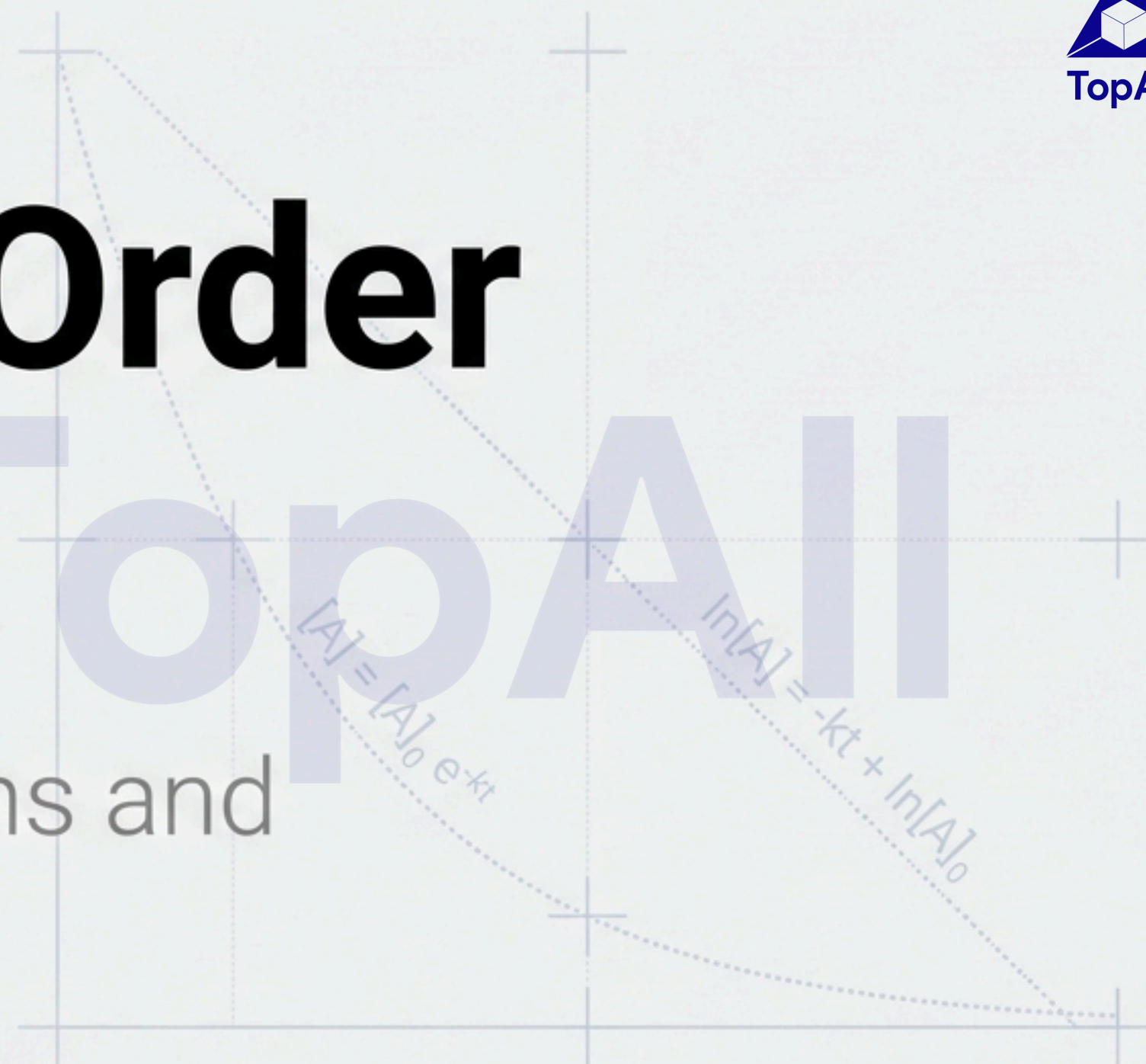


3.3.2 First Order Reactions

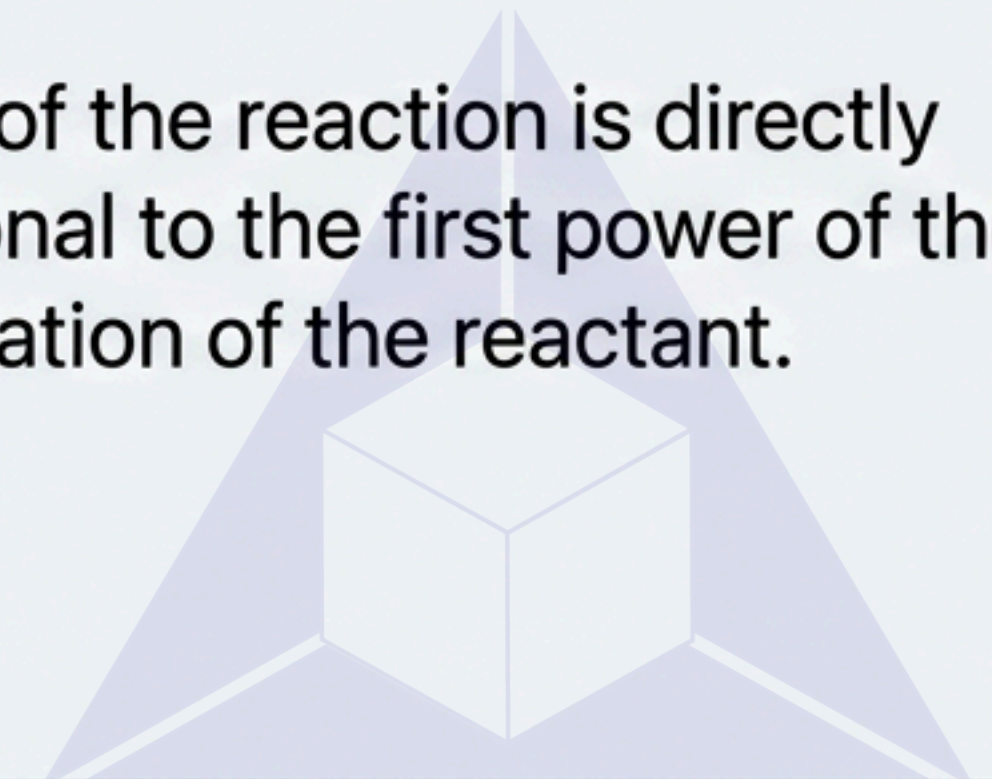
Mathematical derivations and graphical analysis



What First Order Means

The Rule

The rate of the reaction is directly proportional to the first power of the concentration of the reactant.

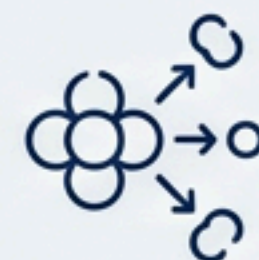

$$\text{Rate} \propto [\text{R}]^1 \longrightarrow \text{Rate} = k[\text{R}]$$

Real-World Examples

Many natural and chemical processes strictly follow first-order kinetics.



- **Radioactive decay:** e.g., ^{226}Ra decaying into ^{222}Rn and He.



- **Decomposition:** e.g., Breakdown of N_2O_5 and N_2O gases.

In a first-order reaction, if you double the reactant concentration, the reaction rate **exactly** doubles.

Differential Form of First Order Reaction

$$-d[R]/dt = k[R]$$

Instantaneous Rate of Disappearance.

(The negative sign is crucial: it accounts for the concentration of reactant R decreasing over time, ensuring the overall rate remains a positive quantity).

First-Order Rate Constant.

For first-order reactions, this value is completely independent of concentration. Units: s^{-1} .

Instantaneous Molar Concentration.

The concentration of the reactant raised to the first power.

Note: This differential form is theoretically perfect but practically difficult to use in the lab because it requires measuring instantaneous slopes at specific moments in time.



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Integrated Form: Connecting Time to Concentration

Integrating $-d[R]/[R] = k dt$ from $t = 0$ to t yields a highly practical formula allowing us to find concentration at any given time.

$$\ln[R] = -kt + \ln[R]_0$$

$$\ln[R] = -kt + \ln[R]_0$$

$$y = mx + c$$

Y-axis: Natural log of concentration at time t

Slope: Negative rate constant

X-axis: Time

Y-intercept: Natural log of initial concentration

Alternative Log Form: The Practical Equation

Why Base 10?

