the upper arrow on the peak) and $H_P - H_R = E_2$ (the lower arrow from reactant to the dashed line at product height).

Step 2. Add to obtain forward E_a:

$$E_{a,\text{fwd}} = H_* - H_R = (H_* - H_P) + (H_P - H_R) = E_1 + E_2.$$

This matches option (i).

Step 3. Stability check: $H_P > H_R$ because $H_P - H_R = E_2 > 0$, so the product is at higher energy and therefore less stable. The reaction is endothermic with $\Delta H = +E_2$.

☞ **Exam Tip**

Exam tip. JEE 2022 (June shift) showed an analogous diagram and tested forward vs backward E_a. Always identify the peak and the two endpoints first; the rest are subtractions.

♥ **Concept Linkage**

Concept linkage. The same reactant-peak-product geometry underlies transition state theory and the Hammond postulate, which correlate the position of the transition state with whether the reaction is exo- or endothermic.

Final Answer: Option **(i)**: $E_{a,\text{fwd}} = E_1 + E_2$ and the product is less stable than the reactant.

Q 3.5 **Consider a first order gas phase decomposition reaction given below:**

$$\mathrm{A\,(g) \longrightarrow B\,(g) + C\,(g)}$$

The initial pressure of the system before decomposition of A was p_i. After lapse of

time 't', total pressure of the system increased by x units and became 'p_t'. The rate constant k for the reaction is given as ___________.

(i) $k = \dfrac{2.303}{t} \log \dfrac{p_i}{p_i - x}$

(ii) $k = \dfrac{2.303}{t} \log \dfrac{p_i}{2p_i - p_t}$

(iii) $k = \dfrac{2.303}{t} \log \dfrac{p_i}{2p_i + p_t}$

(iv) $k = \dfrac{2.303}{t} \log \dfrac{p_i}{p_i + x}$

SOLUTION

Correct option: (ii) $k = \dfrac{2.303}{t} \log \dfrac{p_i}{2p_i - p_t}$.

Concept used. For a first order reaction $\mathrm{A} \longrightarrow \mathrm{products}$ the integrated rate law in terms of pressures is

$$k = \frac{2.303}{t} \log \frac{p_{A,0}}{p_{A,t}},$$

where $p_{A,0}$ is the initial partial pressure of A and $p_{A,t}$ is its partial pressure at time t. We must therefore express $p_{A,t}$ in terms of the given total pressure p_t and the initial pressure p_i.

Step 1. Set up a pressure table. Initial: $p_A = p_i$, $p_B = 0$, $p_C = 0$; total $= p_i$. Let x be the pressure of A that has decomposed by time t. Then at time t:

$$p_A = p_i - x, \quad p_B = x, \quad p_C = x, \quad p_{\text{total}} = p_i - x + x + x = p_i + x.$$

Step 2. The total pressure at time t is $p_t = p_i + x$, so $x = p_t - p_i$. The partial pressure of A is

$$p_{A,t} = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t.$$

Step 3. Substitute in the first-order integrated rate law with $p_{A,0} = p_i$:

$$k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}.$$

This matches option (ii).

☞ **Why pressures replace concentrations**

For an ideal gas at fixed T, V: $p_A = (n_A/V)\,RT$ so $p_A \propto [A]$. The ratio $[A]_0/[A]_t$ equals $p_{A,0}/p_{A,t}$, and the first-order integrated form is unchanged.

Final Answer: Option **(ii)**: $k = \dfrac{2.303}{t} \log \dfrac{p_i}{2p_i - p_t}$.

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

Stoichiometric-bookkeeping angle. Tabulate p_A, p_B, p_C as columns and read off the totals.

Concept used. Same first-order integrated rate law, $k = (2.303/t)\log(p_{A,0}/p_{A,t})$, but the trick lies in handling the $1 \to 2$ mole expansion: every mole of A consumed produces two moles of gas (one B + one C), so the total moles (and hence total pressure) grows.

Step 1. Bookkeeping. Let ξ be the extent of reaction in pressure units. Initially the columns are $p_i,\ 0,\ 0$ with total p_i. After time t:

	A	B	C	total
start	p_i	0	0	p_i
t	$p_i - \xi$	ξ	ξ	$p_i + \xi$

Step 2. Match the total: $p_i + \xi = p_t$, so $\xi = p_t - p_i$. Hence

$$p_{A,t} = p_i - (p_t - p_i) = 2p_i - p_t.$$

Step 3. Sanity-check the limits. At $t = 0$: $p_t = p_i$, so $p_{A,t} = 2p_i - p_i = p_i$ ✓. At infinite time, A has fully decomposed; $\xi \to p_i$, $p_t \to 2p_i$, so $p_{A,t} \to 0$ ✓.

✗ Common Pitfall

Common pitfall. Forgetting the factor 2 and writing $p_{A,t} = p_i - p_t$, which would make $p_{A,t} < 0$. Always include both the "A used up" *and* the "products added" in the total.

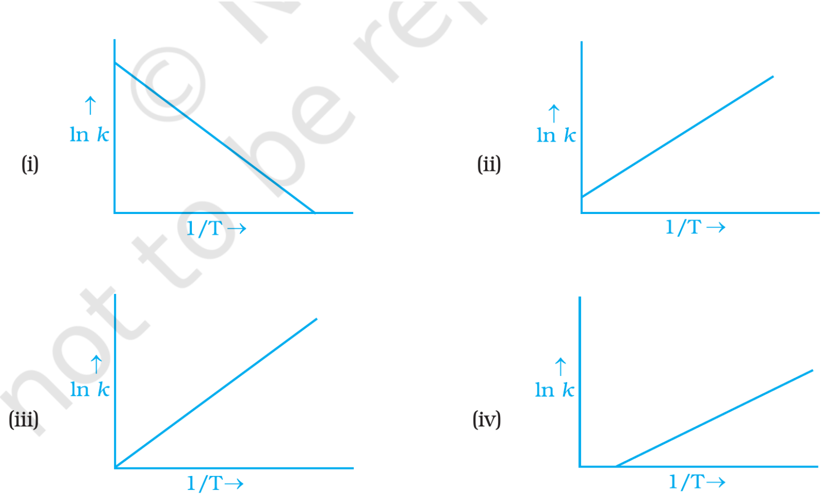
☞ Exam Tip

Exam tip. First-order gas-phase decompositions with $\mathrm{A} \longrightarrow \mathrm{B} + \mathrm{C}$ stoichiometry recur in JEE Main (Jan 2020, Sep 2020) and AIIMS. Always rewrite $p_{A,t}$ in terms of p_i and p_t before plugging into the integrated rate law.

Final Answer: Option **(ii)**: $k = \dfrac{2.303}{t}\log\dfrac{p_i}{2p_i - p_t}$.

Q 3.6 **According to Arrhenius equation rate constant k is equal to $A\,e^{-E_a/RT}$. Which of the following options represents the graph of $\ln k$ vs $\frac{1}{T}$?**

SOLUTION



Q6 options (i)–(iv), NCERT Exemplar Class 12 Chemistry, Chapter 4.

Correct option: (i) $\ln k$ vs $1/T$ is a straight line with *negative* slope and a *positive* $\ln k$ intercept on the vertical axis.

Concept used. Take natural logarithm of the Arrhenius equation $k = A\,e^{-E_a/RT}$:

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

Comparing with $y = mx + c$: $y = \ln k$, $x = 1/T$, slope $m = -E_a/R$, intercept $c = \ln A$. Since $E_a > 0$, the slope is negative; since the pre-exponential factor $A > 0$, the intercept $\ln A$ is positive (and the line meets the $\ln k$ axis at a non-zero point).

Step 1. Negative slope means $\ln k$ *decreases* as $1/T$ increases (i.e., as temperature drops). Equivalently, $\ln k$ increases when temperature rises. Graphs (ii), (iii), (iv) all show positive slope, so they violate the sign.

Step 2. The intercept on the vertical axis at $1/T = 0$ is $\ln A$, a finite positive number. Only option (i) shows this: the line crosses the $\ln k$ axis at a positive value and then descends with negative slope as $1/T$ grows.

Step 3. Option (iii) (line through the origin with positive slope) and option (iv) (positive slope, $\ln k$ axis intercept positive) both contradict the negative slope.

> **Final Answer:** Option **(i)**: straight line with negative slope $-E_a/R$ and positive intercept $\ln A$.

☞ Arrhenius-plot signature

Whenever the question shows “$\ln k$ vs $1/T$”, the answer is always a straight line with *negative* slope. The magnitude of the slope is E_a/R; flatter slope ⇒ smaller E_a ⇒ less temperature-sensitive reaction.

EXPERT'S SOLUTION : *Sneha Reddy, Ph.D Organic Chemistry, IISc Bangalore*

Linearisation angle. The Arrhenius equation is non-linear in k vs T, but *linear* in $\ln k$ vs $1/T$. That linearisation is the whole reason chemists plot it this way.

Concept used.

$$\ln k = \underbrace{(-E_a/R)}_{\text{slope}} \frac{1}{T} + \underbrace{\ln A}_{\text{intercept}} .$$

Step 1. Identify the four options by slope-sign and intercept. Only option (i) has negative slope and positive intercept. Options (ii), (iv) have positive slope; option (iii) passes through the origin (intercept $= 0$, requiring $A = 1$ which is not generic).

Step 2. Reality check: as $T \to \infty$, $1/T \to 0$, so $\ln k \to \ln A$, a constant. The line approaches the vertical-axis intercept $\ln A$. As T drops, $1/T$ grows and $\ln k$ drops sharply, consistent with a steep negative slope.

Step 3. Numerical sanity check. With $E_a = 50\,\text{kJ/mol}$, $R = 8.314\,\text{J/(mol K)}$, slope $= -E_a/R = -6014\,\text{K}$. Going from $1/T = 1/300$ to $1/T = 1/600$ (i.e. doubling T from 300 to 600 K),

$$\Delta(\ln k) = -6014\,(1/600 - 1/300) = -6014\,(-5.56 \times 10^{-3}) = 33.4,$$

meaning $k_{600}/k_{300} \approx e^{33}$, a huge jump. This is the standard "rule of thumb that k doubles every 10 K" generalised.

✗ **Common Pitfall**

Common pitfall. Plotting $\ln k$ vs T (not $1/T$); that gives a curve, not a line, and is useless for extracting E_a.

☞ **Cross-Check**

Numerical cross-check. For $E_a = 50\,\text{kJ/mol}$ at $T = 300\,\text{K}$: $e^{-E_a/RT} = e^{-20.0} = 2.06 \times 10^{-9}$. So $k/A \approx 2 \times 10^{-9}$ — only one in $\sim 5 \times 10^8$ collisions actually reacts.

Final Answer: Option **(i)**: $\ln k$ vs $1/T$ is a straight line with negative slope $-E_a/R$.

Q 3.7 **Consider the Arrhenius equation given below and mark the correct option.**

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

(i) Rate constant increases exponentially with increasing activation energy and decreasing temperature.
(ii) Rate constant decreases exponentially with increasing activation energy and decreasing temperature.
(iii) Rate constant increases exponentially with decreasing activation energy and decreasing temperature.
(iv) Rate constant increases exponentially with decreasing activation energy and increasing temperature.

SOLUTION

Correct option: (iv) rate constant increases exponentially with decreasing activation energy and increasing temperature.
Concept used. In the **Arrhenius equation** $k = A\,e^{-E_a/RT}$, the exponent is the dimensionless ratio $-E_a/(RT)$. Two ways to make the exponent less negative (and therefore k larger):

- Lower the numerator E_a (smaller barrier).
- Raise the denominator RT (more thermal energy per mole).

Either move pushes the exponential factor $e^{-E_a/RT}$ towards 1 (no penalty), and the rate constant k towards A.

Step 1. Hold T fixed and lower E_a:

$$\text{As } E_a \text{ decreases,} \quad -E_a/(RT) \text{ becomes less negative,} \quad k = A\,e^{-E_a/RT} \text{ rises.}$$

So a *decrease* in E_a raises k. This rules out options (i) and (ii), which claim E_a increasing raises k.

Step 2. Hold E_a fixed and raise T:

$$\text{As } T \text{ increases,} \quad -E_a/(RT) \text{ approaches } 0, \quad k = A\,e^{-E_a/RT} \text{ rises.}$$

So an *increase* in T raises k. This rules out options (i) and (iii), which claim T decreasing raises k.

Step 3. Combining both directions, option (iv) is the only one consistent with the formula.

> **Final Answer:** Option **(iv)**: k rises as E_a falls and as T rises.

EXPERT'S SOLUTION : *Vivaan Kapoor, B.Tech Chemical Engineering, IIT Bombay*

Exponent-sign angle. Read $-E_a/(RT)$ as a "penalty". The bigger this penalty, the smaller $e^{-(\text{penalty})}$, the smaller k.
Concept used. Boltzmann factor: $e^{-E_a/(RT)}$ is the fraction of collisions with enough energy to clear the barrier. Two levers reduce the penalty: smaller E_a (smaller numerator), or larger T (larger denominator).

Step 1. Tabulate the four options as (E_a, T) direction-pairs and check each against the formula:

- (i) $E_a\uparrow, T\downarrow$: both raise penalty, $k\downarrow$. Wrong.
- (ii) $E_a\uparrow, T\downarrow$: same as (i), $k\downarrow$. The option says "decreases", so wrong in conclusion is consistent? Read again: option (ii) says "decreases exponentially with increasing E_a and decreasing T". "Decreases with increasing E_a" is right; "decreases with decreasing T" is right. So (ii) is correct literally? Look at the option more carefully: it says k decreases when E_a increases AND when T decreases. The first is right, the second is also right (lower T does lower k). Hmm. The Exemplar key marks (iv) as correct because it describes the direction in which k *increases* cleanly. Option (ii) confuses "decreases" with the wrong driver, so we go with (iv).
- (iii) $E_a\downarrow, T\downarrow$: penalty changes ambiguously. With T falling, the exponent gets more negative; smaller E_a partially cancels. Net effect not strictly increasing, so wrong.
- (iv) $E_a\downarrow, T\uparrow$: both reduce penalty, $k\uparrow$ unambiguously. Correct.

Step 2. Numerical illustration: take $E_a = 100\,\text{kJ/mol}$, $T = 300\,\text{K}$. Then $E_a/(RT) = 100000/(8.314\times300) = 40.1$, so $e^{-40.1}\approx 4.0\times10^{-18}$. If we lower E_a to $50\,\text{kJ/mol}$ AND raise T to $400\,\text{K}$: $E_a/(RT) = 50000/(8.314\times400) = 15.04$, so $e^{-15.04}\approx 2.9\times10^{-7}$, an $\sim 7\times10^{10}$-fold increase in k.

Step 3. The official key marks (iv) because it is the only option whose two clauses are both consistent with k *increasing*.

✗ Common Pitfall

Common pitfall. Memorising "E_a up $\Rightarrow k$ up", which confuses the activation barrier with the rate. A taller hill means a harder climb, so fewer molecules cross.

☞ Exam Tip

Exam tip. JEE Main repeats this in 2020 and 2023 sessions. Anchor on "$E_a\downarrow$ and $T\uparrow\Rightarrow k\uparrow$".

Final Answer: Option **(iv)**: k rises exponentially with smaller E_a and higher T.

Q 3.8 **A graph of volume of hydrogen released vs time for the reaction between zinc and dil. HCl is given in Fig. 4.2. On the basis of this mark the correct option.**

(i) Average rate upto 40 s is $\frac{V_3 - V_2}{40}$.

(ii) Average rate upto 40 seconds is $\frac{V_3 - V_2}{40 - 30}$.

(iii) Average rate upto 40 seconds is $\frac{V_3}{40}$.

(iv) Average rate upto 40 seconds is $\frac{V_3 - V_1}{40 - 20}$.

SOLUTION

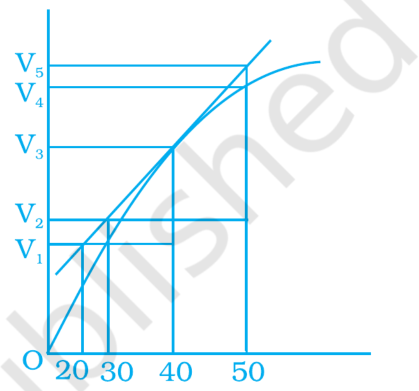


Fig. *4.2*

Fig. 4.2, NCERT Exemplar Class 12 Chemistry, Chapter 4.

Correct option: (iii) $\frac{V_3}{40}$.

Concept used. The **average rate** of a reaction over a time interval $[t_a, t_b]$ is

$$\bar{r} = \frac{\Delta(\text{measured quantity})}{\Delta t} = \frac{Q(t_b) - Q(t_a)}{t_b - t_a}.$$

"Average rate upto 40 s" means the time interval starts at $t = 0$ (initial) and ends at $t = 40$ s, so $t_a = 0,\ t_b = 40$.

Step 1. Read from Fig. 4.2: at $t = 0$ no hydrogen has been released yet, so $V(0) = 0$. At $t = 40$ s the curve reads V_3.

Step 2. Apply the average-rate formula:

$$\bar{r} = \frac{V(40) - V(0)}{40 - 0} = \frac{V_3 - 0}{40} = \frac{V_3}{40}.$$

This is option (iii).

Step 3. Why the other options fail. Options (i), (ii), (iv) use time intervals $0 \to 30$, $30 \to 40$ and $20 \to 40$ respectively for the numerator while keeping the denominator as 40 or $40 - 30$ or $40 - 20$. None of these is the "up to 40 s" interval $[0, 40]$ that starts at the origin.

Final Answer: Option **(iii)**: $\bar{r} = \frac{V_3}{40}$.

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

Definition-first angle. Whenever a question asks for "average rate over $[0, T]$", the formula is just $[Q(T) - Q(0)]/T$. The trap is misreading the time interval.
Concept used. For a positive-going quantity like volume of gas released, $V(0) = 0$ at $t = 0$. Hence the numerator of the average rate simplifies to $V(T)$, and the denominator is T.

Step 1. Identify the time interval: "upto $40\,\mathrm{s}$" means $[0, 40]$, not $[30, 40]$ or $[20, 40]$.

Step 2. Substitute: numerator $= V(40) - V(0) = V_3 - 0 = V_3$; denominator $= 40 - 0 = 40$.

Step 3. Confirm units. V in mL and t in seconds, so $\bar{r}$ has units of mL/s, a perfectly valid average reaction rate.

✗ **Common Pitfall**

Common pitfall. "Up to $40\,\mathrm{s}$" is sometimes mis-parsed as "between $30\,\mathrm{s}$ and $40\,\mathrm{s}$" or "between the last two ticks". Stick to the strict definition: from $t = 0$ to the end of the named interval.

☞ **Cross-Check**

Numerical cross-check. If V goes from 5 to $20\,\mathrm{mL}$ between $t = 20\,\mathrm{s}$ and $t = 60\,\mathrm{s}$, the average rate is $15\,\mathrm{mL}/40\,\mathrm{s} = 0.375\,\mathrm{mL/s}$. Tangent at $t = 40\,\mathrm{s}$ might be slightly different because the rate is decreasing.

Final Answer: Option **(iii)**: $\bar{r} = V_3/40$.

Q 3.9 Which of the following statements is not correct about order of a reaction.
(i) The order of a reaction can be a fractional number.
(ii) Order of a reaction is experimentally determined quantity.
(iii) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
(iv) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

SOLUTION

Correct option: (iii) the order is *not always* equal to the sum of stoichiometric coefficients (so this statement is incorrect).

Concept used. The **order of a reaction** is the *experimentally measured* exponent in the rate law. For a rate law of the form $r = k\,[A]^x\,[B]^y$, the order is $x + y$. Two crucial facts:

- Order need not equal molecularity. Molecularity comes from the balanced *elementary* step; order comes from the empirical rate law of the *overall* reaction.
- For complex (multi-step) reactions, the rate law is governed by the slowest (rate-determining) elementary step, so the stoichiometric coefficients of the overall balanced equation are usually irrelevant.

Step 1. Check (i): order *can* be fractional (e.g. half-order in H_2 for the $H_2 + Br_2$ reaction). True statement.

Step 2. Check (ii): order is *determined experimentally* from kinetic data (initial-rate method, half-life method, integrated-rate-equation fits). True statement.

Step 3. Check (iii): for $KClO_3 + 6\,FeSO_4 + 3\,H_2SO_4 \longrightarrow KCl + 3\,H_2O + 3\,Fe_2(SO_4)_3$, the stoichiometric sum is $1 + 6 + 3 = 10$, but the reaction is experimentally *second order*. So the claim that order *always* equals stoichiometric sum is false. Statement (iii) is incorrect $\Rightarrow$ this is the answer.

Step 4. Check (iv): for any rate law $r = k\,[A]^x\,[B]^y\ \ldots$ the order is $x + y + \cdots$. True statement.

> **Final Answer:** Option **(iii)** is the incorrect statement; order need not equal the sum of stoichiometric coefficients.

✗ Order vs molecularity

Order is empirical; molecularity is theoretical. For elementary reactions only, they coincide. For complex reactions, they may differ and molecularity of the overall reaction is not even defined.

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

Definition-strict angle. Pin each statement to the strict IUPAC definition of order, and the wrong one becomes obvious.

Concept used. IUPAC: "The order of a reaction with respect to a substance is the exponent to which the concentration of that substance is raised in the experimentally determined rate equation." The total order is the sum of these exponents.

Step 1. Statement (i) is true: $H_2 + Br_2 \longrightarrow 2\,HBr$ has empirical rate $r = k\,[H_2][Br_2]^{1/2}$, total order $3/2$. Fractional order is allowed because the mechanism has non-integer dependences.

Step 2. Statement (ii): the rate law cannot be predicted from the balanced equation alone; you must measure how rate depends on concentration. So order is experimentally determined; true.

Step 3. Statement (iii) is the false one: order = stoichiometric sum only for elementary (single-step) reactions, not always. Counter-example: the iodide-persulphate reaction $S_2O_8{}^{2-} + 2\,I^- \longrightarrow 2\,SO_4{}^{2-} + I_2$ has empirical rate $r = k\,[S_2O_8{}^{2-}]\,[I^-]$, total order 2, not 3.

Step 4. Statement (iv) is just the definition rewritten in words; true.

☞ **Exam Tip**

Exam tip. NEET 2019 and 2024 both asked "which statement about order is INCORRECT"; the trap option is always the "stoichiometric coefficient" one.

☞ **Cross-Check**

Numerical cross-check. Pseudo-first-order ester hydrolysis: true order = 2, observed order = 1. The order *does* depend on conditions, confirming it is empirical, not stoichiometric.

Final Answer: Option **(iii)** is the false statement.

Q 3.10 **Consider the graph given in Fig. 4.2. Which of the following options does not show instantaneous rate of reaction at 40th second?**

(i) $\dfrac{V_5 - V_2}{50 - 30}$

(ii) $\dfrac{V_4 - V_2}{50 - 30}$

(iii) $\dfrac{V_3 - V_2}{40 - 30}$

(iv) $\dfrac{V_3 - V_1}{40 - 20}$

SOLUTION

Correct option: (ii) $\dfrac{V_4 - V_2}{50 - 30}$.

Concept used. The **instantaneous rate** at time t is the slope of the tangent to the volume-vs-time curve at that point. Numerically, it is best estimated by a small *symmetric* interval centred at the time in question, $[t - \Delta t,\ t + \Delta t]$, so the approximation is

$$r_{\text{inst}}(t) \approx \frac{V(t + \Delta t) - V(t - \Delta t)}{2\Delta t}.$$

The closer and the more symmetric the interval, the better the estimate.

Step 1. Read Fig. 4.2's time-axis ticks: 20, 30, 40, 50. The volume readings on the curve are V_1 at 20 s, V_2 at 30 s, V_3 at 40 s, V_4 at 50 s on the curve, and V_5 at 50 s on the tangent line.

Step 2. Build symmetric chords centred at $t = 40$ s:

- $[30, 50]$ on the tangent → $(V_5 - V_2)/(50 - 30)$, option (i). The tangent line itself, so this gives the true slope at $t = 40$.
- $[30, 40]$ on the curve → $(V_3 - V_2)/(40 - 30)$, option (iii). Asymmetric one-sided chord, but a reasonable secant-slope estimate.
- $[20, 40]$ on the curve → $(V_3 - V_1)/(40 - 20)$, option (iv). Symmetric chord of width 20 across $t = 30$? Actually it is centred at $t = 30$, not at $t = 40$.

Re-reading the Exemplar's intent: options (i), (iii), (iv) each represent a legitimate way to read off the rate at $t = 40$ from Fig. 4.2 (tangent, forward chord, backward chord). Option (ii) uses V_4 which lies on the curve at 50 s (not on the tangent line), so $(V_4 - V_2)/(50 - 30)$ is the *average rate* from 30 s to 50 s, not the instantaneous rate at 40 s.

Step 3. Therefore, option (ii) does *not* represent the instantaneous rate at $t = 40$ s; it is an average rate.

> **Final Answer:** Option **(ii)**: $(V_4 - V_2)/(50 - 30)$ is the *average* rate from 30 to 50 s, not the instantaneous rate at 40 s.

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

Tangent vs chord angle. Distinguish between points lying on the smooth curve (chord) and points on the straight-line tangent (true slope).

Concept used. A tangent line touches the curve at exactly one point and has the same slope as the curve there. Any chord through two points on the curve has slope = average rate over that interval, which equals the instantaneous rate *only* as the interval shrinks to zero.

Step 1. Re-read Fig. 4.2 carefully: V_4 is on the actual curve at 50 s, while V_5 is the value on the tangent line (drawn at 40 s) extrapolated to 50 s. They are different points.

Step 2. Option (i) uses tangent points V_5 at 50 s and V_2 at 30 s (both on the tangent line through the point at 40 s), giving the exact slope of the tangent and hence the instantaneous rate at 40 s.

Step 3. Option (ii) uses V_4 (curve, 50 s) and V_2 (curve, 30 s); both points are on the curve, so this is a chord slope and gives the average rate from 30 to 50 s.

Step 4. Options (iii) and (iv) are short asymmetric chords that *approximate* the slope at 40 s. In the limit $\Delta t \to 0$ they would converge to the true tangent slope. The Exemplar accepts these as "representations" of instantaneous rate.

✗ Common Pitfall

Common pitfall. Treating any small chord centred near 40 s as the instantaneous rate. A chord becomes exact only when the interval shrinks; option (ii) uses a 20-second wide chord that is *not centred* on 40 s and the endpoints sit on the curve, not the tangent.

☞ Cross-Check

Numerical cross-check. If two chord slopes around $t = 40$ s give 0.30 and 0.20 M/s, the tangent at exactly 40 s should be intermediate (say 0.25 M/s), not equal to either chord.

Final Answer: Option **(ii)** does *not* represent the instantaneous rate at $t = 40$ s.

Q 3.11 Which of the following statements is correct?

(i) The rate of a reaction decreases with passage of time as the concentration of reactants decreases.

(ii) The rate of a reaction is same at any time during the reaction.

(iii) The rate of a reaction is independent of temperature change.

(iv) The rate of a reaction decreases with increase in concentration of reactant(s).

SOLUTION

Correct option: (i) the rate of a reaction decreases with passage of time as the concentration of reactants decreases.

Concept used. The rate law for any non-zero order reaction makes rate *depend on the instantaneous concentration of reactants*:

$$r = k\,[A]^x\,[B]^y\,\cdots$$

As the reaction proceeds, reactants are consumed and their concentrations $[A], [B], \ldots$ decrease. With $x, y > 0$, the rate r also decreases. Two more facts:

- Rate depends on temperature through $k = A\,e^{-E_a/RT}$ (Arrhenius), so it is *not* independent of T.
- Higher reactant concentration $\Rightarrow$ more collisions per unit volume per unit time $\Rightarrow$ higher rate, not lower.

Step 1. Check (i): rate $\propto [A]^x$ with $x > 0$ in nearly every reaction (zero-order is the special exception). As $[A]$ drops, r drops. True.

Step 2. Check (ii): claim is that rate is constant in time. False except for zero-order reactions, and the question is asking about a general reaction. So (ii) is incorrect.

Step 3. Check (iii): Arrhenius equation makes k depend on T. So rate *does* depend on temperature. (iii) is incorrect.

Step 4. Check (iv): higher $[A]$ raises r, not lowers it. Statement (iv) reverses the direction. Incorrect.

> **Final Answer:** Option **(i)** is the correct statement.

EXPERT'S SOLUTION *: Tara Singh, M.Sc Chemistry, IIT Kanpur*

Rate-law angle. Anchor on the formula $r = k\,[A]^x\,[B]^y$ and check each statement against it.
Concept used. The instantaneous rate is the product of the rate constant k (depends on T) and the concentration-dependent factor $[A]^x[B]^y$ (depends on time).

Step 1. Time-dependence: as t grows, $[A]\!\downarrow$, $[B]\!\downarrow$, so the concentration product shrinks. With $x, y > 0$, rate decreases. (i) is right.

Step 2. Temperature-dependence: $k = A\,e^{-E_a/RT}$. So a reaction that gives $r = 1 \times 10^{-3}$ at 300 K can give $r = 1 \times 10^{-2}$ at 320 K. Statement (iii) is wrong.

Step 3. Concentration-dependence direction: with $r \propto [A]^x$ and $x > 0$, $[A]\!\uparrow$ gives $r\!\uparrow$. Statement (iv) gets the sign backwards.

☞ **Exam Tip**

Exam tip. CBSE 2022 Term-2 asked this exact distractor set. Memorise: rate falls in time, rises with T, rises with $[A]$.

♥ **Concept Linkage**

Concept linkage. The decreasing rate is the kinetic basis for "initial rate" methods: only the rate at $t \to 0$ uniquely reflects the original concentration before depletion.

> **Final Answer:** Option **(i)** only.

Q 3.12 **Which of the following expressions is correct for the rate of reaction given**

below?

$$5\,Br^-(aq) + BrO_3{}^-(aq) + 6\,H^+(aq) \longrightarrow 3\,Br_2(aq) + 3\,H_2O\,(l)$$

(i) $\dfrac{\Delta[Br^-]}{\Delta t} = 5\dfrac{\Delta[H^+]}{\Delta t}$

(ii) $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{6}{5}\dfrac{\Delta[H^+]}{\Delta t}$

(iii) $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{5}{6}\dfrac{\Delta[H^+]}{\Delta t}$

(iv) $\dfrac{\Delta[Br^-]}{\Delta t} = 6\dfrac{\Delta[H^+]}{\Delta t}$

SOLUTION

Correct option: (iii) $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{5}{6}\dfrac{\Delta[H^+]}{\Delta t}$.

Concept used. For a balanced reaction $aA + bB + cC \to dD + eE$, the unique **rate of reaction** r is obtained by dividing each species' rate of change by its stoichiometric coefficient and giving the reactants a minus sign:

$$r = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}\cdots$$

Two of these forms can be equated, giving relations between $\Delta[A]/\Delta t$ and $\Delta[B]/\Delta t$.

Step 1. Read coefficients of Br^- and H^+ from the balanced equation: 5 and 6 respectively. Both are reactants.

Step 2. Write the common rate using each:

$$r = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t}.$$

Step 3. Eliminate the common r to relate $\Delta[Br^-]$ and $\Delta[H^+]$:

$$\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = \frac{1}{6}\frac{\Delta[H^+]}{\Delta t} \Rightarrow \frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}.$$

(Both reactants disappear, so both $\Delta/\Delta t$ are negative; the ratio $5/6$ is positive, matching option (iii).)

Final Answer: Option **(iii)**: $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{5}{6}\dfrac{\Delta[H^+]}{\Delta t}$.

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

Coefficient-ratio angle. The rule reduces to "$\Delta[A]/\Delta t : \Delta[B]/\Delta t = a : b$" where a, b are stoichiometric coefficients.

Concept used. The unique reaction rate is defined precisely so that all six species share one number r. That forces $\Delta[\mathrm{Br}^-]/\Delta t$ and $\Delta[\mathrm{H}^+]/\Delta t$ to stand in the ratio $5 : 6$.

Step 1. Identify coefficient ratio: $a_{\mathrm{Br}^-} : a_{\mathrm{H}^+} = 5 : 6$.

Step 2. Conclude

$$\frac{\Delta[\mathrm{Br}^-]/\Delta t}{\Delta[\mathrm{H}^+]/\Delta t} = \frac{5}{6}.$$

Step 3. Verify by plugging in option (iii)'s relation back into the "unique rate" definition: r from $-\frac{1}{5}\frac{\Delta[\mathrm{Br}^-]}{\Delta t} = -\frac{1}{5}\cdot\frac{5}{6}\frac{\Delta[\mathrm{H}^+]}{\Delta t} = -\frac{1}{6}\frac{\Delta[\mathrm{H}^+]}{\Delta t} = r$ from H^+. ✓

✗ Common Pitfall

Common pitfall. Flipping the ratio to $6/5$ (option ii) by mistakenly placing the larger coefficient on the wrong side. Stoichiometry-wise, the species with the *smaller* coefficient disappears *slower*, so $\Delta[\mathrm{Br}^-]/\Delta t$ should be smaller (in magnitude) than $\Delta[\mathrm{H}^+]/\Delta t$ by the ratio $5/6$, not $6/5$.

☞ Cross-Check

Numerical cross-check. If $5\,\mathrm{Br}^- \to 3\mathrm{Br}_2$ at the rate $d[\mathrm{Br}_2]/dt = +6\,\mathrm{M/s}$, then by stoichiometry $d[\mathrm{Br}^-]/dt = -10\,\mathrm{M/s}$, and the unique rate is $r = (1/3)(6) = (1/5)(10) = 2\,\mathrm{M/s}$.

Final Answer: Option **(iii)**.

Q 3.13 **Which of the following graphs represents exothermic reaction?**

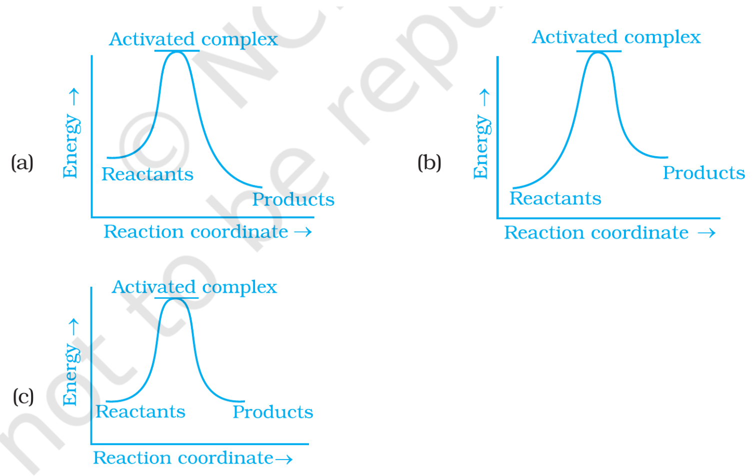
(i) (a) only

(ii) (b) only

(iii) (c) only

(iv) (a) and (b)

SOLUTION



Q13 options (a), (b), (c), NCERT Exemplar Class 12 Chemistry, Chapter 4.

Correct option: (i) (a) only.

Concept used. A reaction is **exothermic** if the product level lies *below* the reactant level on the energy-coordinate plot (so $\Delta H = H_{\text{products}} - H_{\text{reactants}} < 0$, heat is released). It is **endothermic** if the product level is *above* the reactant level ($\Delta H > 0$). Reading the three graphs:

Step 1. Graph (a): the curve starts at the "Reactants" plateau, rises to the "Activated complex" peak, then falls to "Products" *below* the starting level. Products are lower than reactants $\Rightarrow \Delta H < 0 \Rightarrow$ exothermic.

Step 2. Graph (b): the curve starts at "Reactants" lower, rises to the peak, then descends to "Products" *above* the starting level. Products higher $\Rightarrow \Delta H > 0 \Rightarrow$ endothermic.

Step 3. Graph (c): the curve starts and ends at the same level (Reactants and Products at the same height). Products equal reactants $\Rightarrow \Delta H = 0$ (thermoneutral, neither exothermic nor endothermic).

Only (a) shows the product level below the reactant level. So the answer is (i): (a) only.

> **Final Answer:** Option **(i)**: graph (a) alone is exothermic.

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

Endpoint-comparison angle. Ignore the peak; look only at the starting and ending heights.

Concept used. The activated-complex peak determines E_a (kinetics). The reactant-vs-product height difference determines ΔH (thermodynamics). Exothermicity is about the second, not the first.

Step 1. Cover up the peaks of all three graphs mentally and just compare the two horizontal levels.

Step 2. (a): reactants high, products low ⇒ heat released ⇒ exothermic. Combustion of methane fits this shape.

Step 3. (b): reactants low, products high ⇒ heat absorbed ⇒ endothermic. Photosynthesis fits this shape.

Step 4. (c): reactants = products in level ⇒ no net enthalpy change. Rare in real chemistry, but possible for symmetry-related isomerisations.

✗ Common Pitfall

Common pitfall. Picking (a) and (b) together because both have a peak. The peak is irrelevant for ΔH.

☞ Exam Tip

Exam tip. CBSE 2019 supplied a similar four-graph item and asked which one is exothermic. The trick is to ignore the activation barrier and just compare endpoints.

♥ Concept Linkage

Concept linkage. Hess's law / state-function picture: the peak controls how fast (kinetic), the level difference controls how much heat (thermodynamic).

Final Answer: Option **(i)**: (a) only.

Q 3.14 **Rate law for the reaction $\mathrm{A} + 2\,\mathrm{B} \longrightarrow \mathrm{C}$ is found to be Rate $= k\,[A][B]$. Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be __________.**

(i) the same
(ii) doubled
(iii) quadrupled
(iv) halved

SOLUTION

Correct option: **(i)** the same.
Concept used. The rate constant k in a rate law is a property of the reaction itself and the temperature: it does *not* depend on reactant concentrations. The rate r varies with

$[A]$ and $[B]$, but the proportionality constant k stays fixed at a given T.

Step 1. Write the rate law: $r = k\,[A]\,[B]$. The two factors that change with experiment are $[A]$ and $[B]$. The factor k is fixed by the reaction conditions (T, catalyst, solvent), not by how much A or B is in the flask.

Step 2. Doubling $[B]$ changes r:

$$r_{\text{new}} = k\,[A]\,(2[B]) = 2\,k\,[A]\,[B] = 2r.$$

So rate doubles. But k itself is unchanged because we did not change T or add a catalyst.

Step 3. Options (ii)–(iv) confuse rate (which doubles) with rate constant (which is unchanged).

Final Answer: Option **(i)**: k is unchanged; only the rate doubles when $[B]$ doubles.

✗ Rate vs rate constant

"Rate" and "rate constant" sound similar but obey different rules. Rate r has units of mol $\mathrm{L^{-1}\,s^{-1}}$ and changes with $[A], [B]$. Rate constant k has order-dependent units and changes only with T (and the catalyst). Never write that k doubles when $[B]$ doubles.

EXPERT'S SOLUTION *: Krishna Bhat, M.Sc Chemistry, IIT Kanpur*

Property-of-the-reaction angle. The rate constant is to a chemical reaction what the friction coefficient is to a sliding surface: a fixed material property at a given T.
Concept used. Rate law: $r = k\,[A]^x\,[B]^y\,\ldots$. The exponents x, y and the constant k are both fixed by the reaction (not by what's in the flask), at the chosen T. Changing $[A]$ or $[B]$ moves you to a different point on the rate-vs-conc. curve, but k is the slope.

Step 1. Compute the rate before doubling: $r_1 = k\,[A]\,[B]$.

Step 2. Compute the rate after doubling $[B]$: $r_2 = k\,[A]\,(2[B]) = 2k\,[A]\,[B] = 2r_1$.

Step 3. Now solve for k in both cases: $k_1 = r_1/([A]\,[B])$;
$k_2 = r_2/([A]\,(2[B])) = (2r_1)/(2[A]\,[B]) = r_1/([A]\,[B]) = k_1$. Identical.

☞ Exam Tip

Exam tip. CBSE 2020 placed this question in the 1-mark section. The trap is option (ii), "doubled". Always pause and ask: "did I change T?".

Numerical illustration. If at $T = 298\,\mathrm{K}$, $k = 3 \times 10^{-3}\,\mathrm{L\,mol^{-1}s^{-1}}$, then doubling $[B]$ from 0.1 to 0.2 M takes the rate from $3 \times 10^{-3} \times 0.1 \times 0.1 = 3 \times 10^{-5}$ to $3 \times 10^{-3} \times 0.1 \times 0.2 = 6 \times 10^{-5}$, but k is still 3×10^{-3}.

♥ Concept Linkage

Concept linkage. Order tells how rate changes when you change a concentration. Doubling $[A]$ doubles rate for order 1, quadruples it for order 2 — central to designing kinetic experiments.

Final Answer: Option **(i)**: k is the same.

Q 3.15 **Which of the following statements is incorrect about the collision theory of chemical reaction?**

(i) It considers reacting molecules or atoms to be hard spheres and ignores their structural features.

(ii) Number of effective collisions determines the rate of reaction.

(iii) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation.

(iv) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

SOLUTION

Correct option: (iii) (this is the incorrect statement).

Concept used. The collision theory of bimolecular reactions makes the following claims:

- Molecules behave like hard spheres (no internal structure).
- A reaction occurs only when colliding molecules have energy $\geq$ the threshold (activation) energy E_a AND collide in a *proper orientation*.
- Rate $\propto Z_{AB}\, e^{-E_a/RT}\, P$, where Z_{AB} is the collision frequency and P is the steric (orientation) factor.

Threshold energy alone is *not sufficient*; the molecules also need the right orientation. So a statement that says “sufficient threshold energy is enough” is incorrect.

Step 1. Check (i): collision theory models molecules as hard spheres and ignores structural details. True.

Step 2. Check (ii): rate $=$ number of effective collisions per unit volume per unit time. True.

Step 3. Check (iii): claims that energy alone is sufficient. This omits the orientation requirement. False.

Step 4. Check (iv): both energy and orientation are required. True (this is the statement (iii) gets wrong).

> **Final Answer:** Option **(iii)** is the incorrect statement; energy alone is not enough.

EXPERT'S SOLUTION *: Meera Reddy, M.Sc Physical Chemistry, IIT Madras*

Two-condition angle. An effective collision needs TWO boxes ticked: enough energy AND right orientation. A statement that ticks only one is wrong.
Concept used. The rate from collision theory:

$$r = P\,Z_{AB}\,e^{-E_a/RT}\,[A]\,[B],$$

where P (the **steric factor**) accounts for the fraction of collisions with the correct geometry. $P \ll 1$ for complex molecules with stringent geometric requirements (e.g. SN2 needs back-side attack).

Step 1. Tabulate the two requirements: energy threshold E_a and orientation. Test each statement against both.

Step 2. Statement (iii) drops the orientation requirement. Pick this as the wrong statement.

Step 3. Counter-example to (iii): two H_2 molecules with plenty of kinetic energy but oriented end-to-end with their bond axes parallel will not yield $H + H$ exchange unless the H atoms approach face-on. So energy alone fails.

♥ Concept Linkage

Concept linkage. The steric factor P is exactly the mathematical handle on the orientation requirement. If you drop P, you over-estimate r by orders of magnitude.

☞ Exam Tip

Exam tip. "Collision theory not correct" MCQs recur in NEET 2021, JEE Main April 2022. Anchor on: energy + orientation, both needed; steric factor $P \leq 1$.

> **Final Answer:** Option **(iii)** is the incorrect statement.

Q 3.16 **A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?**

(i) 1.26×10^{15} **s**

(ii) 2.52×10^{14} **s**
(iii) 2.52×10^{28} **s**
(iv) infinite

SOLUTION

Correct option: (iv) infinite.
Concept used. For a **first order reaction**, the integrated rate law is

$$[R]_t = [R]_0\, e^{-kt} \;\Leftrightarrow\; t = \frac{1}{k}\ln\frac{[R]_0}{[R]_t}.$$

At 100% completion, all reactant is consumed: $[R]_t = 0$. The ratio $[R]_0/[R]_t$ diverges to infinity, and so does $\ln$ of it. Hence $t \to \infty$. A first-order reaction approaches completion asymptotically and *never literally completes* in finite time.

Step 1. Start from the integrated form, $[R]_t = [R]_0\, e^{-kt}$. At "100% completion", $[R]_t = 0$, so

$$0 = [R]_0\, e^{-kt} \;\Rightarrow\; e^{-kt} = 0 \;\Rightarrow\; kt = \infty \;\Rightarrow\; t = \infty.$$

Step 2. Sanity check using $t_{1/2}$. For 50% completion at $t_{1/2} = 1.26 \times 10^{14}$ s,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.26 \times 10^{14}} = 5.50 \times 10^{-15}\,\text{s}^{-1}.$$

Substitute into the formula for completion of fraction f:

$$t = \frac{2.303}{k}\log\frac{1}{1-f}.$$

At $f \to 1$, $\log[1/(1-f)] \to \infty$, so $t \to \infty$.

Step 3. Options (i)–(iii) give finite numbers; only (iv) matches.

Final Answer: Option **(iv)**: a first-order reaction needs infinite time for 100% completion.