Natural logs (ln) are mathematically elegant, but standard exam log tables and laboratory use Base 10 (log).

To convert $\ln(x)$ to $\log(x)$, we must multiply by **2.303**.

Rearranging the integrated form and isolating k gives us the most common calculation formula:

$$k = \frac{2.303}{t} \log\left(\frac{[R]_0}{[R]}\right)$$

k = Rate constant

t = Elapsed time

$[R]$ = Initial concentration (at t)

$[R]_0$ = Initial concentration (at $t=0$)

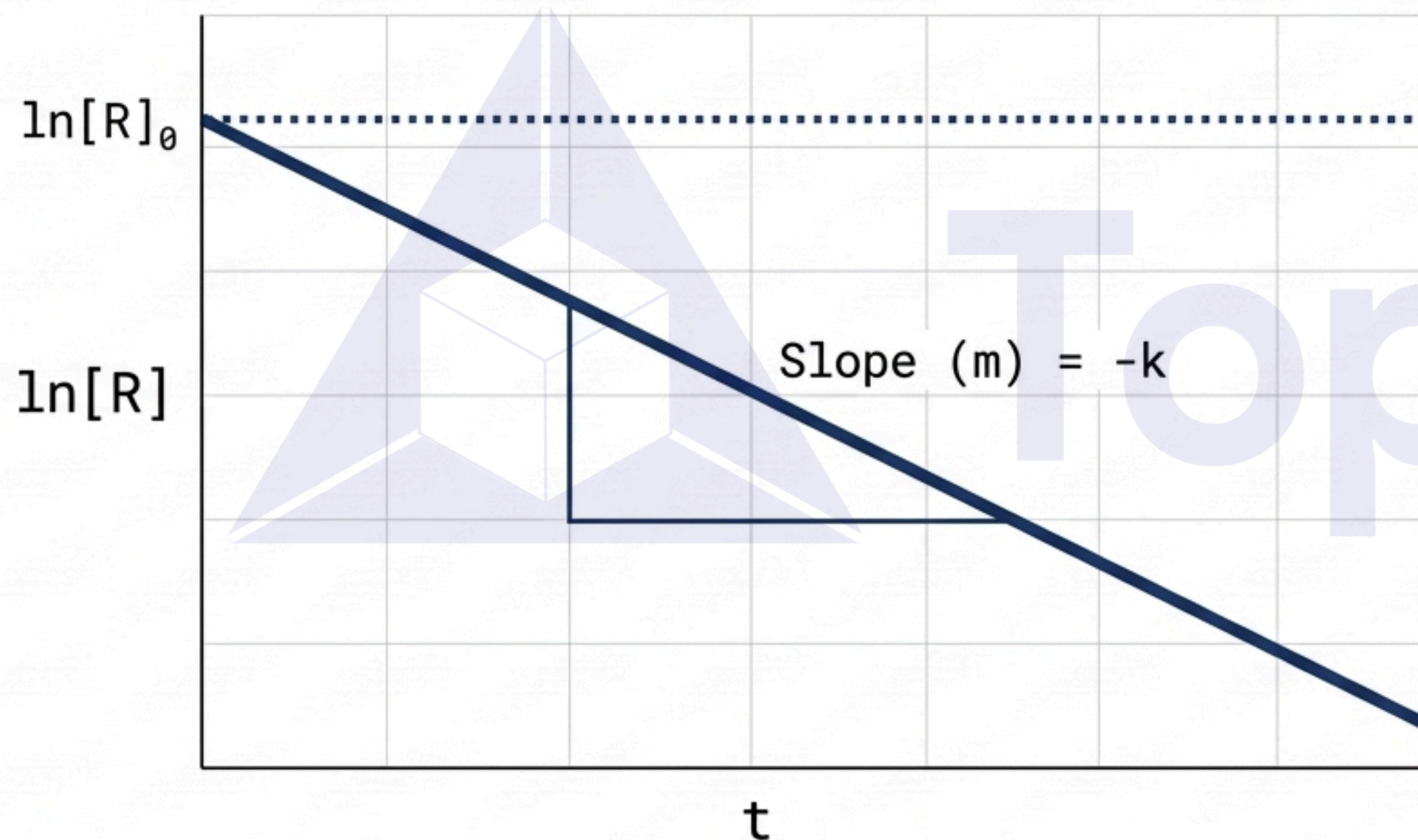
$[R]$ = Final concentration (at time t)



Pro-Tip: This specific form is perfect for calculating the rate constant when given initial and final concentrations over a set period.