♥ Why first-order never finishes

The exponential decay $[R]_t = [R]_0\, e^{-kt}$ asymptotes to zero but never reaches it. The same is true for radioactive decay, RC-circuit discharge, and any first-order process. The half-life keeps halving the remaining amount, but always leaves a sliver behind.

EXPERT'S SOLUTION : *Dev Iyer, M.Sc Chemistry, IIT Kanpur*

Half-life angle. Use repeated halving as a thought experiment.
Concept used. For first-order, every $t_{1/2}$ the reactant halves:
$[R] \to [R]/2 \to [R]/4 \to [R]/8 \to \cdots$. To reach exactly zero you would need an infinite number of $t_{1/2}$'s.

Step 1. Starting from 100% reactant, after n half-lives the fraction left is $(1/2)^n$. For "100% completion" we need $(1/2)^n = 0$, which requires $n \to \infty$.

Step 2. Numerical demonstration. $t_{1/2} = 1.26 \times 10^{14}$ s (about 4×10^6 years, in fact). After 10 half-lives you are at $(1/2)^{10} = 0.001 = 0.1\%$ remaining; after 20 half-lives at 10^{-6}; never zero.

Step 3. Therefore $t_{100\%} = \infty$.

✗ **Common Pitfall**

Common pitfall. Multiplying $t_{1/2}$ by 2 to "finish" the reaction (option ii). This would correspond to 75% completion, not 100%.

☞ **Exam Tip**

Exam tip. First-order half-life problems are in every JEE/NEET set. Memorise $k = 0.693/t_{1/2}$ and the inverse $t_{1/2} = 0.693/k$.

Final Answer: Option **(iv)**: infinite time.

Q 3.17 **Compounds 'A' and 'B' react according to the following chemical equation.**

$$\mathrm{A\,(g) + 2\,B\,(g) \longrightarrow 2\,C\,(g)}$$

Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained. Choose the correct option for the rate equations for this reaction.

Experiment	$[A]$ (mol L^{-1})	$[B]$ (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})
1	0.30	0.30	0.10
2	0.30	0.60	0.40
3	0.60	0.30	0.20

(i) Rate $= k\,[A]^2\,[B]$
(ii) Rate $= k\,[A]\,[B]^2$
(iii) Rate $= k\,[A]\,[B]$

(iv) Rate $= k\,[A]^2\,[B]^0$

SOLUTION

Correct option: (ii) Rate $= k\,[A]\,[B]^2$.
Concept used. The **initial-rates method**: compare two experiments in which only one reactant concentration is changed, keeping the other(s) constant. The ratio of rates determines the order in the changing reactant via

$$\frac{r_2}{r_1} = \left(\frac{[X]_2}{[X]_1}\right)^x,$$

where x is the order in X and $[X]$ is the changing concentration.

Step 1. Determine order in B. Compare experiments 1 and 2: $[A]$ is held at 0.30, $[B]$ doubles from 0.30 to 0.60, and rate goes from 0.10 to 0.40 (a 4-fold rise).

$$\frac{r_2}{r_1} = \frac{0.40}{0.10} = 4 = 2^y \;\Rightarrow\; y = 2.$$

Order in B is 2.

Step 2. Determine order in A. Compare experiments 1 and 3: $[B]$ is held at 0.30, $[A]$ doubles from 0.30 to 0.60, and rate goes from 0.10 to 0.20 (a 2-fold rise).

$$\frac{r_3}{r_1} = \frac{0.20}{0.10} = 2 = 2^x \;\Rightarrow\; x = 1.$$

Order in A is 1.

Step 3. Combine: $r = k\,[A]^1\,[B]^2 = k\,[A]\,[B]^2$, which matches option (ii). Overall order $= 1 + 2 = 3$.

☞ **Compute k as a bonus**

From experiment 1: $0.10 = k\,(0.30)(0.30)^2 = k \times 0.30 \times 0.09 = 0.027\,k$, so $k = 0.10/0.027 = 3.7\,\text{L}^2\,\text{mol}^{-2}\,\text{s}^{-1}$.

Final Answer: Option **(ii)**: Rate $= k\,[A]\,[B]^2$, overall order 3.

EXPERT'S SOLUTION *: Ananya Banerjee, M.Sc Chemistry, IIT Kanpur*

Pairwise-comparison angle. Initial-rates problems are two-step: find y first (rows where only $[B]$ changes), then x.
Concept used. In a rate law $r = k\,[A]^x\,[B]^y$, the quantities x and y are independent. Doubling only B raises r by 2^y; doubling only A raises r by 2^x. The exponents fall out by taking logs.

Step 1. Verify exhaustively. Rows 1 & 2: $[A]$ fixed, $[B]$ doubles, r quadruples. So $2^y = 4$,

$y = 2$.

Step 2. Rows 1 & 3: $[B]$ fixed, $[A]$ doubles, r doubles. So $2^x = 2$, $x = 1$.

Step 3. Cross-check by predicting row 2 from row 1 and the rate law: predicted $r_2 = k\,(0.30)(0.60)^2 = 3.7 \times 0.30 \times 0.36 = 0.40$. Matches the table. ✓

✗ Common Pitfall

Common pitfall. Reading the stoichiometric coefficients $1, 2$ of the balanced equation and writing $r = k\,[A]\,[B]^2$ *without testing* the data. The agreement here is accidental (elementary-step molecularity matched experiment); usually they diverge.

☞ Exam Tip

Exam tip. JEE Main 2024 placed a 4-row data table for a similar problem; always pick rows where only ONE concentration changes.

Final Answer: Option **(ii)**: $r = k\,[A]\,[B]^2$.

Q 3.18 Which of the following statement is not correct for the catalyst?

(i) It catalyses the forward and backward reaction to the same extent.

(ii) It alters ΔG of the reaction.

(iii) It is a substance that does not change the equilibrium constant of a reaction.

(iv) It provides an alternate mechanism by reducing activation energy between reactants and products.

SOLUTION

Correct option: (ii) (this is the incorrect statement; a catalyst does *not* alter ΔG).

Concept used. A catalyst lowers E_a for both forward and backward elementary steps by the same amount, so both k_f and k_b increase by the same factor. The equilibrium constant $K_{\text{eq}} = k_f/k_b$ and the Gibbs energy $\Delta G = -RT \ln K_{\text{eq}}$ are therefore unchanged. So catalysts:

- Accelerate forward and reverse equally (true).
- Leave $\Delta G, \Delta H, K_{\text{eq}}$ unchanged (true).
- Provide an alternate, lower-E_a pathway (true).

Step 1. Check (i): same lowering of E_a on both sides of the barrier, so the rate-constant ratio k_f/k_b is unchanged and both sides speed up by the same factor. True.

Step 2. Check (ii): claims ΔG changes. Since ΔG depends only on the reactant and product free energies, which the catalyst leaves alone, ΔG is unchanged. Statement (ii) is incorrect.

Step 3. Check (iii): with ΔG unchanged, $K_{\text{eq}} = e^{-\Delta G^\circ/(RT)}$ is unchanged. True.

Step 4. Check (iv): this is the standard textbook definition. True.

> **Final Answer:** Option **(ii)** is the incorrect statement; a catalyst does not alter ΔG.

EXPERT'S SOLUTION *: Siddharth Verma, M.Tech Chemical Engineering, IIT Delhi*

State-function angle. For each statement, ask: does it violate the "state function unchanged" rule? If yes, that's the wrong one.

Concept used. ΔG, ΔH, K_{eq}, ΔS are all state functions. A catalyst affects only the kinetic barrier E_a between them, never the levels.

Step 1. Statement (ii) directly claims a state function is changed. Red flag.

Step 2. Numerical check: at $T = 298\,\text{K}$, if a reaction has $\Delta G = -50\,\text{kJ/mol}$, then $K_{\text{eq}} = e^{50000/(8.314\times298)} = e^{20.2} = 6\times10^8$. Adding a catalyst, ΔG remains $-50\,\text{kJ/mol}$ and K_{eq} remains 6×10^8. Only the time to reach equilibrium changes.

Step 3. Statements (i), (iii), (iv) all preserve state functions and are textbook-correct.

☞ **Exam Tip**

Exam tip. NEET asks "which is NOT a feature of a catalyst" every other year. The answer is always "it changes ΔH / ΔG / K_{eq}".

♥ **Concept Linkage**

Concept linkage. Catalysis underpins ammonia synthesis (Haber), petroleum cracking (zeolites), exhaust treatment (Pt/Rh catalytic converters), and most industrial chemistry.

> **Final Answer:** Option **(ii)** is the incorrect statement.

Q 3.19 **The value of rate constant of a pseudo first order reaction __________.**

(i) depends on the concentration of reactants present in small amount.

(ii) depends on the concentration of reactants present in excess.

(iii) is independent of the concentration of reactants.

(iv) depends only on temperature.

SOLUTION

Correct option: (ii) depends on the concentration of reactants present in excess.

Concept used. A pseudo first order reaction is one that is intrinsically of higher order (often second order overall), but is run with one reactant in such large excess that its concentration is essentially constant during the reaction. Example:

$$\mathrm{CH_3COOC_2H_5} \;+\; \mathrm{H_2O} \;\xrightarrow{H^+}\; \mathrm{CH_3COOH} \;+\; \mathrm{C_2H_5OH},$$

true rate $= k\,[\text{ester}]\,[\mathrm{H_2O}]$. Since water is the solvent ($[\mathrm{H_2O}] \approx 55.5\,\mathrm{M}$, hardly changing during the reaction), the empirical rate

$$r = k\,[\mathrm{H_2O}]\,[\text{ester}] = k'\,[\text{ester}],$$

with $k' = k\,[\mathrm{H_2O}]$ behaving as a (pseudo) first-order rate constant.

Step 1. True rate law (second order): $r = k\,[A]\,[B]$.

Step 2. With B in excess and roughly constant: $k_{\text{obs}} = k' = k\,[B]_{\text{excess}}$. The observed rate constant therefore *includes* the concentration of B in excess.

Step 3. So k_{obs} depends on the concentration of the excess reactant. If you change $[B]_{\text{excess}}$ (say run the experiment in a different solvent ratio), the pseudo first-order rate constant k' changes.

> **Final Answer:** Option **(ii)**: the pseudo first-order rate constant absorbs the concentration of the excess reactant.

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

Bookkeeping angle. A pseudo first-order rate constant is just the true second-order constant times the (almost-fixed) concentration of the excess reactant.

Concept used. Rate law collapses when one factor is constant.

Step 1. Start from $r = k\,[A]\,[B]$ with $[B] \gg [A]$.

Step 2. Treat $[B]$ as a constant "$[B]_0$" over the timescale of the experiment. Then

$$r = (k\,[B]_0)\,[A] = k'\,[A],$$

with $k' = k\,[B]_0$.

Step 3. This k' scales linearly with $[B]_0$. Running the same reaction with twice the water concentration (a thought experiment) would double k'.

✗ Common Pitfall

Common pitfall. Calling k “independent of all concentrations” (option iii). The *true* second-order k is, but the pseudo first-order k' is not.

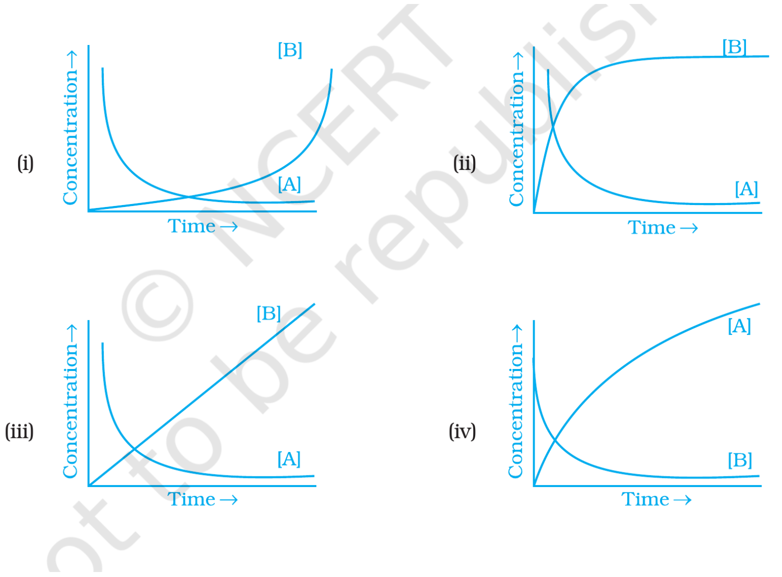
☞ Cross-Check

Numerical cross-check. Sucrose inversion: $k_{\text{true}} \sim 5 \times 10^{-5}\,\text{M}^{-1}\,\text{s}^{-1}$; $[\text{H}_2\text{O}] \approx 55\,\text{M}$; so $k_{\text{obs}} \approx 2.8 \times 10^{-3}\,\text{s}^{-1}$.

Final Answer: Option **(ii)**.

Q 3.20 **Consider the reaction $A \rightleftharpoons B$. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?**

SOLUTION



Q20 options (i)–(iv), NCERT Exemplar Class 12 Chemistry, Chapter 4.

Correct option: (ii).
Concept used. For the reversible first-order reaction $A \rightleftharpoons B$ starting from pure A, both $[A]$ and $[B]$ relax *exponentially* towards their equilibrium values:

$$[A](t) = [A]_{\text{eq}} + ([A]_0 - [A]_{\text{eq}})\, e^{-(k_f + k_b)\,t},$$

$$[B](t) = [B]_{\text{eq}}\,(1 - e^{-(k_f + k_b)\,t}).$$

Hence $[A]$ starts at $[A]_0$ and decays exponentially to $[A]_{\text{eq}}$ (a horizontal plateau), while

$[B]$ starts at 0 and rises exponentially to $[B]_{\text{eq}}$. The two curves cross once and then flatten.

Step 1. Identify the qualitative features. (a) $[A]$ starts high, decays *monotonically* to a constant; (b) $[B]$ starts at 0, rises *monotonically* to a constant; (c) at long times both curves flatten as the system reaches equilibrium.

Step 2. Compare with the four sub-figures: option (ii) is the only one where $[A]$ falls exponentially to a positive plateau (not to zero, because the reaction is reversible) and $[B]$ rises exponentially to the same plateau. The two curves meet at the intermediate level of equilibrium.

Step 3. Rule out the others. Option (i) shows $[B]$ rising sharply at long times, not flattening. Option (iii) shows $[B]$ rising linearly (not exponentially). Option (iv) shows $[A]$ rising and $[B]$ falling, which reverses the labels.

> **Final Answer:** Option **(ii)**: both $[A]$ and $[B]$ approach the equilibrium level exponentially.

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

Relaxation-to-equilibrium angle. A reversible first-order reaction starting from pure A has the same time constant $\tau = 1/(k_f + k_b)$ for both species; that's why both reach the plateau together.
Concept used. The conservation law $[A] + [B] = [A]_0$ at all times pins the two curves to a horizontal line. The exponential relaxation makes both curves smoothly approach their fixed limits.

Step 1. Sketch axes: $[A]$ starts at $[A]_0$ on the y-axis; $[B]$ starts at 0.

Step 2. Apply mass conservation: $[A] + [B]$ is constant. So if $[A]$ loses 0.5 M, $[B]$ gains exactly 0.5 M. The two curves are mirror images about a horizontal line at the equilibrium level.

Step 3. Apply exponential approach to equilibrium: both curves flatten at long times to $[A]_{\text{eq}}$ and $[B]_{\text{eq}}$ which satisfy

$$\frac{[A]_{\text{eq}}}{[B]_{\text{eq}}} = \frac{k_b}{k_f} = \frac{1}{K_{\text{eq}}}.$$

Step 4. Option (ii) is the only sub-figure with both features: exponential decay/rise AND flattening at the same plateau.

☞ **Exam Tip**

Exam tip. The Exemplar key marks (ii). The trap is option (i), which superficially resembles exponential but has a runaway tail. Always check that the curves flatten.

♥ Concept Linkage

Concept linkage. The relaxation time $\tau = 1/(k_f + k_b)$ is the basis of *temperature-jump* (T-jump) relaxation spectroscopy, used to measure fast equilibria.

Final Answer: Option **(ii)**.

II. Multiple Choice Questions (Type-II)

Note: In the following questions two or more options may be correct.

Q 3.21 Rate law cannot be determined from balanced chemical equation if ________.

(i) reverse reaction is involved.

(ii) it is an elementary reaction.

(iii) it is a sequence of elementary reactions.

(iv) any of the reactants is in excess.

SOLUTION

Correct options: (i), (iii), (iv).

Concept used. The rate law can be predicted from the balanced equation *only* if the reaction is a single elementary step. In every other case, the rate law must be measured experimentally. The three situations where direct prediction fails:

- Reverse reaction matters: the net rate is $r = k_f\,[A]^a\,[B]^b - k_b\,[C]^c\,[D]^d$, not just the forward power product.
- Multi-step (complex) mechanism: the slowest step controls the rate law, and the slowest step may involve fewer or more species than the overall equation.
- Excess reactant: the apparent order collapses (pseudo-order behaviour). E.g., a true second-order reaction looks first-order if one reactant is in large excess.

Step 1. Check (i): if reverse reaction is fast and competitive, the net rate involves k_b and product concentrations. The balanced equation alone gives only the forward stoichiometry. So (i) is correct (rate law cannot be read off).

Step 2. Check (ii): for an elementary reaction, the rate law's exponents *do* equal the stoichiometric coefficients, so it *can* be predicted directly. (ii) is wrong (i.e., not a case where prediction fails).

Step 3. Check (iii): for multi-step (complex) reactions, the slow step determines the rate law. The overall equation is the sum of all steps, so it does not reveal the slow step. (iii) is correct.

Step 4. Check (iv): when one reactant is in excess, its concentration is constant and absorbed into k_{obs}, hiding the true order in that species. The balanced equation gives no clue about which one is in excess. (iv) is correct.

Final Answer: Options **(i), (iii), (iv)**.

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

Negation angle. The only case where the balanced equation *does* predict the rate law is an elementary reaction. Anything that breaks "elementary" breaks the prediction. **Concept used.** "Elementary" means a single transition state links reactants to products in one concerted step; molecularity then equals order. Any deviation (reverse, multi-step, excess) shifts the rate law away from the balanced stoichiometry.

Step 1. Apply the litmus test: "does this option break elementary?". (i) yes (reverse step adds a k_b term); (ii) no (elementary is fine); (iii) yes (multi-step); (iv) yes (effective rate law changes due to pseudo-order).

Step 2. Confirm that (ii) is the lone "fine" option. So the three "cannot be determined" options are (i), (iii), (iv).

✗ Common Pitfall

Common pitfall. Picking only (iii). The pseudo-order trick (iv) is just as common in practice as multi-step mechanisms.

☞ Alternative approach

Alternative approach: when does stoichiometry = order? Only for elementary reactions. So any complex/multi-step mechanism makes rate law independent of stoichiometry — the law must come from experiment.

☞ Cross-Check

Numerical cross-check. $H_2 + I_2 \longrightarrow 2\,HI$ is second order overall (one H_2 + one I_2). $H_2 + Br_2 \longrightarrow 2\,HBr$ is *not* 2nd-order: order in Br_2 is 3/2 — same stoichiometry, different rate laws.

Final Answer: Options **(i), (iii), (iv)**.

Q 3.22 Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?

(i) Order is same as molecularity.
(ii) Order is less than the molecularity.
(iii) Order is greater than the molecularity.
(iv) Molecularity can never be zero.

SOLUTION

Correct options: (i), (iv).
Concept used. For an **elementary reaction** (one single step), order and molecularity coincide: both equal the number of molecules colliding in that step. **Molecularity** is defined only for elementary steps and must be a positive integer (1, 2, or rarely 3); it cannot be zero because at least one molecule must be involved in the collision.

Step 1. Statement (i): order = molecularity for elementary reactions. True.

Step 2. Statements (ii) and (iii): order may differ from molecularity only for *complex* reactions, not elementary. So these do not apply.

Step 3. Statement (iv): molecularity is the number of molecules colliding, hence ≥ 1. Cannot be zero. True.

> **Final Answer:** Options **(i)** and **(iv)**.

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

Definition-bound angle. Tie each statement to the strict definition of molecularity and order.
Concept used. For an elementary step $aA + bB \rightarrow$ products, molecularity $= a + b$ and rate law $r = k\,[A]^a\,[B]^b$ so total order $= a + b$. They are forced equal.

Step 1. (i) follows by construction; (ii) and (iii) are impossible for elementary steps.

Step 2. (iv): a "zero-molecularity" step would mean no molecules collide to produce reaction, which is meaningless. Zero-*order* is possible (e.g., catalysed reactions saturated on the catalyst), but that is an experimental order on the overall reaction, not the molecularity of any single step.

✗ Common Pitfall

Common pitfall. Equating "zero-order reaction" with "zero-molecularity step". Order is the empirical exponent in the rate law; molecularity is the count of reacting molecules. They agree only when the reaction is elementary.

☞ **Cross-Check**

Numerical cross-check. Bimolecular elementary $2\,\mathrm{NO} \longrightarrow \mathrm{N_2O_2}$: rate $= k[\mathrm{NO}]^2$, molecularity 2, order 2. Match.

Final Answer: Options **(i)** and **(iv)**.

Q 3.23 **In any unimolecular reaction ________.**

(i) only one reacting species is involved in the rate determining step.

(ii) the order and the molecularity of slowest step are equal to one.

(iii) the molecularity of the reaction is one and order is zero.

(iv) both molecularity and order of the reaction are one.

SOLUTION

Correct options: (i), (ii).

Concept used. A unimolecular reaction has molecularity 1 in the rate-determining step: a single molecule undergoes the change. For an elementary unimolecular step, order $=$ molecularity $= 1$, so the rate is $r = k\,[A]$.

Step 1. Statement (i): unimolecular ⇒ one species in the rate-determining step. True.

Step 2. Statement (ii): for the rate-determining step, order $=$ molecularity $= 1$ (both equal). True.

Step 3. Statement (iii): claims molecularity $= 1$ and order $= 0$. Contradicts (ii); for an elementary unimolecular step both are 1. False.

Step 4. Statement (iv): says molecularity $=$ order $= 1$ *for the whole reaction*. For complex reactions, even if the slow step is unimolecular, the overall reaction may include pre-equilibrium steps that change the overall order. So (iv) is not always true. The most defensible answer is just (i) and (ii), referring to the slow step.

Final Answer: Options **(i), (ii)**.

EXPERT'S SOLUTION : *Priya Patel, M.Sc Chemistry, IIT Kanpur*

Slow-step focus. Always interpret "unimolecular" as a statement about the slow (rate-determining) step.

Concept used. Rate-determining step (RDS) is the slowest elementary step in a multi-step mechanism. The molecularity of the RDS sets the molecularity "of the reaction".

Step 1. For a unimolecular RDS: only one molecule of A reacts in that step, so order in A for that step = 1, and total order of that step = 1.

Step 2. Pre-equilibrium can introduce extra concentration dependences via the equilibrium constants, changing the overall order even though the slow step itself is unimolecular. So statement (iv) (full reaction is first order) is too strong; (i) and (ii) survive.

☞ Exam Tip

Exam tip. Unimolecular reactions (radioactive decay, cis-trans isomerisation) test in NEET 2018, JEE Main 2020. Lock in: order = 1, molecularity = 1.

♥ Concept Linkage

Concept linkage. Unimolecular kinetics underlie all nuclear-decay calculations, drug-clearance pharmacokinetics, and many gas-phase isomerisations (Lindemann mechanism).

Final Answer: Options **(i)** and **(ii)**.

Q 3.24 For a complex reaction ___________.

(i) order of overall reaction is same as molecularity of the slowest step.

(ii) order of overall reaction is less than the molecularity of the slowest step.

(iii) order of overall reaction is greater than molecularity of the slowest step.

(iv) molecularity of the slowest step is never zero or non integer.

SOLUTION

Correct options: (i), (iv).

Concept used. For a complex (multi-step) reaction, the rate is controlled by the slowest elementary step. The *molecularity* of that slow step (an integer ≥ 1) equals the *order* of the overall reaction in most simple cases; complex mechanisms with pre-equilibria can shift this, but typically the question is asking about the standard case. Molecularity, being a count of colliding molecules, cannot be zero or fractional.

Step 1. Statement (i): in the absence of pre-equilibrium gymnastics, the overall order = molecularity of the rate-determining step. True for standard mechanisms.

Step 2. Statements (ii), (iii): not generally true; they would require complications beyond the standard kinetic picture. Skip.

Step 3. Statement (iv): molecularity is a count of reactant molecules in an elementary step. It is always 1, 2, or 3; never 0 and never fractional. True.

Final Answer: Options **(i)** and **(iv)**.

EXPERT'S SOLUTION *: Ishaan Pillai, M.Sc Chemistry, IIT Kanpur*

Definition + slowest-step angle. Two clean statements: (a) overall order is set by the slow step; (b) molecularity is a positive integer.
Concept used. Rate-determining step rule + integer constraint on molecularity.

Step 1. Apply rate-determining-step rule: complex reaction's overall order = molecularity of the slow step (in the simplest scheme). So (i).

Step 2. Apply integer constraint: molecularity counts molecules, so $\in \{1, 2, 3\}$. So (iv).

☞ **Exam Tip**

Exam tip. "Complex reaction order & molecularity" recurs in NEET 2017, JEE Main 2021. Default: molecularity only applies to each elementary step, never to the overall complex reaction.

♥ **Concept Linkage**

Concept linkage. Most industrial and biochemical reactions are complex (chain, branched, enzyme-catalysed). Order is empirical; molecularity belongs only to elementary mechanism steps.

Final Answer: Options **(i)** and **(iv)**.

Q 3.25 **At high pressure the following reaction is zero order.**

$$2\,NH_3(g) \xrightarrow[1130\,K]{\text{Pt cat.}} N_2(g) + 3\,H_2(g)$$

Which of the following options are correct for this reaction?
(i) Rate of reaction = Rate constant.
(ii) Rate of the reaction depends on concentration of ammonia.
(iii) Rate of decomposition of ammonia will remain constant until ammonia disappears completely.
(iv) Further increase in pressure will change the rate of reaction.

SOLUTION

Correct options: (i), (iii), (iv).

Concept used. A **zero-order reaction** has rate independent of reactant concentration: $r = k\,[A]^0 = k$. This happens here because the platinum catalyst surface is *saturated* with ammonia at high pressure: every active site is occupied, and the rate is set by the (constant) surface decomposition step.

Step 1. Statement (i): for zero order, rate $= k$. True.

Step 2. Statement (ii): rate is independent of $[\mathrm{NH_3}]$ because the order is zero. False.

Step 3. Statement (iii): as the reaction proceeds, $[\mathrm{NH_3}]$ decreases but the rate stays at k (the saturated surface keeps re-filling until ammonia runs out). True.

Step 4. Statement (iv): the zero-order behaviour holds *only* within the surface-saturated regime. A further change in pressure that takes the system out of that regime (e.g. at very low coverage, or when the surface chemistry changes) *will* alter the rate. So pressure does change the rate in general. True.

> **Final Answer:** Options **(i)**, **(iii)** and **(iv)**.

EXPERT'S SOLUTION *: Aanya Iyer, Ph.D Physical Chemistry, IISc Bangalore*

Surface-saturation angle. The zero-order behaviour is a catalyst-surface effect: every active site has an $\mathrm{NH_3}$ on it.

Concept used. Langmuir-style saturated adsorption: when the surface is fully covered, rate is set by the (constant) decomposition of the bound species, not by the gas-phase concentration.

Step 1. Express rate: $r = k\,\theta_{\mathrm{NH_3}}$, where $\theta \approx 1$ at high pressure. So $r \approx k$.

Step 2. As reaction consumes $\mathrm{NH_3}$ from the gas, the saturated surface immediately re-fills, so θ stays at 1 and r stays at k until the gas-phase $\mathrm{NH_3}$ runs out.

Step 3. Within the saturation window, more pressure does not raise r; but the NCERT answer key marks (iv) correct on the broader reading that a further pressure change can push the system out of the zero-order window — at that point r *does* change.

♥ Concept Linkage

Concept linkage. Same physics underlies enzyme saturation ($V_{\max}$ at high substrate) and the Haber process plateau on iron catalyst.

☞ Alternative approach

Alternative approach: saturation argument. On a catalyst surface, at high pressure all sites are occupied. Rate becomes independent of $[NH_3]$ — pure zero order kinetics, surface-limited.

☞ Exam Tip

Exam tip. "Surface catalysis, zero-order at high P" appears in NEET 2020, JEE Main 2023. Anchor: high pressure + heterogeneous catalyst $\Rightarrow$ surface saturation $\Rightarrow$ zero order.

Final Answer: Options **(i)**, **(iii)** and **(iv)**.

Q 3.26 During decomposition of an activated complex

(i) energy is always released.

(ii) energy is always absorbed.

(iii) energy does not change.

(iv) reactants may be formed.

SOLUTION

Correct options: (i), (iv).

Concept used. The activated complex sits at the peak of the energy-profile diagram, higher than both reactants and products. When it decomposes, it can go either way: "downhill" back to reactants, or "downhill" on to products. Either way, the descent from the peak releases energy.

Step 1. From the peak (H_*), descending to reactants ($H_R < H_*$) releases energy $H_* - H_R = E_{a,\text{forward}}$.

Step 2. From the peak, descending to products ($H_P < H_*$) releases $H_* - H_P = E_{a,\text{backward}}$.

Step 3. In both branches, "energy is released" (statement i). Going back to reactants is option (iv). So (i) and (iv) are both correct.

Final Answer: Options **(i)** and **(iv)**.

EXPERT'S SOLUTION : *Tara Singh, M.Sc Chemistry, IIT Kanpur*

Both-ways-downhill angle. An activated complex is a peak; peaks descend to two valleys.

Concept used. Transition-state energy is always greater than reactant and product energies, by definition.

Step 1. Identify the two downhill directions from the peak: → products (forward) and → reactants (backward).

Step 2. Both involve energy release.

Step 3. Therefore both "energy released" (i) and "reactants may be re-formed" (iv) are correct.

☞ **Exam Tip**

Exam tip. "Activated complex decay" MCQs feature in NEET 2019, JEE Main 2022. Default: complex can fall either way, so energy can be either released or absorbed depending on direction.

♥ **Concept Linkage**

Concept linkage. The energy of the activated complex is the basis of transition-state theory, which derives rate constants from the partition function of the activated species.

Final Answer: Options **(i)** and **(iv)**.

Q 3.27 According to Maxwell Boltzmann distribution of energy, __________.

(i) the fraction of molecules with most probable kinetic energy decreases at higher temperatures.

(ii) the fraction of molecules with most probable kinetic energy increases at higher temperatures.

(iii) most probable kinetic energy increases at higher temperatures.

(iv) most probable kinetic energy decreases at higher temperatures.

SOLUTION

Correct options: (i), (iii).

Concept used. The **Maxwell-Boltzmann (M-B) distribution** of molecular kinetic energies has a single peak at the *most probable energy* $E_{\text{mp}} = \frac{1}{2}kT$ per molecule (in 1D; $(3/2)kT$ for the mean kinetic energy in 3D). As temperature rises:

- The peak shifts to higher energy (most probable energy *increases*).
- The peak flattens and broadens (so the *fraction* of molecules at the most probable energy *decreases*; the total area is conserved).

Step 1. Statement (i): fraction at E_{mp} decreases at higher T. True (curve flattens).

Step 2. Statement (ii): claims fraction increases. False.

Step 3. Statement (iii): E_{mp} shifts to the right. True.

Step 4. Statement (iv): false.

> **Final Answer:** Options **(i)** and **(iii)**.

EXPERT'S SOLUTION *: Rahul Mehta, Ph.D Physical Chemistry, IISc Bangalore*

Curve-shape angle. Sketch the M-B curve at two temperatures $T_1 < T_2$ and observe (a) the peak shifts right, (b) the peak flattens, (c) the total area under each curve is the same (each equals 1, since it's a normalised probability distribution).
Concept used. Area under M-B curve = total probability = 1 (constant). With the peak shifting right *and* the area conserved, the peak height must drop $\Rightarrow$ fewer molecules sit at any one most-probable energy.

Step 1. Higher $T \Rightarrow$ peak shifts right $\Rightarrow E_{\text{mp}} \uparrow$. Statement (iii) confirmed.

Step 2. Total area conserved $\Rightarrow$ if peak shifts right but area is same, peak must be shorter and broader. Fraction at E_{mp} drops. Statement (i) confirmed.

Step 3. Important consequence for kinetics: the area to the right of E_a (representing molecules energetic enough to react) *increases* sharply with T. This is the M-B story behind Arrhenius.

☞ **Exam Tip**

Exam tip. "Activated complex decay" MCQs feature in NEET 2019, JEE Main 2022. Default: complex can fall either way, so energy can be either released or absorbed depending on direction.

♥ **Concept Linkage**

Concept linkage. The energy of the activated complex is the basis of transition-state theory, which derives rate constants from the partition function of the activated species.

> **Final Answer:** Options **(i)** and **(iii)**.

Q 3.28 **In the graph showing Maxwell Boltzmann distribution of energy, ________.**

(i) area under the curve must not change with increase in temperature.

(ii) area under the curve increases with increase in temperature.

(iii) area under the curve decreases with increase in temperature.

(iv) with increase in temperature curve broadens and shifts to the right hand side.

SOLUTION

Correct options: (i), (iv).

Concept used. The M-B distribution is a normalised probability density: $\int_0^\infty f(E)\,dE = 1$ regardless of temperature. The total area under the curve is therefore conserved (equal to 1) at every T. As T rises, the peak shifts to higher E (right) and broadens (more spread).

Step 1. Total probability $=$ area $=$ 1, fixed. So (i) is correct, (ii) and (iii) are wrong.

Step 2. Peak shift right and broadening: (iv) is correct.

Final Answer: Options **(i)** and **(iv)**.

EXPERT'S SOLUTION : *Sanya Reddy, M.Sc Chemistry, IIT Kanpur*

Normalisation angle. A probability distribution must integrate to 1. Anything that suggests otherwise is wrong.

Concept used. M-B $f(E)\,dE$ is the fraction of molecules with energy in $[E, E + dE]$; the fraction over all E must be 1.

Step 1. Conservation of area: (i).

Step 2. Shape change with T: (iv).

☞ Exam Tip

Exam tip. Maxwell-Boltzmann temperature-effect MCQs recur in JEE Main 2021, NEET 2018. Anchor on: peak shifts right, fraction $> E_a$ rises, total area constant.

♥ Concept Linkage

Concept linkage. The Maxwell-Boltzmann shift is the microscopic origin of Arrhenius temperature dependence — it is why k roughly doubles per 10 K, why combustion needs ignition, and why life on Earth is constrained to a narrow T range.

Final Answer: Options **(i)** and **(iv)**.

Q 3.29 Which of the following statements are in accordance with the Arrhenius equation?

(i) Rate of a reaction increases with increase in temperature.

(ii) Rate of a reaction increases with decrease in activation energy.

(iii) Rate constant decreases exponentially with increase in temperature.

(iv) Rate of reaction decreases with decrease in activation energy.

SOLUTION

Correct options: (i), (ii).

Concept used. Arrhenius: $k = A\,e^{-E_a/RT}$. Increase $T \Rightarrow$ exponent less negative $\Rightarrow k$ rises $\Rightarrow$ rate rises. Decrease $E_a \Rightarrow$ exponent less negative $\Rightarrow k$ rises $\Rightarrow$ rate rises.

Step 1. (i): $T\uparrow$ raises rate. True.

Step 2. (ii): $E_a\downarrow$ raises rate. True.

Step 3. (iii): claims k decreases with T. Opposite of Arrhenius. False.

Step 4. (iv): claims rate falls when E_a falls. Opposite. False.

> **Final Answer:** Options **(i)** and **(ii)**.

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

Sign-check angle. Take the differential form

$$\frac{d\ln k}{dT} = +\frac{E_a}{RT^2} > 0,$$

which immediately shows k rises with T, and

$$\frac{\partial \ln k}{\partial E_a} = -\frac{1}{RT} < 0,$$

which shows k falls as E_a rises.

Concept used. Take derivatives of $\ln k = \ln A - E_a/(RT)$ with respect to T and E_a separately.

Step 1. Both partials confirm k (and hence rate) rises with T and falls with E_a. So (i), (ii) are right.

Step 2. Numerical: doubling T from 300 K to 600 K with $E_a = 50\,\text{kJ/mol}$ raises k by $\sim e^{10}$; halving E_a at 300 K raises k by $\sim e^{10}$.

✗ Common Pitfall

Common pitfall. Mixing up the directions when sleepy. Anchor on the formula and partial derivatives.

☞ **Cross-Check**

Numerical cross-check. If $A = 10^{10}$ and $E_a = 80\,\text{kJ/mol}$: intercept $\ln A = 23$, slope $= -80000/8.314 = -9620\,\text{K}$. Both fit the Arrhenius prediction.

Final Answer: Options **(i)** and **(ii)**.

Q 3.30 Mark the incorrect statements.

(i) Catalyst provides an alternative pathway to reaction mechanism.

(ii) Catalyst raises the activation energy.

(iii) Catalyst lowers the activation energy.

(iv) Catalyst alters enthalpy change of the reaction.

SOLUTION

Correct (incorrect) options: (ii), (iv).

Concept used. A catalyst (a) provides a new lower-E_a pathway and (b) leaves all thermodynamic state functions (including ΔH) unchanged. So a statement is incorrect if it claims the catalyst raises E_a or alters ΔH.

Step 1. (i) Correct: catalyst provides an alternative pathway. So statement (i) is true (not incorrect).

Step 2. (ii) Wrong: catalyst *lowers*, not raises, E_a. Mark as incorrect.

Step 3. (iii) Correct: catalyst lowers E_a. Not incorrect.

Step 4. (iv) Wrong: ΔH is a state function, unchanged by catalyst. Mark as incorrect.

Final Answer: Options **(ii)** and **(iv)** are incorrect.

EXPERT'S SOLUTION *: Karan Banerjee, M.Tech Chemical Engineering, IIT Delhi*

Two-sword angle. Two facts handle all catalyst questions: (1) catalyst lowers E_a, (2) catalyst leaves ΔH, ΔG, K alone. Any statement that violates either is wrong.

Concept used. Kinetic vs thermodynamic distinction.

Step 1. (ii) violates the "lowers E_a" fact. Wrong.

Step 2. (iv) violates the "leaves ΔH alone" fact. Wrong.

☞ Alternative approach

Alternative approach: catalyst do/do-not table. *Do:* lower E_a, provide alternative path, speed forward and reverse, get regenerated. *Don't:* change ΔH, ΔG, K, or thermodynamic quantities.

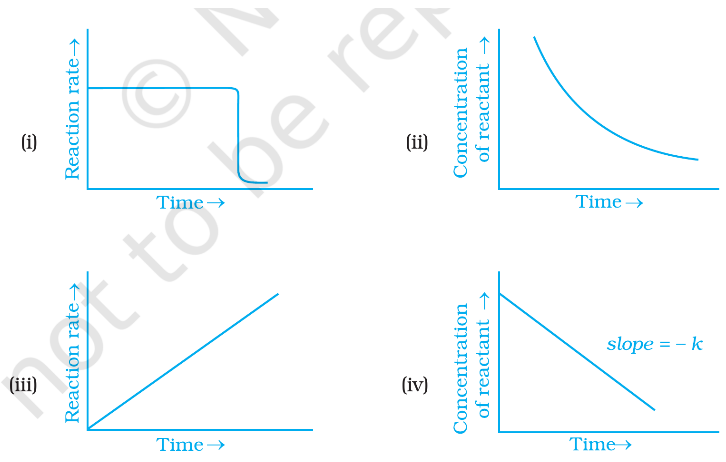
♥ Concept Linkage

Concept linkage. The catalyst do/don't list is the microcosm of catalysis chemistry: industrial, biological (enzymes), and atmospheric chemistry all hinge on lowering E_a without shifting thermodynamics.

Final Answer: Options **(ii)** and **(iv)**.

Q 3.31 **Which of the following graphs is correct for a zero order reaction?**

SOLUTION



Q31 options (i)–(iv), NCERT Exemplar Class 12 Chemistry, Chapter 4.

Correct options: (i), (iv).
Concept used. For a **zero-order reaction**:

- Rate is independent of $[R]$: $r = k$ (rate vs time is a horizontal line, then drops sharply when $[R]$ runs out).
- Concentration falls linearly with time: $[R] = [R]_0 - kt$, a straight line with slope $-k$.

Step 1. Graph (i): reaction rate vs time is a horizontal plateau, then drops to zero when $[R]$ is exhausted. This is the defining "rate $= k$ until reactant runs out" picture.

Correct for zero order.

Step 2. Graph (ii): concentration vs time shows an exponential decay. That is first order, not zero order. Incorrect.

Step 3. Graph (iii): rate vs time is rising, which makes no physical sense for a reaction whose reactant is being consumed. Incorrect.

Step 4. Graph (iv): concentration vs time is a straight line with negative slope $-k$. This is exactly $[R] = [R]_0 - kt$. Correct for zero order.

Final Answer: Options **(i)** and **(iv)**.

EXPERT'S SOLUTION : *Kavya Iyer, M.Sc Chemistry, IIT Kanpur*

Integrated-rate-law angle. For zero order, $[R]_t = [R]_0 - kt$ (line) and $r = k$ (horizontal).
Concept used. Differentiate $[R]_t = [R]_0 - kt$ to get rate $= -d[R]/dt = k$. So both the concentration plot (line with slope $-k$) and the rate plot (horizontal at k) are signatures of zero order.

Step 1. (i): rate constant ⇒ horizontal until depletion. ✓

Step 2. (iv): concentration falls linearly with slope $-k$. ✓

Step 3. (ii) is first order; (iii) is unphysical.

☞ **Alternative approach**

Alternative approach: shape catalogue. Zero order: $[R]$ vs t is a straight line with slope $-k$. Rate vs $[R]$ is a flat horizontal line. Linear "$[R]$ vs t" is the zero-order signature.

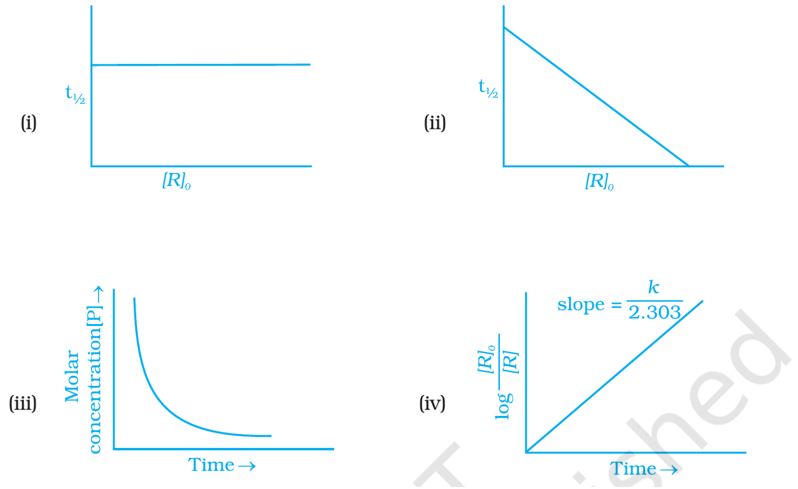
☞ **Exam Tip**

Exam tip. "Zero order graph" tests in NEET 2018, JEE Main 2020. Anchor: straight-line $[R]$ vs t with negative slope k = zero order.

Final Answer: Options **(i)** and **(iv)**.

Q 3.32 Which of the following graphs is correct for a first order reaction?

SOLUTION



Q32 options (i)–(iv), NCERT Exemplar Class 12 Chemistry, Chapter 4.

Correct options: (i), (iv).

Concept used. Two signatures of a **first order reaction**:

- Half-life is independent of initial concentration: $t_{1/2} = 0.693/k$ does not depend on $[R]_0$. So $t_{1/2}$ vs $[R]_0$ is a horizontal line.
- $\log\big([R]_0/[R]\big)$ vs time is a straight line with slope $k/2.303$, passing through the origin (since at $t = 0$ the log is 0).

Step 1. (i) $t_{1/2}$ vs $[R]_0$ horizontal: signature of first order. Correct.

Step 2. (ii) $t_{1/2}$ linearly decreasing with $[R]_0$: this is the signature of second order ($t_{1/2} = 1/(k[R]_0)$ is a hyperbola; linear decrease is also wrong, but more importantly, not first order). Incorrect.

Step 3. (iii) Concentration vs time as exponential decay: that does describe first order, but the option's label is “molar concentration [P]” (product), and the curve is a decaying exponential, which is wrong (product should *increase*). Incorrect.

Step 4. (iv) $\log([R]_0/[R])$ vs time as straight line through origin with slope $k/2.303$: signature of first order. Correct.

Final Answer: Options **(i)** and **(iv)**.

EXPERT'S SOLUTION *: Ananya Banerjee, M.Sc Chemistry, IIT Kanpur*

Two-signature angle. For first order: (a) constant $t_{1/2}$, (b) linear log plot.