Straight Line Plot of $\ln[R]$ vs t

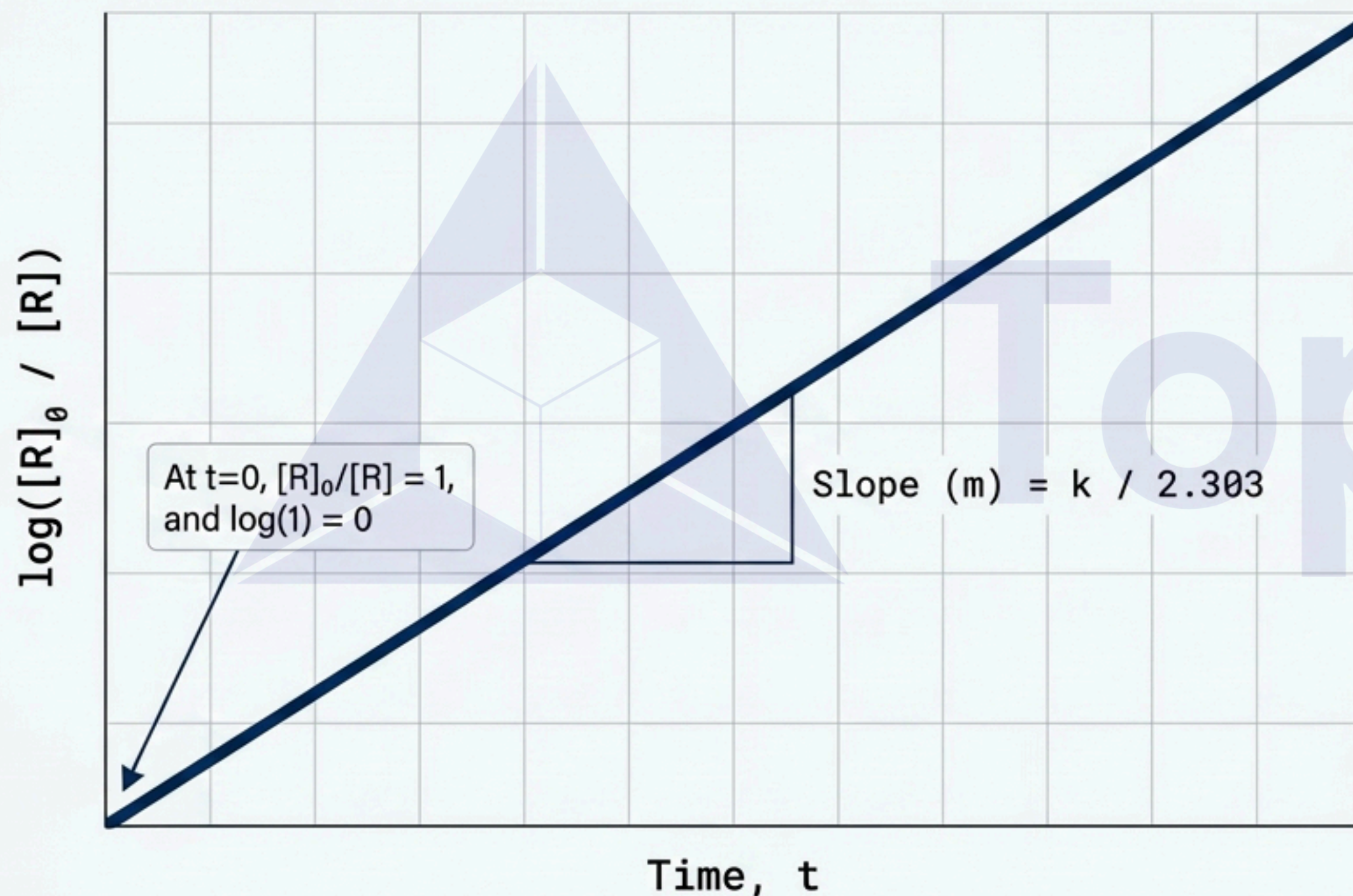
Graph Card



Key-Takeaway Box

- Plotting the natural log of concentration against time yields a perfect straight line for first-order reactions.
- The steepness of the line instantly reveals the rate constant: $k = -\text{Slope}$.