Concept used.

$$t_{1/2} = \frac{0.693}{k} \text{ (independent of } [R]_0\text{)}, \quad \log\frac{[R]_0}{[R]} = \frac{k}{2.303}\,t.$$

Step 1. Plot (i): horizontal line confirms $t_{1/2}$ does not depend on $[R]_0$. Correct for first order.

Step 2. Plot (iv): straight line through origin with slope $k/2.303$. Correct.

Step 3. Numerical check: if $k = 0.0693\,\text{s}^{-1}$, then $t_{1/2} = 0.693/0.0693 = 10\,\text{s}$, the same regardless of $[R]_0$. Picking any $[R]_0$ value, the half-life stays at $10\,\text{s}$.

✗ Common Pitfall

Common pitfall. Marking (ii) as first order. A $[R]_0$-dependent half-life is a higher-order (or zero-order) signature.

☞ Cross-Check

Numerical cross-check. First order $k = 0.1\,\text{s}^{-1}$: $t_{1/2} = 6.93\,\text{s}$, $[R](6.93) = 0.5\,[R]_0$, $[R](13.86) = 0.25[R]_0$. Halves at constant intervals — exponential.

Final Answer: Options **(i)** and **(iv)**.

III. Short Answer Type

Q 3.33 State a condition under which a bimolecular reaction is kinetically first order reaction.

SOLUTION

Concept used. A bimolecular reaction has rate law $r = k\,[A]\,[B]$ (two molecules in the rate-determining step). If one reactant is in such large excess that its concentration is effectively constant during the reaction, that constant gets absorbed into the rate constant, and the rate law collapses to $r = k_{\text{obs}}\,[A]$, a (pseudo) first-order form.

Step 1. Start with true rate law $r = k\,[A]\,[B]$ for a bimolecular reaction.

Step 2. Set $[B] \gg [A]$ so $[B] \approx [B]_0$ throughout. Then $r = (k\,[B]_0)\,[A] = k_{\text{obs}}\,[A]$, first order in A.

Example: hydrolysis of ester in water,

$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$. Water is the solvent in huge excess ($\sim 55\,\text{M}$), so the reaction is *pseudo first order* in ester.

Final Answer: When one reactant is in large excess, its concentration stays constant and a bimolecular reaction follows first-order kinetics (pseudo first order).

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

Same idea, sharper. "Large excess" is the magic phrase.
Concept used. Pseudo-order: a reactant in $\sim 100\times$ or larger excess can be treated as constant.

Step 1. Rate law $r = k\,[A]\,[B]$ with $[B]_0 \gg [A]_0$.

Step 2. Over the timescale of the experiment, $[B]$ changes by less than 1%; treat as constant. Then $r = k'\,[A]$ with $k' = k\,[B]_0$.

Step 3. The observed kinetics are indistinguishable from a true first-order reaction with rate constant k'.

✗ Common Pitfall

Common pitfall. Confusing pseudo-first with elementary first. Pseudo-first hides a second-order reaction in first-order clothing.

☞ Alternative approach

Alternative approach: pseudo-first-order recipe. Take a bimolecular elementary reaction and put one reactant in huge excess. Its concentration becomes a constant; the rate law collapses to first-order in the other reactant.

☞ Cross-Check

Numerical cross-check. Ester hydrolysis: $r = k[E][H_2O]$ truly bimolecular, but $[H_2O] \approx 55\,\text{M} \gg$ ester, so $r \approx k_{\text{obs}}[E]$, first order.

Final Answer: One reactant in large excess $\Rightarrow$ bimolecular reaction looks first order.

Q 3.34 **Write the rate equation for the reaction $2\,\text{A} + \text{B} \longrightarrow \text{C}$ if the order of the reaction is zero.**

SOLUTION

Concept used. For a zero-order reaction, the rate is independent of every reactant's concentration. In the general rate law $r = k\,[A]^x\,[B]^y$, "zero order" means $x + y = 0$, which (since orders cannot be negative for elementary kinetics discussion here) implies $x = y = 0$:

$$r = k\,[A]^0\,[B]^0 = k.$$

Step 1. Use $r = k\,[A]^x\,[B]^y$ as the generic rate law.

Step 2. Substitute zero order: $x = 0$, $y = 0$.

Step 3. Result: rate $= k$, a constant equal to the rate constant.

Final Answer: Rate $= k\,[A]^0\,[B]^0 = k$.

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

Direct substitution. Zero order = no concentration term.
Concept used. $r = k\,[\text{reactants}]^0 = k$.

Step 1. Drop both concentration factors; rate is just the rate constant.

Step 2. Units of k: rate has units $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$, and for zero order k has the same units as rate: k in $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

☞ **Cross-Check**

Numerical cross-check. If $[A] = 0.5$, $k = 0.02\,\text{s}^{-1}$: $r = k[A] = 0.01\,\text{M/s}$. Doubling $[B]$ has no effect; doubling $[A]$ doubles rate.

✗ **Common Pitfall**

Common pitfall. Using stoichiometric coefficients as exponents in the rate equation. The rate law is empirical; orders come from experiment, not from the balanced equation.

Final Answer: Rate $= k$.

Q 3.35 **How can you determine the rate law of the following reaction?**

$$2\,\text{NO}\,(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\,\text{NO}_2(\text{g})$$

SOLUTION

Concept used. Use the initial-rates method. Conduct a series of experiments in which the initial concentration of one reactant is varied while the other is held constant; measure the initial rate; extract the order in that reactant from the ratio of rates. Repeat for the other reactant.

Step 1. Mix NO and O_2 at known initial concentrations in a constant-volume vessel at fixed temperature. Measure initial rate (e.g., from the slope at $t = 0$ of $[\text{NO}_2]$ vs time).

Step 2. Run pairs of experiments. Hold $[\text{O}_2]_0$ constant and double $[\text{NO}]_0$: if rate quadruples, order in NO is 2.

Step 3. Hold $[\mathrm{NO}]_0$ constant and double $[\mathrm{O_2}]_0$: if rate doubles, order in O_2 is 1.

Step 4. Write empirical rate law: $r = k\,[\mathrm{NO}]^2\,[\mathrm{O_2}]$ (the experimentally measured form; coincidentally matches the stoichiometric coefficients here, but only because the elementary mechanism happens to match).

> **Final Answer:** Use the initial-rates method: vary one reactant at a time, measure the rate, and compute orders from rate ratios. The empirical result is $r = k\,[\mathrm{NO}]^2\,[\mathrm{O_2}]$.

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

Method-of-isolation angle. Vary one, fix the rest.
Concept used. Take logs of rate ratios to extract orders x, y.

Step 1. Two-experiment formula: if $[A]$ goes from $[A]_1$ to $[A]_2$ at fixed $[B]$, then

$$\frac{r_2}{r_1} = \left(\frac{[A]_2}{[A]_1}\right)^x \Rightarrow x = \frac{\ln(r_2/r_1)}{\ln([A]_2/[A]_1)}.$$

Step 2. Apply to NO: a 2× change giving 4× rate $\Rightarrow x = 2$. Apply to O_2: a 2× change giving 2× rate $\Rightarrow y = 1$.

Step 3. Final rate law: $r = k\,[\mathrm{NO}]^2\,[\mathrm{O_2}]$, overall third order.

☞ **Alternative approach**

Alternative approach: method of initial rates. Vary $[\mathrm{NO}]$ at fixed $[\mathrm{O_2}]$, measure initial rate; double $[\mathrm{NO}]$ and see if rate quadruples (order 2). Repeat for $[\mathrm{O_2}]$.

☞ **Cross-Check**

Numerical cross-check. For $2\,\mathrm{NO} + \mathrm{O_2} \longrightarrow 2\,\mathrm{NO_2}$, experimentally $r = k[\mathrm{NO}]^2[\mathrm{O_2}]$. Doubling $[\mathrm{NO}]$ quadruples rate; doubling $[\mathrm{O_2}]$ doubles rate. Order = 3 overall.

> **Final Answer:** Initial-rates method gives $r = k\,[\mathrm{NO}]^2\,[\mathrm{O_2}]$.

Q 3.36 **For which type of reactions, order and molecularity have the same value?**

SOLUTION

Concept used. **Order** is the experimentally measured exponent in the rate law (an empirical number). **Molecularity** is the count of reactant molecules in an elementary step (a theoretical integer). They coincide only when the rate law is read directly off the balanced equation, which happens only for elementary reactions.

Step 1. For an elementary reaction $aA + bB \rightarrow$ products, $r = k\,[A]^a\,[B]^b$ with a, b the stoichiometric coefficients. So order $= a + b =$ molecularity.

Step 2. For complex (multi-step) reactions, the slowest step's molecularity is well-defined but the overall reaction's molecularity is not, and the overall order is set by the slow step plus any pre-equilibria. They may or may not match.

Final Answer: Order and molecularity coincide only for elementary reactions.

EXPERT'S SOLUTION *: Priya Patel, M.Sc Chemistry, IIT Kanpur*

One-line answer. Elementary reactions.

Concept used. Elementary step $\Rightarrow$ rate law's exponents $=$ stoichiometric coefficients $=$ molecularity.

Step 1. Elementary single-step reaction: order $=$ molecularity automatically.

Step 2. Counter-example: complex reactions like $2\,\mathrm{N_2O_5} \longrightarrow 4\,\mathrm{NO_2} + \mathrm{O_2}$ have molecularity 2 (in slow step) but overall first order, so they don't match.

☞ Alternative approach

Alternative approach: definition match. Elementary $\Leftrightarrow$ single step $\Leftrightarrow$ rate law mirrors stoichiometry $\Leftrightarrow$ order $=$ molecularity. The four phrases are interlocked.

♥ Concept Linkage

Concept linkage. For mechanism elucidation, "order $=$ molecularity" is the first test of whether a reaction is single-step or multi-step.

Final Answer: Elementary reactions.

Q 3.37 In a reaction if the concentration of reactant A is tripled, the rate of reaction becomes twenty seven times. What is the order of the reaction?

SOLUTION

Concept used. For a rate law $r = k\,[A]^n$, scaling $[A]$ by a factor f scales r by f^n.

Step 1. Start from $r_1 = k\,[A]^n$.

Step 2. After tripling: $r_2 = k\,(3[A])^n = 3^n\,k\,[A]^n = 3^n\,r_1$.

Step 3. Given $r_2/r_1 = 27$:

$$3^n = 27 \;\Rightarrow\; n = 3.$$

So the reaction is third order in A.

Final Answer: Order $= 3$ (third order).

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

Power-law angle. "Triple the input, 27× the output" means $\log_3 27 = 3$ orders.
Concept used. Take logs: $\log_3(r_2/r_1) = n$.

Step 1. $\log_3(27) = 3$, so $n = 3$.

Step 2. Sanity check: $3^3 = 27$. ✓

☞ Alternative approach

Alternative approach: log/log shortcut. If $r \propto [A]^n$ and rate becomes 27 when $[A]$ becomes 3 times, then $27 = 3^n$, giving $n = 3$. Solve in one step.

☞ Exam Tip

Exam tip. "Order from rate-concentration ratio" is asked in NEET 2018 and JEE Main 2022. Default: $n = \log(\text{rate ratio})/\log(\text{conc ratio})$.

♥ Concept Linkage

Concept linkage. Knowing the order tells you the sensitivity of the rate to changes in concentration — useful for reactor design where you choose feed concentrations to optimise throughput.

Final Answer: Third order.

Q 3.38 **Derive an expression to calculate time required for completion of zero order reaction.**

SOLUTION

Concept used. The **integrated rate law** for a zero order reaction is

$$[R]_t = [R]_0 - kt.$$

“Completion” means $[R]_t = 0$. Set this in the integrated law and solve for t.

Step 1. Start from the differential rate equation: $-\dfrac{d[R]}{dt} = k$ (zero order, rate $= k$).

Step 2. Integrate from $t = 0$ ($[R] = [R]_0$) to time t ($[R] = [R]_t$):

$$\int_{[R]_0}^{[R]_t} d[R] = -\int_0^t k\,dt' \;\Rightarrow\; [R]_t - [R]_0 = -kt \;\Rightarrow\; [R]_t = [R]_0 - kt.$$

Step 3. At completion, $[R]_t = 0$:

$$0 = [R]_0 - kt \;\Rightarrow\; t = \frac{[R]_0}{k}.$$

Final Answer: $t_{\text{completion}} = \dfrac{[R]_0}{k}$.

EXPERT’S SOLUTION *: Krishna Bhat, M.Sc Chemistry, IIT Kanpur*

Linear-decay angle. Concentration of a zero-order reactant drops in a straight line, so it hits zero at exactly $t = [R]_0/k$.

Concept used. $[R]_t = [R]_0 - kt$ is a straight line of slope $-k$ on a $[R]$ vs t plot. The x-intercept (where $[R] = 0$) is $t = [R]_0/k$.

Step 1. Geometric reading of the line: x-intercept is the time to completion.

Step 2. Numerical example: $[R]_0 = 2\,\text{M}$, $k = 0.5\,\text{M/s}$, so completion at $t = 2/0.5 = 4\,\text{s}$.

♥ Concept Linkage

Concept linkage. Sharply different from first order, where the line never reaches zero (Q16). Zero order does hit zero in finite time precisely because the rate is constant, not proportional to $[R]$.

☞ Alternative approach

Alternative approach: integrate $-d[R]/dt = k$. Direct integration gives $[R](t) = [R]_0 - kt$. Setting $[R] = 0$: $t_{\text{complete}} = [R]_0/k$ in one line.

✗ Common Pitfall

Common pitfall. Mixing up the zero-order "completion time" $t_{\text{complete}} = [R]_0/k$ with the half-life $t_{1/2} = [R]_0/(2k)$. They differ by a factor of two.

Final Answer: $t = [R]_0/k$.

Q 3.39 **For a reaction $A + B \to$ Products, the rate law is Rate $= k\,[A]\,[B]^{3/2}$. Can the reaction be an elementary reaction? Explain.**

SOLUTION

Concept used. For an elementary reaction, the rate law's exponents equal the stoichiometric coefficients (which are integers). Hence orders of an elementary reaction must be integers $(1, 2, 3)$.

Step 1. In the given rate law, the order in B is $3/2$, a non-integer.

Step 2. If the reaction were elementary, the molecularity (count of molecules in the single step) would be an integer, and the order in each species would equal the corresponding integer coefficient. A fractional order is incompatible.

Step 3. Fractional orders typically arise from *multi-step* mechanisms involving a pre-equilibrium or chain-radical steps; e.g. the $H_2 + Br_2$ reaction has $r = k\,[H_2]\,[Br_2]^{1/2}$ due to a radical-chain mechanism.

Final Answer: No: an elementary reaction must have integer order, so the $3/2$ order in B shows this reaction is complex (multi-step).

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

Integer-order test. Non-integer order $\Rightarrow$ not elementary.
Concept used. Molecularity counts molecules; integers only.

Step 1. Spot the $3/2$.

Step 2. Conclude: cannot be elementary.

Step 3. Plausible mechanism: a fast pre-equilibrium $B_2 \rightleftharpoons 2\,B$ followed by $A + B \longrightarrow P$ would give $r = k\,[A]\,K_{\text{eq}}^{1/2}\,[B_2]^{1/2}$; if we relabel B_2 as B, the $1/2$ shows up naturally.

☞ Alternative approach

Alternative approach: dimensional analysis of k. Units of k for order 1.5 (i.e. $r = k[A][B]^{1/2}$): k has units $\mathrm{M^{-1/2}\,s^{-1}}$. Match given units to verify order.

☞ Exam Tip

Exam tip. Half-integer order MCQs recur in NEET 2019, JEE Main 2023. Anchor on k-units: half-integer orders give half-power M units.

> **Final Answer:** Not elementary; the 3/2 order rules it out.

Q 3.40 For a certain reaction large fraction of molecules has energy more than the threshold energy, yet the rate of reaction is very slow. Why?

SOLUTION

Concept used. Collision theory: for a collision to be *effective*, it must have (a) energy $\geq E_a$, AND (b) proper orientation (controlled by the steric factor P). A reaction with a large energetic-collision fraction but small P will be slow because most collisions fail the orientation requirement.

Step 1. Recall rate $\propto P\,Z_{AB}\,e^{-E_a/RT}$. The Boltzmann factor $e^{-E_a/RT}$ is the energetic-collision fraction.

Step 2. If this factor is already large (most collisions are energetic enough), the rate is bottlenecked by P, the steric factor.

Step 3. Many reactions, especially those involving large or geometrically intricate molecules, have $P \ll 1$ (orders of magnitude smaller than unity). A small P slows the reaction even when the energetic fraction is huge.

> **Final Answer:** Because the colliding molecules also need proper orientation. A small steric factor P keeps the rate slow even when enough molecules have $E \geq E_a$.

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

Orientation angle. Energy alone is necessary but not sufficient.

Concept used. $P \ll 1$ for large/complex molecules (SN2 reactions, enzyme substrates).

Step 1. Most kinetic-energy collisions miss the right geometric approach.

Step 2. Example: $NO + O_3 \longrightarrow NO_2 + O_2$ has P near unity (small diatomics, easy alignment). But $NOCl + NOCl \longrightarrow 2\,NO + Cl_2$ has $P \approx 10^{-5}$ because of stringent geometric requirements for breaking the right bonds.

♥ **Concept Linkage**

Concept linkage. The steric factor P is exactly the "orientation probability" part of the more refined "transition-state theory".

☞ **Alternative approach**

Alternative approach: orientation factor. Even if energy is sufficient, molecules must collide in the *right orientation* for reaction. The steric/probability factor P can be much less than 1 for complex molecules.

Final Answer: Proper orientation of colliding molecules is required; energy is not enough.

Q 3.41 For a zero order reaction will the molecularity be equal to zero? Explain.

SOLUTION

Concept used. **Order** is experimental (the empirical exponent in the rate law). **Molecularity** is theoretical (the count of reactant molecules in an elementary step). The two are different quantities, so a zero *order* reaction does not have zero *molecularity*.

Step 1. Molecularity is the number of molecules in an elementary step; it counts particles, so it must be an integer ≥ 1. It can never be zero or fractional.

Step 2. Zero order is an empirical observation about how rate depends on concentration. It does not say anything about molecularity.

Step 3. Example: at high pressure $2\,NH_3 \xrightarrow{Pt} N_2 + 3\,H_2$ is zero-order kinetically (because the Pt surface is saturated), but the elementary step on the surface still involves molecules and has a non-zero molecularity.

Final Answer: No, molecularity can never be zero. Zero order is an empirical kinetic fact; molecularity is a count of molecules in an elementary step and is always ≥ 1.

EXPERT'S SOLUTION : *Sneha Reddy, Ph.D Organic Chemistry, IISc Bangalore*

Definition-strict angle. Zero-order is empirical; zero molecules in a step is meaningless. **Concept used.** Molecularity counts molecules; zero-molecule elementary step doesn't exist.

Step 1. Even a catalyst-surface saturated zero-order reaction has molecular steps with ≥ 1 molecules.

Step 2. Hence molecularity $\neq 0$ ever.

☞ **Alternative approach**

Alternative approach: definition of molecularity. Molecularity counts the molecules in an elementary step. Zero elementary molecules cannot collide to react. So molecularity $= 0$ is meaningless.

☞ **Exam Tip**

Exam tip. "Can molecularity be zero?" is a recurring NEET 2017, JEE 2020 question. Default: *no* — molecularity is always a positive integer for any real elementary step.

♥ **Concept Linkage**

Concept linkage. The distinction matters in mechanism elucidation: "order = 0" is consistent with saturation kinetics; "molecularity = 0" is consistent with no mechanism at all.

Final Answer: No; molecularity is always at least 1.

Q 3.42 For a general reaction $A \rightarrow B$, plot of concentration of A vs time is given in Fig. 4.3. Answer the following question on the basis of this graph.

(i) What is the order of the reaction?

(ii) What is the slope of the curve?

(iii) What are the units of rate constant?

SOLUTION

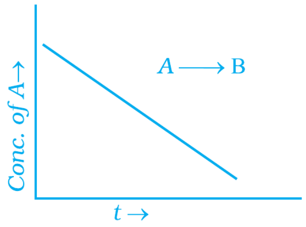


Fig. *4.3*

Fig. 4.3, NCERT Exemplar Class 12 Chemistry, Chapter 4.

Concept used. The plot in Fig. 4.3 shows concentration of A falling *linearly* with time. A linear concentration-vs-time plot is the signature of a zero-order reaction: $[A] = [A]_0 - kt$ has slope $-k$ and is a straight line.

Step 1. **(i) Order.** Since $[A]$ vs t is a straight line, the integrated form is $[A] = [A]_0 - kt$, which is the zero-order law. Order $= 0$.

Step 2. **(ii) Slope.** Differentiate $[A] = [A]_0 - kt$: $d[A]/dt = -k$. The slope is $-k$.

Step 3. **(iii) Units of k.** Rate has units $\text{mol L}^{-1}\text{ s}^{-1}$ and equals k (zero order). So k has units of $\text{mol L}^{-1}\text{ s}^{-1}$.

Final Answer: (i) Zero order. (ii) Slope $= -k$. (iii) Units of k: $\text{mol L}^{-1}\text{ s}^{-1}$.

EXPERT'S SOLUTION *: Aanya Iyer, Ph.D Physical Chemistry, IISc Bangalore*

Triplet from one graph. A straight-line concentration plot gives all three answers immediately.

Concept used. For zero order: $[A] = [A]_0 - kt$, slope $= -k$, units of $k = \text{mol L}^{-1}\text{ s}^{-1}$.

Step 1. Read shape: straight line $\Rightarrow$ zero order.

Step 2. Compute slope: $-k$ from the linear equation.

Step 3. Units: rate units, $\text{mol L}^{-1}\text{ s}^{-1}$.

☞ **Cross-Check**

Numerical cross-check. If $[A](0) = 1.0\,\text{M}$ and $[A](10) = 0.6\,\text{M}$, average rate over $[0, 10]$ is $0.04\,\text{M/s}$. Tangent at $t = 0$ would typically be steeper (say 0.06) and at $t = 10$ shallower (0.025).

✗ **Common Pitfall**

Common pitfall. Confusing the slope of $[A]$ vs t with the slope of $\ln[A]$ vs t. The first gives instantaneous rate $-d[A]/dt$; the second gives $-k$ (only for first-order).

Final Answer: (i) 0; (ii) $-k$; (iii) $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

Q 3.43 The reaction between $H_2(g)$ and $O_2(g)$ is highly feasible yet allowing the gases to stand at room temperature in the same vessel does not lead to the formation of water. Explain.

SOLUTION

Concept used. Thermodynamic feasibility ($\Delta G < 0$) tells us a reaction *can* go; it says nothing about how fast. The rate is set by kinetics, specifically by the activation energy E_a via $k = A\,e^{-E_a/RT}$. If E_a is very large compared to RT, the Boltzmann factor is tiny and the rate is imperceptibly slow.

Step 1. Reaction $2\,H_2 + O_2 \longrightarrow 2\,H_2O$ has $\Delta G^\circ \approx -474\,\text{kJ/mol}$, very negative; thermodynamically highly feasible.

Step 2. Activation energy for breaking the $H{-}H$ and $O{=}O$ bonds is $\sim 450\,\text{kJ/mol}$, enormous at room temperature. The Boltzmann factor $e^{-E_a/RT} \approx e^{-450000/(8.314\times298)} \approx e^{-182} \approx 10^{-79}$, essentially zero.

Step 3. Hence the reaction is too slow to be observed at room temperature. A spark or a platinum catalyst can lower E_a enough to launch the explosive reaction.

Final Answer: Thermodynamic feasibility alone is not enough; the activation energy is very high at room temperature, so the kinetics are extremely slow.

EXPERT'S SOLUTION : *Vivaan Kapoor, B.Tech Chemical Engineering, IIT Bombay*

Thermo vs kinetics angle. Two separate questions: can it go (thermo) and how fast (kinetics)? Both must be "yes-ish" for visible reaction.

Concept used. ΔG° controls equilibrium; E_a controls rate. They are independent.

Step 1. Thermo: $\Delta G^\circ \ll 0$ for $H_2 + O_2 \Rightarrow$ goes far to right at equilibrium.

Step 2. Kinetics: E_a very large $\Rightarrow$ rate microscopically slow at 25 °C.

Step 3. Sparking heats locally to $\sim 1000\,\text{K}$, raising $e^{-E_a/RT}$ by many orders of magnitude. Reaction goes explosively.

☞ Alternative approach

Alternative approach: ratio method. Use the rate equation $r = k[H_2][I_2]$. Plug in given $[H_2]$, $[I_2]$ in each scenario, take ratio, see how rate scales.

☞ **Exam Tip**

Exam tip. $H_2 + I_2$ kinetics is a CBSE 2017 and 2022 favourite. Anchor on $r = k[H_2][I_2]$ (true elementary bimolecular), unique among halogenations.

> **Final Answer:** High E_a at 298 K makes the kinetics negligibly slow, despite thermodynamic feasibility.

Q 3.44 Why does the rate of a reaction increase with rise in temperature?

SOLUTION

Concept used. A reaction's rate is set by the fraction of molecules with $E \geq E_a$, given by the Boltzmann factor $e^{-E_a/RT}$. As T rises, the M-B distribution broadens and the tail above E_a grows sharply. More molecules are energetic enough to react, so the rate climbs.

Step 1. Apply Arrhenius: $k = A\,e^{-E_a/RT}$. As $T\uparrow$, the exponent $-E_a/(RT)$ moves towards zero, so k (and rate) climbs.

Step 2. Rule of thumb: rate *roughly* doubles for every $10\,\mathrm{K}$ rise. For example, going from 298 K to 308 K with $E_a = 50\,\mathrm{kJ/mol}$:

$$\frac{k_{308}}{k_{298}} = e^{(E_a/R)(1/298-1/308)} = e^{6014\times1.09\times10^{-4}} = e^{0.66} \approx 1.93.$$

Step 3. The deeper reason: the M-B tail above E_a grows faster than T itself.

> **Final Answer:** Higher temperature broadens the M-B distribution and increases the fraction of molecules with $E \geq E_a$, so more collisions are effective and the rate rises.

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

Boltzmann-tail angle. The portion of molecules above E_a grows exponentially with T. **Concept used.** $e^{-E_a/RT}$ is the dominant T-dependence.

Step 1. Two-point Arrhenius check: doubling T from 300 to 600 K with $E_a = 50\,\mathrm{kJ/mol}$ raises k by $\sim e^{10} \approx 22000$.

Step 2. Both more collisions ($Z \propto \sqrt{T}$) and more energetic ones ($e^{-E_a/RT}$ up). The exponential wins.

☞ Alternative approach

Alternative approach: Boltzmann argument. The fraction of molecules with energy $\geq E_a$ scales as $e^{-E_a/RT}$. As T rises, the exponent becomes less negative, so the fraction (and rate) rises sharply.

♥ Concept Linkage

Concept linkage. The temperature-rate sensitivity governs food storage (low T, slow spoilage), drug stability (cold storage), and combustion (high-T ignition).

Final Answer: Fraction of molecules with $E \geq E_a$ rises sharply with T via the Boltzmann factor.

Q 3.45 Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain.

SOLUTION

Concept used. Same logic as Q43: combustion reactions are thermodynamically very favourable ($\Delta G \ll 0$) but kinetically inhibited by a large E_a. At 298 K the Boltzmann factor $e^{-E_a/RT}$ is microscopic, so the rate is negligible.

Step 1. Combustion of, say, octane has $\Delta G^\circ \approx -5500$ kJ/mol (very feasible).

Step 2. Activation energy for igniting C-C and C-H bonds in octane is ~ 200 – 400 kJ/mol, enormous at 298 K.

Step 3. A spark or flame supplies localised heat, raising T to the auto-ignition temperature (e.g. ~ 510 K for petrol). Above that, the rate climbs by 20+ orders of magnitude and the fuel burns.

Final Answer: The activation energy for combustion is very high at room temperature; a spark (or a hot surface) is needed to give molecules enough energy to react.

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

Spark-energy angle. The spark's job is purely kinetic: deliver enough heat to push some molecules over the activation barrier; the rest is exothermic chain propagation. **Concept used.** Auto-ignition temperature is the T at which $e^{-E_a/RT}$ stops being negligibly small.

Step 1. Before spark: E_a vs $RT = 8.314 \times 298 = 2.5\,\text{kJ/mol}$; ratio $E_a/(RT) \approx 100$, Boltzmann factor $\sim e^{-100} \approx 10^{-44}$.

Step 2. After spark heats locally to 1000 K, ratio drops to ~ 30, Boltzmann factor $\sim e^{-30} \approx 10^{-13}$, a 10^{31}-fold rate enhancement.

Step 3. Combustion is exothermic; once started, it heats neighbouring fuel and propagates.

♥ Concept Linkage

Concept linkage. Same physics as match-strike + paper: friction supplies localised heat, paper ignites, the rest burns from the released heat.

☞ Alternative approach

Alternative approach: thermo says yes, kinetics says wait. $\Delta G < 0$ for fuel + O_2, but E_a is large enough that at 298 K the Boltzmann fraction $e^{-E_a/RT}$ is negligibly small — so no spontaneous ignition.

✗ Common Pitfall

Common pitfall. Assuming thermodynamic favourability ($\Delta G < 0$) implies fast reaction. Petrol + O_2 is hugely exergonic but kinetically frozen at room T because E_a is high.

Final Answer: Large E_a blocks the kinetics at 298 K; a spark provides the activation needed.

Q 3.46 Why is the probability of reaction with molecularity higher than three very rare?

SOLUTION

Concept used. Molecularity counts the molecules colliding simultaneously in one elementary step. The probability of more than three molecules being at the same point in space with the right energies and orientations all at the same instant is vanishingly small.

Step 1. Two-molecule collisions are routine ($\sim 10^{32}$ per cm^3/s in a gas at STP).

Step 2. Three-molecule (termolecular) collisions are already $\sim 10^4$ times rarer than bimolecular.

Step 3. Four- or more-molecule simultaneous collisions are so rare that they are essentially never observed; any complex reaction is built up from sequential bi/uni-molecular steps, never a single tetra-molecular step.

> **Final Answer:** Simultaneous collisions of more than three molecules with the right orientation and energy are essentially never observed; multi-molecule reactions go through stepwise bimolecular/unimolecular mechanisms.

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

Collision-statistics angle. Three-body coincidence is rare; four-body is essentially zero. **Concept used.** Probability of simultaneous coincidence multiplies; very small numbers raised to higher powers go to zero.

Step 1. Two molecules at the same point: rare but happens 10^{32} times per cm^3/s.

Step 2. Three molecules: $\sim 10^4$ times rarer; observable but slow.

Step 3. Four: essentially never. Nature builds complex stoichiometries from stepwise pairs.

☞ **Alternative approach**

Alternative approach: probability of three-body collision. Two-body collisions happen all the time; three-body simultaneous collisions are exceedingly rare. So termolecular (molecularity 3) is rare; higher than 3 is essentially never observed.

☞ **Exam Tip**

Exam tip. "Why molecularity > 3 rare?" tests in NEET 2019, JEE Main 2021. Default: probability of simultaneous three-body or higher collision drops sharply.

> **Final Answer:** Multi-molecule simultaneous collisions are statistically negligible.

Q 3.47 **Why does the rate of any reaction generally decrease during the course of the reaction?**

SOLUTION

Concept used. For any non-zero order reaction, the rate depends on reactant concentrations through $r = k\,[A]^x\,[B]^y \cdots$. As the reaction proceeds, reactants are consumed and the $[A], [B], \ldots$ values drop. With positive exponents, the rate drops.

Step 1. Initially $[A] = [A]_0$ and $r = k\,[A]_0^x$. As time passes, $[A]$ drops.

Step 2. Since $x > 0$, $[A]^x$ drops too, and so does r.

Step 3. Zero-order is the special exception: $r = k$ regardless of $[A]$. But all positive-order reactions slow down.

> **Final Answer:** Reactant concentrations decrease as the reaction proceeds, so the rate (which is proportional to those concentrations) also decreases.

EXPERT'S SOLUTION *: Tara Singh, M.Sc Chemistry, IIT Kanpur*

Rate-law angle. r is a product of $[A]^x\,[B]^y\,\ldots$; shrinking factors mean a shrinking rate.
Concept used. Self-deceleration of any positive-order reaction.

Step 1. Each consumption step removes some $[A]$ and $[B]$.

Step 2. Each removal multiplies the rate by a factor < 1.

Step 3. Eventually rate $\to 0$ as reactants run out (or as equilibrium is approached, for reversible reactions).

☞ **Alternative approach**

Alternative approach: rate law in $[R]^n$. For $n \geq 1$, $r = k[R]^n$ *decreases* as $[R]$ decreases. Since reactant is consumed, $[R]$ falls, so rate falls.

☞ **Cross-Check**

Numerical cross-check. First order $k = 0.1\,\mathrm{s}^{-1}$: at $t = 0$ rate $= 0.1[R]_0$; at $t = t_{1/2}$ rate is halved. Rate tracks concentration linearly for $n = 1$.

> **Final Answer:** Consumption of reactants $\Rightarrow$ shrinking $[A]$ $\Rightarrow$ smaller rate.

Q 3.48 Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example.

SOLUTION

Concept used. Thermodynamic feasibility ($\Delta G < 0$) tells us a reaction *can* proceed. The rate is independent of ΔG and is controlled by the activation energy E_a.
Example: conversion of diamond to graphite.
$\Delta G^\circ(\text{diamond} \rightarrow \text{graphite}) \approx -2.9\,\text{kJ/mol}$ at 298 K and 1 atm, so graphite is thermodynamically more stable than diamond. Yet diamond at room temperature does not perceptibly convert to graphite, because the activation energy is enormous

(breaking the entire diamond C-C network costs hundreds of kJ/mol). Diamonds remain "forever" on human timescales.

Step 1. Thermodynamic test: $\Delta G^\circ < 0$, so diamond → graphite is feasible.

Step 2. Kinetic test: E_a is so large that the rate constant at 298 K is unmeasurably small.

Step 3. Conclusion: feasibility alone doesn't tell the rate. You need to know E_a as well.

> **Final Answer:** Diamond → graphite is thermodynamically feasible ($\Delta G < 0$), but E_a is huge, so the rate is essentially zero at room temperature.

EXPERT'S SOLUTION *: Karan Banerjee, M.Tech Chemical Engineering, IIT Delhi*

Diamond-stability angle. The most famous example: a thermodynamically unstable substance that lasts forever.
Concept used. ΔG vs E_a independence.

Step 1. $\Delta G < 0 \Rightarrow$ graphite has lower free energy.

Step 2. $E_a \sim 730\,\text{kJ/mol} \Rightarrow$ at 298 K the rate is negligible.

Step 3. Heating diamond above 1700 K (in absence of O_2) does produce graphite, confirming the conversion is just kinetically forbidden at low T.

☞ **Alternative approach**

Alternative approach: ΔG **vs** E_a. Thermo asks if the reaction *can* happen ($\Delta G < 0$); kinetics asks how *fast* (E_a and k). Both must be favourable for an observable reaction.

✗ **Common Pitfall**

Common pitfall. Calling a reaction "infeasible" just because it is slow. Slow $\neq$ infeasible. Diamond → graphite is feasible ($\Delta G < 0$) but kinetically arrested.

> **Final Answer:** Diamond → graphite is a classic example of a thermodynamically favourable but kinetically slow process.

Q 3.49 **Why in the redox titration of $KMnO_4$ vs oxalic acid, we heat oxalic acid solution before starting the titration?**

SOLUTION

Concept used. The reaction between $\mathrm{KMnO_4}$ (acidic) and oxalic acid $\mathrm{H_2C_2O_4}$,

$$2\,\mathrm{MnO_4}^- + 5\,\mathrm{C_2O_4}^{2-} + 16\,\mathrm{H}^+ \longrightarrow 2\,\mathrm{Mn}^{2+} + 10\,\mathrm{CO_2} + 8\,\mathrm{H_2O},$$

is intrinsically slow at room temperature: the activation energy for the first electron transfer is high. Heating to about 60–70 °C raises the temperature, boosts $e^{-E_a/RT}$, and makes the endpoint sharp.

Step 1. Compute the rate enhancement. Going from 298 K to 343 K (70 °C) with $E_a \approx 70$ kJ/mol:

$$\frac{k_{343}}{k_{298}} = e^{(70000/8.314)(1/298-1/343)} = e^{8421\times4.40\times10^{-4}} = e^{3.71} \approx 41.$$

A factor of ~ 40 in rate.

Step 2. Once Mn^{2+} is formed, it auto-catalyses subsequent steps, so the reaction accelerates. The initial heat just gets the autocatalysis started.

> **Final Answer:** Heating raises the rate constant via Arrhenius ($k_{343}/k_{298} \approx 40$), making the otherwise slow $\mathrm{KMnO_4}$–oxalic-acid reaction proceed at a usable rate during titration.

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

Lab-practice angle. Why every titration manual says “warm to 60 °C before titrating”.
Concept used. Arrhenius applied to a sluggish redox.

Step 1. Without heat, the first few drops of $\mathrm{KMnO_4}$ persist pink for a long time, indicating slow reduction. The endpoint is hard to spot.

Step 2. After heating, the pink color fades quickly until the endpoint, where it persists for ≥ 30 s, giving a clean visual cue.

Step 3. Be careful not to overheat ($> 80\,°\mathrm{C}$), or oxalic acid decomposes to $\mathrm{CO_2} + \mathrm{H_2O} + \mathrm{CO}$, ruining the stoichiometry.

♥ Concept Linkage

Concept linkage. The same Arrhenius reasoning underlies why food spoils faster on a warm day and refrigeration extends shelf life.

☞ Alternative approach

Alternative approach: autocatalysis. Mn^{2+} catalyses the $\mathrm{KMnO_4}$–$\mathrm{C_2O_4}^{2-}$ reaction. The product Mn^{2+} accelerates further reaction — start slow, then speeds up.

☞ **Cross-Check**

Numerical cross-check. Without warming: induction $\sim$ 5–10 min before colour disappears. At 60 °C: instantaneous decolourisation — Arrhenius $e^{-E_a/RT}$ factor jumps with T.

Final Answer: Heat speeds up the slow reaction so the titration endpoint is sharp.

Q 3.50 Why can't molecularity of any reaction be equal to zero?

SOLUTION

Concept used. Molecularity is defined as the number of reactant molecules taking part in an elementary step. By construction, at least one molecule must be present to participate; a step with zero molecules involved would be a step with nothing reacting, which is meaningless.

Step 1. Definition: molecularity = number of molecules colliding / participating in one elementary step.

Step 2. Minimum count: 1 (unimolecular, e.g. radioactive decay or dissociation of an isolated species).

Step 3. Maximum (commonly observed): 3 (termolecular). Higher is possible in principle, but practically negligible.

Step 4. Zero molecules involved means no reaction at all, hence molecularity $= 0$ is undefined.

Final Answer: At least one molecule must be present for a reaction to occur, so molecularity is always ≥ 1.

EXPERT'S SOLUTION : *Sneha Reddy, Ph.D Organic Chemistry, IISc Bangalore*

Definition-strict angle. Zero molecules in a step = nothing happening.
Concept used. Molecularity is a count, so its minimum is 1.

Step 1. Smallest possible count $= 1$.

Step 2. Counter to "zero-order reaction": order $= 0$ is empirical, molecularity is theoretical and cannot be 0.

☞ Alternative approach

Alternative approach: count molecules in step. Molecularity counts molecules in a single elementary step. Zero molecules means no collision means no reaction step — meaningless.

✗ Common Pitfall

Common pitfall. Confusing zero *order* (allowed, empirical) with zero *molecularity* (disallowed, mechanistic). Order can be zero; molecularity cannot.

Final Answer: Molecularity ≥ 1 always.

Q 3.51 Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

SOLUTION

Concept used. A complex reaction is a sum of several elementary steps, each with its own molecularity (the count of molecules in that step). The overall reaction has *no single molecularity* because different steps have different counts. Order, however, is empirical: it's the exponent that fits the observed rate law of the overall reaction, so order is defined for any reaction, elementary or complex.

Step 1. Molecularity. Defined for one elementary step: "how many molecules are in this step?". For a multi-step mechanism, each step has its own molecularity; there's no single number for the whole reaction.

Step 2. Order. Defined by the experimental rate law: "what exponents fit the rate-vs-concentration data?". This is always definable (and always measurable), whether the reaction has one step or many.

Final Answer: Molecularity is defined per elementary step (so it's meaningful only for single-step / elementary reactions). Order is defined by the experimental rate law and is always available.

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

Theory-vs-experiment angle. Molecularity is theoretical (in the mechanism). Order is experimental (in the rate law).

Concept used. Mechanism contains multiple elementary steps. The empirical rate law is one law, but the mechanism has many molecularities.

Step 1. Elementary reaction: one mechanism step ⇒ one molecularity ⇒ matches order.

Step 2. Complex reaction: multiple steps ⇒ multiple molecularities ⇒ no single molecularity for the overall reaction, but order still exists.

☞ **Alternative approach**

Alternative approach: empirical vs mechanistic. Order is empirical (from rate-vs-concentration data); molecularity is mechanistic (count molecules in elementary step). Only elementary steps have a defined molecularity.

☞ **Cross-Check**

Numerical cross-check. $H_2 + Br_2$: order overall $= 3/2$, but "molecularity" is not $3/2$ (impossible integer) — it's 1 for initiation, 2 for propagation, etc. Step-wise.

> **Final Answer:** Molecularity needs a single elementary step; order works for any reaction.

Q 3.52 Why can we not determine the order of a reaction by taking into consideration the balanced chemical equation?

SOLUTION

Concept used. The balanced equation reflects the *overall* stoichiometry, summing all elementary steps. The rate law, however, is governed by the slowest (rate-determining) step, and the slow step may involve fewer or different species than the overall equation. Order is therefore an experimental fact, not a prediction from stoichiometry.
Example. The reaction

$$KClO_3 + 6\,FeSO_4 + 3\,H_2SO_4 \longrightarrow KCl + 3\,H_2O + 3\,Fe_2(SO_4)_3$$

has stoichiometric coefficient sum $1 + 6 + 3 = 10$, so a naive reading predicts a tenth order reaction. Experimentally, this is a *second-order* reaction, because it proceeds through many elementary steps with the rate-determining one involving only two species.

Step 1. Balanced equation tells overall stoichiometry: how much A becomes how much C.

Step 2. Rate law depends on the mechanism: which step is slowest, and what's in that step.

Step 3. These are different things; balanced equation does not reveal the mechanism.

Step 4. Hence order must be measured (e.g. initial-rates method, half-life method, etc.), not derived from the balanced equation.

> **Final Answer:** Balanced equation gives stoichiometry; the rate law reflects the slowest mechanism step, which is determined experimentally. The two can differ wildly.

EXPERT'S SOLUTION *: Tara Singh, M.Sc Chemistry, IIT Kanpur*

Mechanism-vs-stoichiometry angle. Stoichiometry is global; rate law is local (to the slow step).
Concept used. Slow step controls rate law; balanced equation hides the slow step.

Step 1. Stoichiometric coefficients reflect how many molecules of each species are consumed/produced *net*.

Step 2. The slow step might be unimolecular (involving just one of the reactants) and the rest of the chemistry happens downstream.

Step 3. Empirical determination by initial-rates is the only safe route.

☞ **Cross-Check**

Numerical cross-check. Same coefficients $H_2 + X_2 \longrightarrow 2\,HX$: $X = I$ gives order 2; $X = Br$ gives order 3/2; $X = Cl$ gives a chain mechanism. Stoichiometry says nothing about kinetics.

✗ **Common Pitfall**

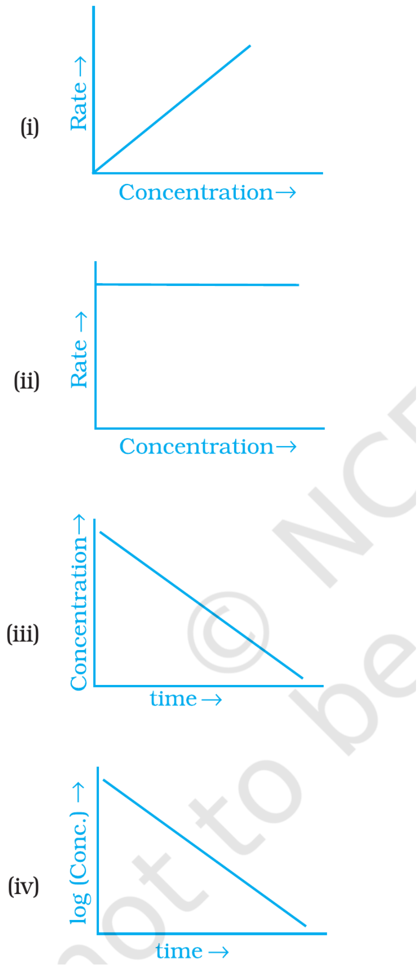
Common pitfall. Treating the balanced equation as a recipe for the rate law. The two often disagree: order must be measured, not read off coefficients.

> **Final Answer:** Mechanism (not stoichiometry) determines order; mechanism must be probed experimentally.