Straight Line Plot of $\log([R]_0/[R])$ vs t

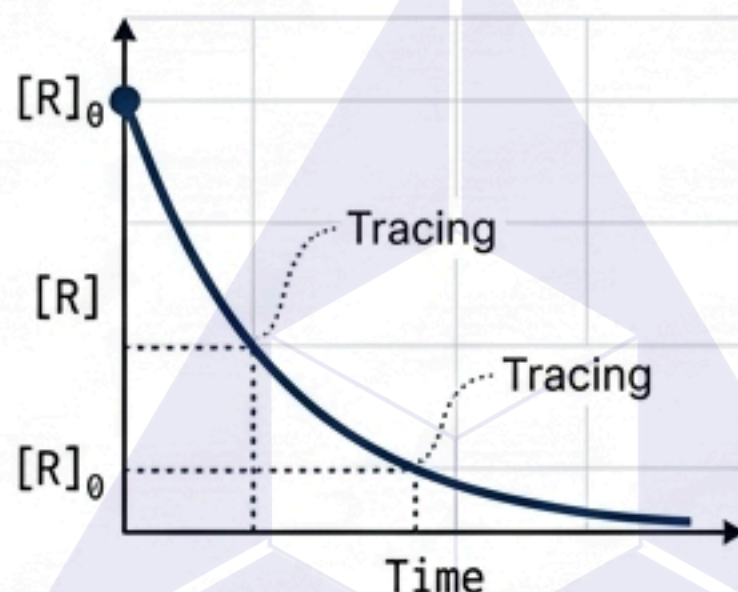


- Because we are plotting a ratio of initial vs. current concentration, the value grows over time.
- Calculating the slope of this specific plot provides the rate constant using the formula:
 $k = \text{Slope} \times 2.303$.

Final Recap: Reality vs. Analysis

The Reality (Exponential Decay)

How nature behaves.

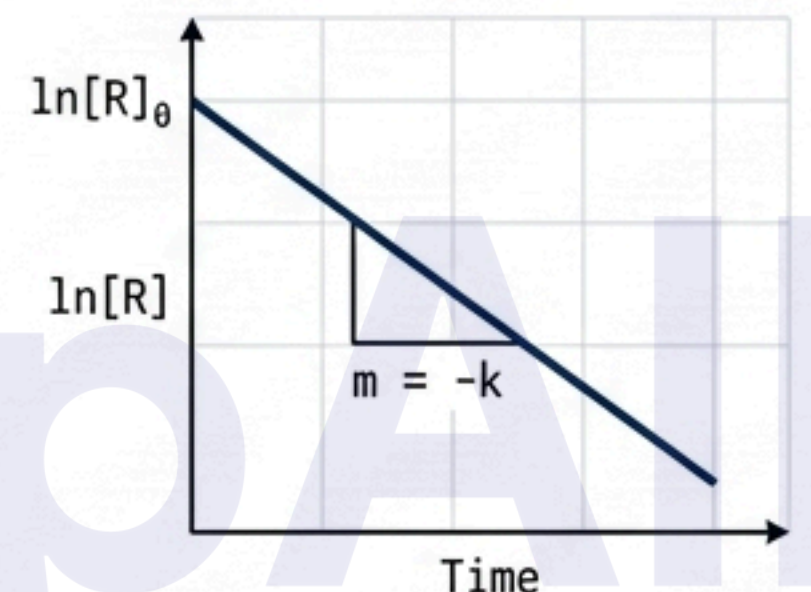


$$\text{Antilog Equation: } [R] = [R]_0 e^{-kt}$$

Concentration drops infinitely but theoretically never reaches absolute zero.

The Analysis (Log-Linear)

How chemists measure it.



$$\text{Linear Equation: } \ln[R] = -kt + \ln[R]_0$$

Transforming the data with logarithms allows us to easily calculate constants using simple linear regression.

The Half-Life Rule

For all first-order reactions, the half-life ($t_{1/2} = 0.693 / k$) is strictly constant and completely independent of the initial concentration.



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