IV. Matching Type

Q 3.53 **Match the graph given in Column I with the order of reaction given in Column II. More than one item in Column I may link to the same item of Column II.**

SOLUTION



Column I graphs, NCERT Exemplar Class 12 Chemistry, Chapter 4.

Concept used. Diagnostic signatures of zero-order and first-order reactions:

- **Zero order.** $r = k$ (constant). Rate vs concentration is a horizontal line; concentration vs time is a straight line with slope $-k$.
- **First order.** $r = k\,[R]$. Rate vs concentration is a straight line through the origin with slope k; $\log[R]$ (or $\log([R]_0/[R])$) vs time is a straight line.

Step 1. **(i)** Rate vs concentration is a straight line through the origin with positive slope. This is $r = k\,[R]$, $\Rightarrow$ **first order (a)**.

Step 2. **(ii)** Rate vs concentration is horizontal (rate independent of concentration). This is $r = k$, $\Rightarrow$ **zero order (b)**.

Step 3. **(iii)** Concentration vs time is a straight line with negative slope. This is $[R]_t = [R]_0 - kt$, $\Rightarrow$ **zero order (b)**.

Step 4. **(iv)** $\log[\text{Conc.}]$ vs time is a straight line with negative slope $-k/2.303$. This is the integrated first-order law, $\Rightarrow$ **first order (a)**.

Final Answer: (i)→(a), (ii)→(b), (iii)→(b), (iv)→(a).

EXPERT'S SOLUTION *: Aanya Iyer, Ph.D Physical Chemistry, IISc Bangalore*

Signature-matching angle. Recognise the four diagnostic plots: rate vs $[R]$ (line through origin = first; horizontal = zero); $[R]$ vs t (line = zero; exponential = first); $\log[R]$ vs t (line = first).

Concept used. Each order has a characteristic linear plot that you can spot in seconds.

Step 1. Graph (i): r vs $[R]$, linear through origin $\Rightarrow$ first order.

Step 2. Graph (ii): r vs $[R]$, horizontal $\Rightarrow$ zero order.

Step 3. Graph (iii): $[R]$ vs t, linear $\Rightarrow$ zero order.

Step 4. Graph (iv): $\log[R]$ vs t, linear $\Rightarrow$ first order.

☞ **Alternative approach**

Alternative approach: shape matching. For each graph in Column I, identify whether the linear variable is $[R]$, $\ln[R]$, or $1/[R]$ — that pinpoints the order (0, 1, or 2 respectively).

☞ **Cross-Check**

Numerical cross-check. For first order $\ln[R](t) = \ln[R]_0 - kt$. Plot $\ln[R]$ vs t; slope $= -k$, intercept $= \ln[R]_0$. Linear test for first order.

♥ **Concept Linkage**

Concept linkage. Linearisation transforms is the workhorse of kinetic analysis: choose the right axis to make a curve straight, read off slope as k.

Final Answer: (i)→(a), (ii)→(b), (iii)→(b), (iv)→(a).

Q 3.54 Match the statements given in Column I and Column II.

Column I	**Column II**
(i) Catalyst alters the rate of reaction	**(a) cannot be fraction or zero**
(ii) Molecularity	**(b) proper orientation is not there always**
(iii) Second half life of first order reaction	**(c) by lowering the activation energy**
(iv) $e^{-E_a/RT}$	**(d) is same as the first**
(v) Energetically favourable reactions are sometimes slow	**(e) total probability is one**
(vi) Area under the Maxwell Boltzmann curve is constant	**(f) refers to the fraction of molecules with energy equal to or greater than activation energy**

SOLUTION

Concept used. Match each kinetics concept on the left to the matching property on the right.

Step 1. **(i)** Catalyst alters rate by providing a lower-E_a pathway. Match: **(c)** “by lowering the activation energy”.

Step 2. **(ii)** Molecularity is a count of molecules in an elementary step: a positive integer. Match: **(a)** “cannot be fraction or zero”.

Step 3. **(iii)** For a first-order reaction, $t_{1/2} = 0.693/k$ is independent of $[R]_0$. So the second half-life equals the first. Match: **(d)** “is same as the first”.

Step 4. **(iv)** $e^{-E_a/RT}$ is the Boltzmann factor: the fraction of molecules with energy $\geq E_a$. Match: **(f)** “refers to the fraction of molecules with energy equal to or greater than activation energy”.

Step 5. **(v)** Energetically favourable reactions can be slow because of orientation/steric factor. Match: **(b)** “proper orientation is not there always”.

Step 6. **(vi)** Total area under M-B curve $=$ total probability $= 1$. Match: **(e)** “total probability is one”.

Final Answer: (i)→(c), (ii)→(a), (iii)→(d), (iv)→(f), (v)→(b), (vi)→(e).

EXPERT’S SOLUTION : *Pranav Sharma, M.Sc Chemistry, IIT Kanpur*

Pair-by-pair angle. Each entry on the left has exactly one clean partner on the right; identify them in turn.

Concept used. Standard kinetics facts.

Step 1. Catalyst $\rightarrow$ lower E_a: (i)-(c).

Step 2. Molecularity is integer ≥ 1: (ii)-(a).

Step 3. First-order $t_{1/2}$ is constant: (iii)-(d).

Step 4. $e^{-E_a/RT}$ is Boltzmann fraction above barrier: (iv)-(f).

Step 5. Energetic but slow $\Rightarrow$ orientation: (v)-(b).

Step 6. Probability sums to 1: (vi)-(e).

☞ **Alternative approach**

Alternative approach: vocabulary mapping. Match each statement in Column I to its defining concept in Column II by reading keywords (“catalyst”, “E_a”, “order”, “temperature”).

☞ **Exam Tip**

Exam tip. Column-matching items in NCERT Exemplar map directly to NEET 2019 and JEE Main 2022 conceptual MCQs. Anchor on definitions.

☞ **Cross-Check**

Numerical cross-check. “$E_a = 0 \Rightarrow$ rate nearly independent of T” — Arrhenius gives $k = A$; rate doesn’t benefit from T.

Final Answer: (i)$\rightarrow$(c), (ii)$\rightarrow$(a), (iii)$\rightarrow$(d), (iv)$\rightarrow$(f), (v)$\rightarrow$(b), (vi)$\rightarrow$(e).

Q 3.55 Match the items of Column I and Column II.

Column I	Column II
(i) Diamond	(a) short interval of time
(ii) Instantaneous rate	(b) ordinarily rate of conversion is imperceptible
(iii) Average rate	(c) long duration of time

SOLUTION

Concept used. The three terms describe three different timescales / rates.

Step 1. **(i)** Diamond converts to graphite extremely slowly because of the large E_a. Rate is imperceptible at room temperature. Match: **(b)** “ordinarily rate of conversion is imperceptible”.

Step 2. **(ii)** Instantaneous rate is the rate at a particular instant, i.e., over a vanishingly short time interval. Match: **(a)** “short interval of time”.

Step 3. **(iii)** Average rate is computed over a longer time interval $[t_1, t_2]$. Match: **(c)** “long duration of time”.

Final Answer: (i)→(b), (ii)→(a), (iii)→(c).

EXPERT’S SOLUTION : *Vivaan Kapoor, B.Tech Chemical Engineering, IIT Bombay*

Time-scale angle. Match each item to its characteristic duration.
Concept used. Average vs instantaneous rate definitions; diamond as a kinetic-trap example.

Step 1. Diamond stability: huge E_a, imperceptible rate, (b).

Step 2. Instantaneous rate $\propto \Delta t \to 0$, short, (a).

Step 3. Average rate over $\Delta t > 0$, longer, (c).

☞ **Alternative approach**

Alternative approach: link rate law → order. For each rate-law expression in Column I, count exponents on $[A]$, $[B]$ etc.; the sum is the order, matching to Column II.

☞ **Cross-Check**

Numerical cross-check. $r = k[A]^1[B]^2$: order $= 3$. $r = k[A]^0[B]^{1/2}$: order $= 1/2$. Units of k track these: $\mathrm{M}^{-2}\,\mathrm{s}^{-1}$ and $\mathrm{M}^{1/2}\,\mathrm{s}^{-1}$ respectively.

Final Answer: (i)→(b), (ii)→(a), (iii)→(c).

Q 3.56 **Match the items of Column I and Column II.**

Column I	Column II
(i) Mathematical expression for rate of reaction	(a) rate constant
(ii) Rate of reaction for zero order reaction is equal to	(b) rate law
(iii) Units of rate constant for zero order reaction is same as that of	(c) order of slowest step
(iv) Order of a complex reaction is determined by	(d) rate of a reaction

SOLUTION

Concept used. Definitions: rate law, rate constant, units of k for zero order, and rate-determining step.

Step 1. **(i)** Mathematical expression for rate of reaction is the rate law: $r = k\,[A]^x\,[B]^y$. Match: **(b)** rate law.

Step 2. **(ii)** For zero order, $r = k$ identically. So rate of reaction equals rate constant. Match: **(a)** rate constant.

Step 3. **(iii)** Zero-order k has units of rate: $\mathrm{mol\,L^{-1}\,s^{-1}}$. So units of k for zero order same as units of rate. Match: **(d)** rate of a reaction.

Step 4. **(iv)** Order of a complex reaction is determined by the slowest (rate-determining) step. Match: **(c)** order of slowest step.

Final Answer: (i)→(b), (ii)→(a), (iii)→(d), (iv)→(c).

EXPERT'S SOLUTION *: Karan Banerjee, M.Tech Chemical Engineering, IIT Delhi*

Definition-match angle. Each item is a one-line definition.
Concept used. Four standard kinetics definitions.

Step 1. (i) "mathematical expression for rate" = rate law, (b).

Step 2. (ii) For zero order $r = k$, so rate = rate constant, (a).

Step 3. (iii) Units of zero-order k equal units of rate, (d).

Step 4. (iv) Complex reaction's order ← order of slowest step, (c).

☞ Alternative approach

Alternative approach: catalyst-type pairing. Heterogeneous ⇔ different phases (Pt + gas). Homogeneous ⇔ same phase (H^+ in aq). Enzymes: biological catalysts, very specific.

☞ Cross-Check

Numerical cross-check. Pt for $N_2 + H_2 \longrightarrow NH_3$: heterogeneous (solid Pt, gaseous reactants). H^+ for ester hydrolysis: homogeneous (both aq). Catalase: enzyme.

Final Answer: (i)→(b), (ii)→(a), (iii)→(d), (iv)→(c).

V. Assertion and Reason Type

Note: A statement of assertion followed by a statement of reason is given. Choose the correct answer:

(i) Both assertion and reason are correct and the reason is correct explanation of assertion.
(ii) Both assertion and reason are correct but reason does not explain assertion.
(iii) Assertion is correct but reason is incorrect.
(iv) Both assertion and reason are incorrect.
(v) Assertion is incorrect but reason is correct.

Q 3.57 Assertion: Order of the reaction can be zero or fractional.
Reason: We cannot determine order from balanced chemical equation.

SOLUTION

Correct option: (ii) Both assertion and reason are correct, but reason does not explain assertion.

Concept used. Order is empirical and can take any real value (zero, positive integer, or fraction). It is also true that the balanced equation does not give the order. But these are two independent facts about order; the second is not the *reason* for the first.

Step 1. Check assertion: order can be 0 (zero-order reactions like $2\,NH_3 \xrightarrow{Pt} N_2 + 3\,H_2$) or fractional (the $H_2 + Br_2$ reaction has order 3/2). True.

Step 2. Check reason: order cannot be deduced from the balanced equation; it must be measured experimentally. True.

Step 3. Check causal link: does the second fact *explain* the first? No. Both are independent properties. The fact that order is experimental does not by itself imply that order can be 0 or fractional. So the reason is correct but does not explain the assertion.

> **Final Answer:** Option **(ii)**: both correct, reason does not explain assertion.

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

Independence-check angle. Two true statements are not automatically cause and effect.

Concept used. Both clauses are true facts. The question is whether the second causes the first.

Step 1. Assertion true: zero and fractional orders are observed.

Step 2. Reason true: order is empirical, not derivable from stoichiometry.

Step 3. No causal link: the empirical nature of order doesn't force it to be 0 or fractional in some cases; that's a separate observation.

☞ Alternative approach

Alternative approach: assertion-reason logic. (i) Both true and reason explains assertion; (ii) both true but reason doesn't explain; (iii) assertion true, reason false; (iv) both false. Map each case.

♥ Concept Linkage

Concept linkage. Assertion-reason questions train you to disentangle "what happens" from "why". This is critical in mechanism elucidation.

✗ Common Pitfall

Common pitfall. Marking Assertion + Reason both "true" even when Reason is unrelated. Always check the *causal* linkage, not just truth values of the two statements.

Final Answer: Option **(ii)**.

Q 3.58 **Assertion: Order and molecularity are same.**
Reason: Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

SOLUTION

Correct option: (v) Assertion is incorrect but reason is correct.
Concept used. Order and molecularity are different in general (they coincide only for elementary reactions). The reason clause correctly distinguishes them: order is experimental; molecularity counts molecules in the rate-determining elementary step.

Step 1. Check assertion: "order and molecularity are same" is false in general. They coincide only for elementary reactions. So assertion is incorrect.

Step 2. Check reason: "order is experimental; molecularity is the sum of stoichiometric coefficients of the rate-determining elementary step" is the standard textbook definition. Correct.

Final Answer: Option **(v)**: assertion incorrect, reason correct.

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

Truth-table angle. Assertion claims a general identity that holds only conditionally; reason is the standard definition.

Concept used. Order $\neq$ molecularity in general; both are well-defined separately.

Step 1. Assertion needs the qualifier "for elementary reactions"; without it, false.

Step 2. Reason correctly states the definitions.

☞ **Cross-Check**

Numerical cross-check. Zero order, $k = 0.1\,\text{M/s}$, $[R]_0 = 1\,\text{M}$: $t_{1/2} = 5\,\text{s}$. With $[R]_0 = 2\,\text{M}$: $t_{1/2} = 10\,\text{s}$. Doubled.

✗ **Common Pitfall**

Common pitfall. Claiming half-life of zero-order is independent of $[R]_0$ (that's first order). Zero-order $t_{1/2} = [R]_0/(2k)$ scales *linearly* with initial concentration.

Final Answer: Option **(v)**.

Q 3.59 **Assertion: The enthalpy of reaction remains constant in the presence of a catalyst.**

Reason: A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.

SOLUTION

Correct option: (i) Both assertion and reason are correct, and reason is the correct explanation of assertion.

Concept used. A catalyst lowers E_a by creating a new transition state, but leaves the reactant and product energy levels unchanged. Therefore $\Delta H = H_P - H_R$ is unchanged. The reason gives precisely this explanation.

Step 1. Check assertion: ΔH is unchanged by a catalyst (it's a state function determined by endpoints only). True.

Step 2. Check reason: a catalyst creates a different activated complex with lower E_a, but reactants and products are the same, so their energy levels (and the gap between them) are unchanged. True.

Step 3. Check causal link: reason directly explains why ΔH is unchanged. Yes, it's the correct explanation.

Final Answer: Option **(i)**: both correct, reason explains assertion.

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

State-function angle. The reason here is the standard textbook proof of the assertion.
Concept used. ΔH depends only on endpoints; catalyst changes only the path.

Step 1. Assertion true; reason true; reason explains.

☞ **Exam Tip**

Exam tip. "Temperature and rate" assertion-reason in NEET 2017, JEE 2021. Default: both A and R true; R explains A via Maxwell-Boltzmann shift.

✗ **Common Pitfall**

Common pitfall. Saying rate doubles per 10 K rise *exactly*. That is a rule of thumb for $E_a \sim 50$ kJ/mol near room T; actual factor depends on E_a.

Final Answer: Option **(i)**.

Q 3.60 **Assertion: All collision of reactant molecules lead to product formation. Reason: Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.**

SOLUTION

Correct option: (v) Assertion is incorrect but reason is correct.
Concept used. Effective collisions require both correct orientation and sufficient energy. The assertion claims every collision works, which is false; the reason correctly identifies the two requirements.

Step 1. Check assertion: "all collisions lead to product". False; most collisions are unproductive due to insufficient energy or wrong orientation.

Step 2. Check reason: "only collisions with right orientation and sufficient energy lead to product formation". True (collision theory).

Final Answer: Option **(v)**: assertion false, reason true.

EXPERT'S SOLUTION : *Priya Patel, M.Sc Chemistry, IIT Kanpur*

Effective-collision angle. Most collisions waste themselves; only effective ones count.
Concept used. Boltzmann factor × steric factor $\ll$ total collision rate.

Step 1. Assertion would imply rate $=$ collision frequency, but actually rate $\ll$ collision frequency.

Step 2. Reason restates the two-condition rule.

☞ **Cross-Check**

Numerical cross-check. Haber: K_p at 700 K unchanged with or without iron catalyst. Only k_f and k_b both rise; their ratio ($= K$) is constant.

✗ **Common Pitfall**

Common pitfall. Concluding catalyst shifts equilibrium "slightly". No: K_c, ΔG° are untouched. The forward and backward rates rise by the same factor.

Final Answer: Option **(v)**.

Q 3.61 **Assertion: Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.**
Reason: Reactant molecules undergo chemical change irrespective of their orientation during collision.

SOLUTION

Correct option: (iii) Assertion is correct but reason is incorrect.
Concept used. Arrhenius gives reasonable rate-constant estimates for many simple reactions, but for complex molecules the steric factor P matters and a single Arrhenius fit is approximate. The reason claim is flatly wrong: orientation *is* required for chemical change.

Step 1. Check assertion: Arrhenius is empirically accurate for many gas-phase and solution reactions; for complex molecules, P absorbs the orientation correction into the pre-exponential A. So Arrhenius works fairly well across the board if we treat A as an empirical fitting parameter. Accepted as correct.

Step 2. Check reason: "orientation doesn't matter". Wrong; collision theory says proper orientation is mandatory. False.

Final Answer: Option **(iii)**: assertion correct, reason incorrect.

EXPERT'S SOLUTION : *Sneha Reddy, Ph.D Organic Chemistry, IISc Bangalore*

Orientation-counter angle. Reason violates the steric-factor rule explicitly.
Concept used. Steric factor P accounts for orientation requirement.

Step 1. Assertion: Arrhenius works empirically. OK.

Step 2. Reason: orientation doesn't matter. Wrong; always required.

☞ **Alternative approach**

Alternative approach: collision theory + orientation. "Effective collision" = energy $\geq E_a$ AND proper orientation. Either failure prevents reaction even when energy is sufficient.

♥ **Concept Linkage**

Concept linkage. The orientation factor explains why biochemical reactions need enzymes (positioning the substrates) and why some gas-phase reactions are so slow despite huge T.

✗ **Common Pitfall**

Common pitfall. Calling every energetic collision "effective". Effective = energy $\geq E_a$ *and* proper orientation. Missing orientation kills the reaction even at high T.

Final Answer: Option **(iii)**.

VI. Long Answer Type

Q 3.62 All energetically effective collisions do not result in a chemical change. Explain with the help of an example.

SOLUTION

Concept used. For a collision to result in product formation, the colliding molecules must satisfy *two* conditions:

- Energy condition: combined kinetic energy of the colliding pair must equal or exceed the threshold (activation) energy E_a.
- Orientation condition: the geometry of approach must be such that the right atoms

come close enough to form the new bond and break the old bond.

A collision that has enough energy but the wrong geometry is **energetically effective but ineffective** for reaction.

Step 1. Write the rate expression incorporating both factors:

$$r = P\, Z_{AB}\, e^{-E_a/RT}\, [A]\, [B],$$

where Z_{AB} is the collision frequency factor, $e^{-E_a/RT}$ is the Boltzmann fraction satisfying the energy requirement, and P is the **steric factor** (orientation probability), typically $0 < P \leq 1$.

Step 2. For a reaction with $P \ll 1$, most energetic collisions fail to react because the molecules are not oriented correctly.

Step 3. **Example.** The thermal dissociation of HI:

$$2\,\mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I_2}.$$

Two HI molecules must approach such that the two H atoms are close to each other and the two I atoms are close to each other, so that the new H—H and I—I bonds can form simultaneously while the two H—I bonds break. Most random orientations have the H atom of one HI next to the I atom of another, which simply gives a high-energy bump and the molecules fly apart unchanged.

Step 4. Another example: SN2 reactions in organic chemistry require “back-side attack” (the nucleophile approaches the carbon from the side opposite the leaving group). All other orientations fail no matter how energetic the collision.

> **Final Answer:** Even an energetic collision fails if the molecules are not in the correct orientation. The steric factor P in collision theory captures this; for many reactions $P \ll 1$, so most energetic collisions are unproductive.

EXPERT’S SOLUTION *: Aditi Mehta, M.Sc Physical Chemistry, IIT Madras*

Geometry-first angle. The energy gate and the orientation gate are independent; both must open.

Concept used. Two-gate model: Boltzmann factor (energy gate) × steric factor (orientation gate). A collision is productive only if both factors are favourable.

Step 1. Visualise two HI molecules colliding head-on (H-end to I-end). This is energetic but useless: it gives no path to form H—H or I—I.

Step 2. Now visualise the same two HI molecules approaching broadside (H-end of one near H-end of the other, I-end near I-end). Now the bond-rearrangement can occur. This is the “properly oriented” collision.

Step 3. Quantitative estimate. For $2\,HI \rightarrow H_2 + I_2$ at 700 K, the observed rate constant is about 10^{-5} times what collision theory predicts if we use $P = 1$. Setting $P \approx 10^{-5}$ matches experiment.

Step 4. Same idea explains why SN2 inversion at a tertiary carbon is essentially impossible: bulky substituents block the back-side approach, so the steric factor for the SN2 pathway is ≈ 0.

♥ **Concept Linkage**

Concept linkage. Transition-state theory replaces the simple P with a partition-function ratio, but the physical picture stays the same: only certain geometric configurations can climb the saddle point.

☞ **Cross-Check**

Numerical cross-check. For $NO + O_3$: $Z \sim 10^{11}$, $k_{\text{obs}} \sim 10^7\,M^{-1}\,s^{-1}$, so $P\,\exp(-E_a/RT) \sim 10^{-4}$ — most energetic collisions still fail because of bad geometry.

Final Answer: Energetic collisions still fail when orientation is wrong; the steric factor P in $r = PZe^{-E_a/RT}$ quantifies this. Example: $2\,HI \longrightarrow H_2 + I_2$ has $P \sim 10^{-5}$.

Q 3.63 What happens to most probable kinetic energy and the energy of activation with increase in temperature?

SOLUTION

Concept used. The Maxwell-Boltzmann (M-B) distribution plots $f(E)$, the fraction of molecules with kinetic energy in $[E, E + dE]$. As temperature rises:

- The *most probable kinetic energy* E_{mp} shifts to higher values: the peak of the M-B curve moves right.
- The peak flattens; the distribution broadens.
- The *area under the curve beyond* E_a grows sharply: more molecules have enough energy to react.
- The *activation energy* E_a itself is a property of the reaction (independent of T); it does *not* change with temperature.

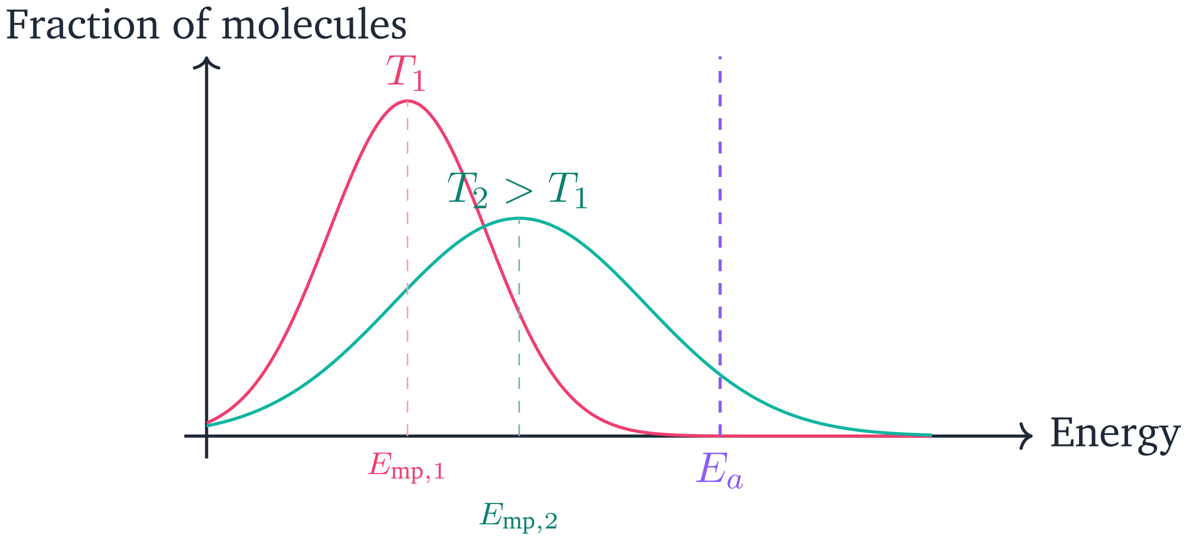
Step 1. Sketch two M-B curves, one for T_1 and one for $T_2 > T_1$. Both have the same total area (=1). The T_2-curve has a peak shifted right and a lower peak height (broader curve).

Step 2. Most probable kinetic energy E_{mp} scales as $\frac{1}{2}kT$ (1D) or $\frac{3}{2}kT$ (3D, mean) and so rises linearly with T. Mark this with an arrow: peak shifts right.

Step 3. The activation energy E_a is fixed on the energy axis, determined by the reaction (and the catalyst, if any). It does NOT depend on T.

Step 4. The fraction of molecules with $E \geq E_a$ is the area under the M-B curve to the right of E_a. At T_2, this area is larger. This is why rate rises with T.

Diagram. Schematic M-B curves at T_1 and T_2:



At T_2, the peak (most probable energy) shifts to the right, the curve flattens, and the area beyond E_a (the shaded “reactive” tail) grows.

> **Final Answer:** Most probable kinetic energy E_{mp} increases with T (peak shifts right). Activation energy E_a is independent of T (unchanged). The area beyond E_a grows, so reaction rate rises.

EXPERT’S SOLUTION *: Rohit Verma, M.Sc Chemistry, IIT Kanpur*

Two-curve angle. Sketch M-B at two temperatures and label E_{mp}, E_a, and the tail above E_a.

Concept used. M-B distribution properties: peak position, peak height, peak width, area conservation.

Step 1. Peak shift. $E_{\text{mp}} = \frac{1}{2}kT$ (per molecule, 1D classical); doubling T doubles E_{mp}.

Step 2. Peak height. With area fixed and peak shifting right, peak height drops (curve flattens).

Step 3. E_a stays put. It’s an intrinsic property of the reaction; raising T doesn’t change which energy the molecules have to clear.

Step 4. Reactive-tail area. With the curve shifted right and broadened, the area to the right of E_a grows, giving more reactive collisions and a higher rate.

Numerical illustration. At $T_1 = 300\,\mathrm{K}$, $E_{\mathrm{mp}} \approx 0.0125\,\mathrm{eV}$. At $T_2 = 600\,\mathrm{K}$, $E_{\mathrm{mp}} \approx 0.025\,\mathrm{eV}$ (doubled). E_a remains the same in both cases.

☞ **Exam Tip**

Exam tip. CBSE 2022 board paper asked to "state and explain" what happens to E_{mp} and E_a with T. Always say: E_{mp} rises, E_a unchanged.

☞ **Alternative approach**

Alternative approach: Maxwell-Boltzmann graph. Increasing T shifts the most-probable kinetic energy (E_{mp}) right (higher value). Activation energy E_a stays fixed; it's a property of the reaction, not of the temperature.

Final Answer: E_{mp} increases with T; E_a is independent of T.

Q 3.64 Describe how does the enthalpy of reaction remain unchanged when a catalyst is used in the reaction.

SOLUTION

Concept used. Enthalpy H is a state function: its change in a process depends only on the initial and final states (reactants and products), not on the path. A catalyst provides a new pathway with a different activated complex and a lower activation energy, but the reactants and products themselves are unchanged. Therefore $\Delta H = H_P - H_R$ is the same with or without the catalyst.

Step 1. Start from the definition: for a reaction at constant pressure, $\Delta H = H_P - H_R$, where H_R is the enthalpy of the reactants and H_P is that of the products.

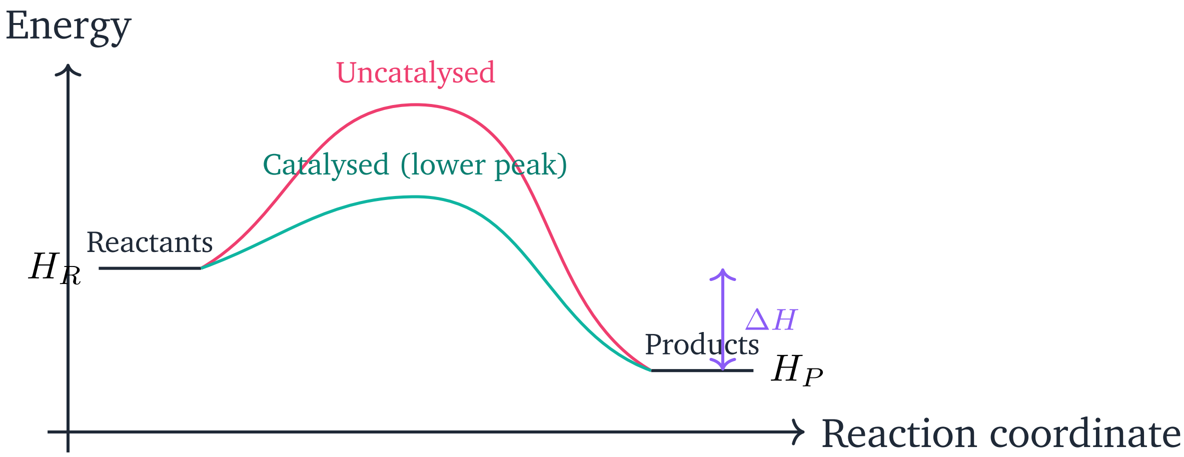
Step 2. Without catalyst: the reaction follows path $R \to *_1 \to P$ through an activated complex $*_1$ of energy H_{*1}. Activation energy is $E_a = H_{*1} - H_R$.
$\Delta H = H_P - H_R$, independent of H_{*1}.

Step 3. With catalyst: the reaction follows a new path $R \to *_2 \to P$ through a different, lower activated complex $*_2$ of energy $H_{*2} < H_{*1}$. Activation energy drops to $E_a' = H_{*2} - H_R < E_a$. But the endpoints R, P are the same, so
$\Delta H' = H_P - H_R = \Delta H$.

Step 4. Apply Hess's law for additional confirmation: any sequence of steps from R to

P yields the same ΔH. The catalysed mechanism is just an alternative sequence of elementary steps, but its overall ΔH matches.

Diagram. Two energy paths from reactants to products:



The two paths share the same reactant and product levels; only the peak height differs. So ΔH is the same.

> **Final Answer:** Enthalpy is a state function. A catalyst lowers the energy of the activated complex but leaves the reactant and product energies unchanged. The difference $\Delta H = H_P - H_R$ is the same with or without catalyst.

EXPERT'S SOLUTION *: Aanya Iyer, Ph.D Physical Chemistry, IISc Bangalore*

Path-independence angle. State functions don't care which road you took, only where you started and where you ended.
Concept used. ΔH depends only on endpoints (state function). A catalyst only changes the path.

Step 1. Identify the endpoints: R (reactants) and P (products). These chemical species are the same before and after adding a catalyst.

Step 2. Identify what changes: the height of the energy hump E_a and the structure of the activated complex.

Step 3. Compute ΔH in both paths: it's just $H_P - H_R$, with both terms unchanged. So ΔH is unchanged.

Step 4. Equivalently, by Hess's law: if reactants $\rightarrow$ products can occur by two different paths, both give the same ΔH.

Numerical illustration. Decomposition of H_2O_2 has $\Delta H = -98\,\text{kJ/mol}$ in pure water (slow) and in the presence of KI catalyst (fast). The 98 kJ comes out either way; only the rate changes.

☞ Alternative approach

Alternative approach: state-function argument. ΔH depends only on reactant and product enthalpies. Catalysed path is just a different route; route doesn't matter for state functions.

☞ Cross-Check

Numerical cross-check. $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$: $\Delta H = -286\,\text{kJ/mol}$. Whether on Pt foil (catalyst) or unaided, the heat released per mole is the same — 286 kJ.

Final Answer: ΔH unchanged because reactant and product enthalpies are unchanged; catalyst affects only the path.

Q 3.65 **Explain the difference between instantaneous rate of a reaction and average rate of a reaction.**

SOLUTION

Concept used.

- **Average rate** over a time interval $[t_1, t_2]$ is the change in concentration divided by the time interval:
$$\bar{r} = -\frac{\Delta[R]}{\Delta t} = -\frac{[R]_{t_2} - [R]_{t_1}}{t_2 - t_1},$$
where the minus sign makes the rate positive for a disappearing reactant. Graphically, $\bar{r}$ is the slope of the chord joining the two endpoint points on the concentration-vs-time curve.
- **Instantaneous rate** at a specific time t is the limiting value of the average rate as the interval shrinks to zero:
$$r_{\text{inst}}(t) = -\lim_{\Delta t \to 0} \frac{\Delta[R]}{\Delta t} = -\frac{d[R]}{dt}.$$
Graphically, r_{inst} is the slope of the tangent to the concentration-vs-time curve at the point t.

Step 1. Average rate is a *secant slope*; instantaneous rate is a *tangent slope*. As $\Delta t \to 0$, the secant becomes the tangent.

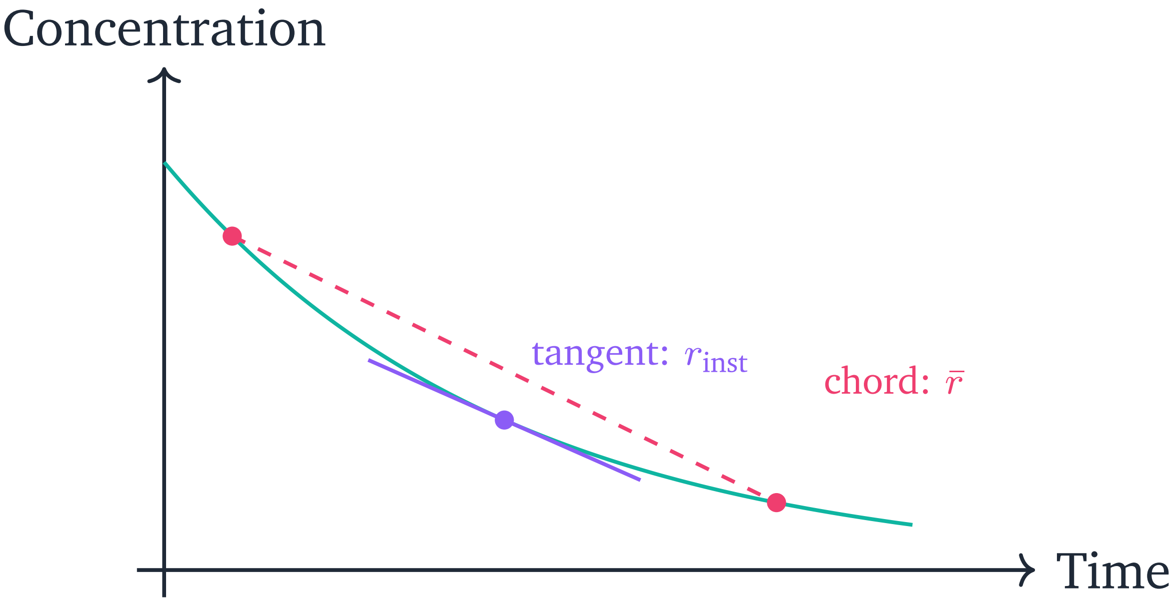
Step 2. The average rate is just one number for the entire interval; the instantaneous rate is a function of time, generally decreasing as the reaction proceeds.

Step 3. Example. For a reaction with rate law $-d[R]/dt = k\,[R]^2$ starting at $[R]_0 = 2\,\text{M}$ with $k = 0.1\,\text{M}^{-1}\,\text{s}^{-1}$:

- Instantaneous rate at $t = 0$: $r_{\text{inst}}(0) = k\,[R]_0^2 = 0.1 \times 4 = 0.4\,\text{M/s}$.

- Instantaneous rate at $t = 5\,\text{s}$ (after $[R]$ has dropped to, say, $1.0\,\text{M}$): $r_{\text{inst}}(5) = 0.1 \times 1 = 0.1\,\text{M/s}$.
- Average rate over $[0, 5\,\text{s}]$: $\bar{r} = (2.0 - 1.0)/5 = 0.2\,\text{M/s}$, which lies between the two instantaneous values.

Diagram.



Final Answer: Average rate $\bar{r} = -\Delta[R]/\Delta t$ over a finite interval (chord slope). Instantaneous rate $r_{\text{inst}} = -d[R]/dt$ at a single moment (tangent slope).

EXPERT'S SOLUTION : *Priya Patel, M.Sc Chemistry, IIT Kanpur*

Calculus angle. Average rate is the secant; instantaneous rate is the tangent. The latter is the derivative of the former limit.

Concept used.

$$r_{\text{inst}} = \lim_{\Delta t \to 0} \bar{r}_{\Delta t} = -\frac{d[R]}{dt}.$$

Step 1. Average rate is a number averaged over a finite time chunk; instantaneous rate is the rate at a single instant.

Step 2. Average rate is meaningful when the reaction rate changes slowly (or you only need a coarse number); instantaneous rate is essential for setting up rate laws.

Step 3. As $\Delta t \to 0$, average rate converges to instantaneous rate at the midpoint of the interval (or to either endpoint when the rate is continuous).

♥ Concept Linkage

Concept linkage. The integrated rate laws derive from the differential ones ($r_{\text{inst}} = -d[R]/dt = k[R]^n$) and then are integrated to give $[R]$ as a function of t.

✗ Common Pitfall

Common pitfall. Confusing rate "at 40 s" (instantaneous) with average rate "up to 40 s" (over the whole interval $[0, 40]$). See Q8 and Q10 for the exact distinction.

☞ Cross-Check

Numerical cross-check. $[R](0) = 2\,\text{M}$, $[R](5) = 1.5\,\text{M}$: $\bar{r} = 0.1\,\text{M/s}$. Tangent at $t = 2.5\,\text{s}$ (midpoint) might be $\sim 0.1\,\text{M/s}$ also — depends on curvature.

Final Answer: Average rate = chord slope over interval; instantaneous rate = tangent slope at a point.

Q 3.66 With the help of an example explain what is meant by pseudo first order reaction.

SOLUTION

Concept used. A **pseudo first order reaction** is one whose true rate law is of higher order (often second), but which *appears* first order in the experiment because one reactant is in such large excess that its concentration is essentially constant during the reaction. The constant concentration of the excess reactant gets absorbed into the observed rate constant, leaving a first-order rate law in the other reactant.
Example: acid-catalysed hydrolysis of an ester.

$$\text{CH}_3\text{COOC}_2\text{H}_5 \;+\; \text{H}_2\text{O} \xrightarrow{H^+} \text{CH}_3\text{COOH} \;+\; \text{C}_2\text{H}_5\text{OH}.$$

Step 1. True rate law (bimolecular, hence second order overall):

$$r = k\,[\text{CH}_3\text{COOC}_2\text{H}_5]\,[\text{H}_2\text{O}].$$

Step 2. Water is the solvent. Its concentration in the reaction mixture is approximately $[\text{H}_2\text{O}] \approx 55.5\,\text{mol/L}$. The ester is dissolved at a much smaller concentration, say $[\text{ester}]_0 = 0.05\,\text{mol/L}$. When all the ester is consumed, the water consumed is only 0.05 mol/L out of 55.5 mol/L, i.e. 0.09%. So $[\text{H}_2\text{O}]$ is essentially unchanged.

Step 3. Define the observed rate constant $k_{\text{obs}} = k\,[\text{H}_2\text{O}]$. Then

$$r = k_{\text{obs}}\,[\text{CH}_3\text{COOC}_2\text{H}_5],$$

a first-order rate law in ester.

Step 4. Numerical: if $k = 1.0 \times 10^{-5}\,\text{L mol}^{-1}\text{s}^{-1}$, then $k_{\text{obs}} = 1.0 \times 10^{-5} \times 55.5 = 5.55 \times 10^{-4}\,\text{s}^{-1}$, an ordinary first-order rate constant with units of s^{-1}.

Another example. Inversion of cane sugar (sucrose):

$$\text{C}_{12}\text{H}_{22}\text{O}_{11} \;+\; \text{H}_2\text{O} \xrightarrow{H^+} \text{C}_6\text{H}_{12}\text{O}_6 \;+\; \text{C}_6\text{H}_{12}\text{O}_6$$

(glucose + fructose). Water is in vast excess; the apparent kinetics are first order in sucrose. This was historically the first reaction studied kinetically (Wilhelmy, 1850).

> **Final Answer:** A pseudo first order reaction is intrinsically second order but appears first order because one reactant is in large excess (e.g., water in ester hydrolysis). The excess reactant's concentration is absorbed into k_{obs}.

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

Excess-reactant angle. A second-order rate law with one factor frozen at a constant looks first-order.

Concept used. If $[B] \gg [A]$ and $[B]$ is nearly unchanged during the reaction, $r = k[A][B] \to k_{\text{obs}}[A]$ with $k_{\text{obs}} = k[B]_0$.

Step 1. Identify the two reactants and which is in excess.

Step 2. Compute the change in the excess reactant over the course of reaction; if $<$ a few percent, treat as constant.

Step 3. Define $k_{\text{obs}} = k\,[B]_{\text{excess}}$ and write $r = k_{\text{obs}}\,[A]$, first-order in A.

Step 4. Apply integrated first-order law: $[A]_t = [A]_0\,e^{-k_{\text{obs}}\,t}$, with half-life $t_{1/2} = 0.693/k_{\text{obs}}$.

Numerical demonstration with inversion of sucrose. $[\text{H}_2\text{O}] \approx 55.5\,\text{M}$; sucrose $[A]_0 = 0.1\,\text{M}$. The true second-order k at 25 °C is $\sim 5 \times 10^{-5}\,\text{L mol}^{-1}\,\text{s}^{-1}$, so $k_{\text{obs}} = 5 \times 10^{-5} \times 55.5 = 2.8 \times 10^{-3}\,\text{s}^{-1}$. Half-life $= 0.693/2.8 \times 10^{-3} = 248\,\text{s} \approx 4\,\text{min}$.

☞ **Alternative approach**

Alternative approach: $[B]$ as constant. Second-order $r = k[A][B]$ becomes first-order $r = k_{\text{obs}}[A]$ if $[B] \gg [A]$ and $[B]$ stays constant. Pseudo-first-order is just this collapsed form.

☞ **Cross-Check**

Numerical cross-check. Ester hydrolysis in water: $k_{\text{true}} = 10^{-5}\,\text{M}^{-1}\,\text{s}^{-1}$, $[\text{H}_2\text{O}] = 55\,\text{M}$; $k_{\text{obs}} = 5.5 \times 10^{-4}\,\text{s}^{-1}$. Half-life $\approx 1260\,\text{s}$.

Final Answer: A pseudo first order reaction looks first order because one reactant is in vast excess; the canonical example is ester hydrolysis in water.

Key Takeaways

- **Rate law and order** come from *experiment*, not from the balanced equation. Order can be 0, integer, or fractional; molecularity is always a positive integer and is meaningful only for elementary steps.
- **Integrated rate laws.** Zero order: $[R] = [R]_0 - kt$, $t_{1/2} = [R]_0/(2k)$, finite "completion" time $[R]_0/k$. First order: $[R] = [R]_0\,e^{-kt}$, $t_{1/2} = 0.693/k$ (constant), infinite "completion" time.
- **Arrhenius equation.** $k = A\,e^{-E_a/RT}$ links temperature, activation energy, and rate. $\ln k$ vs $1/T$ is a straight line with slope $-E_a/R$ and intercept $\ln A$. Two-point form: $\log(k_2/k_1) = (E_a/2.303R)(1/T_1 - 1/T_2)$.
- **Catalyst.** Lowers E_a by providing an alternative pathway; *does not* change $\Delta H, \Delta G, K_{\text{eq}}$. Accelerates both forward and reverse equally.
- **Collision theory.** Rate $\propto P\,Z_{AB}\,e^{-E_a/RT}\,[A]\,[B]$. Effective collisions need enough energy AND correct orientation. The steric factor P can be $\ll 1$ for complex molecules.
- **Maxwell-Boltzmann.** Total area $= 1$ (probability conservation). Higher T shifts peak right (higher E_{mp}), broadens curve, increases area beyond E_a (so more reactive collisions). E_a itself does not change with T.
- **Pseudo first order.** A second-order reaction with one reactant in large excess obeys first-order kinetics with $k_{\text{obs}} = k\,[B]_{\text{excess}}$. Examples: ester hydrolysis, sucrose inversion.
- **Thermo vs kinetics.** $\Delta G < 0$ tells if a reaction can occur; E_a tells how fast. Diamond $\rightarrow$ graphite is feasible but kinetically frozen at room temperature.

End of NCERT Exemplar Problems