

must integrate $-\frac{d[A]}{dt} = k_0$

$$d[A] = -k_0 dt$$
$$\int_{[A]_0}^{[A]} d[A] = -k_0 \int_0^t dt$$

$$[A] - [A]_0 = -k_0 t$$

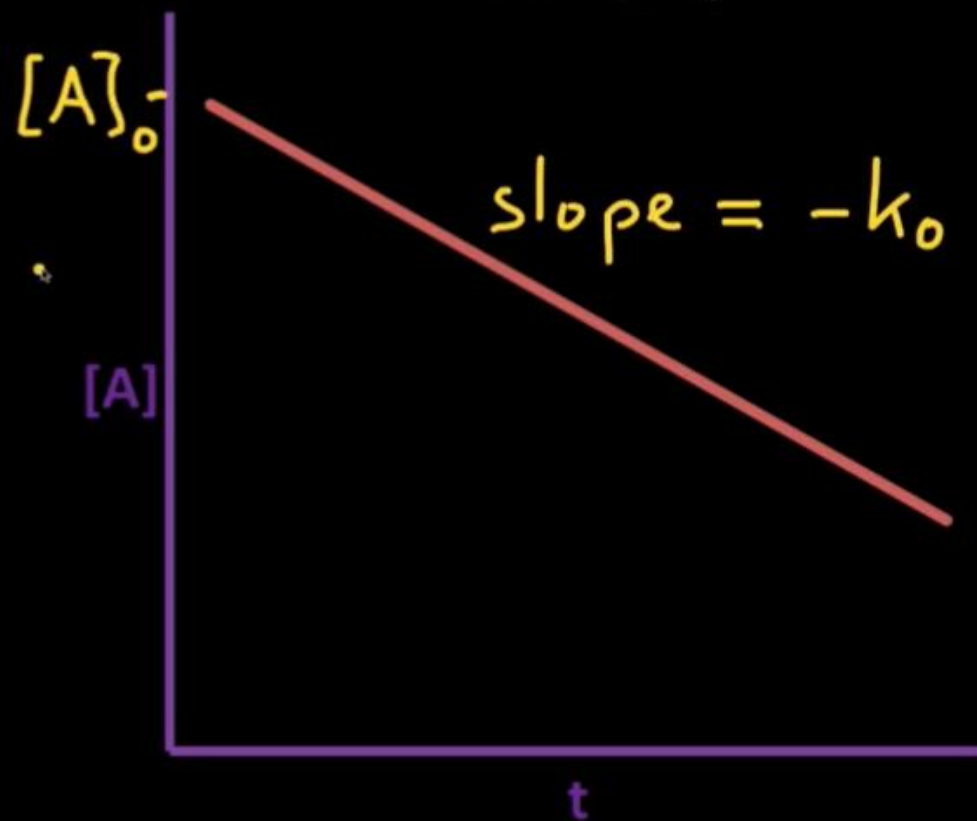
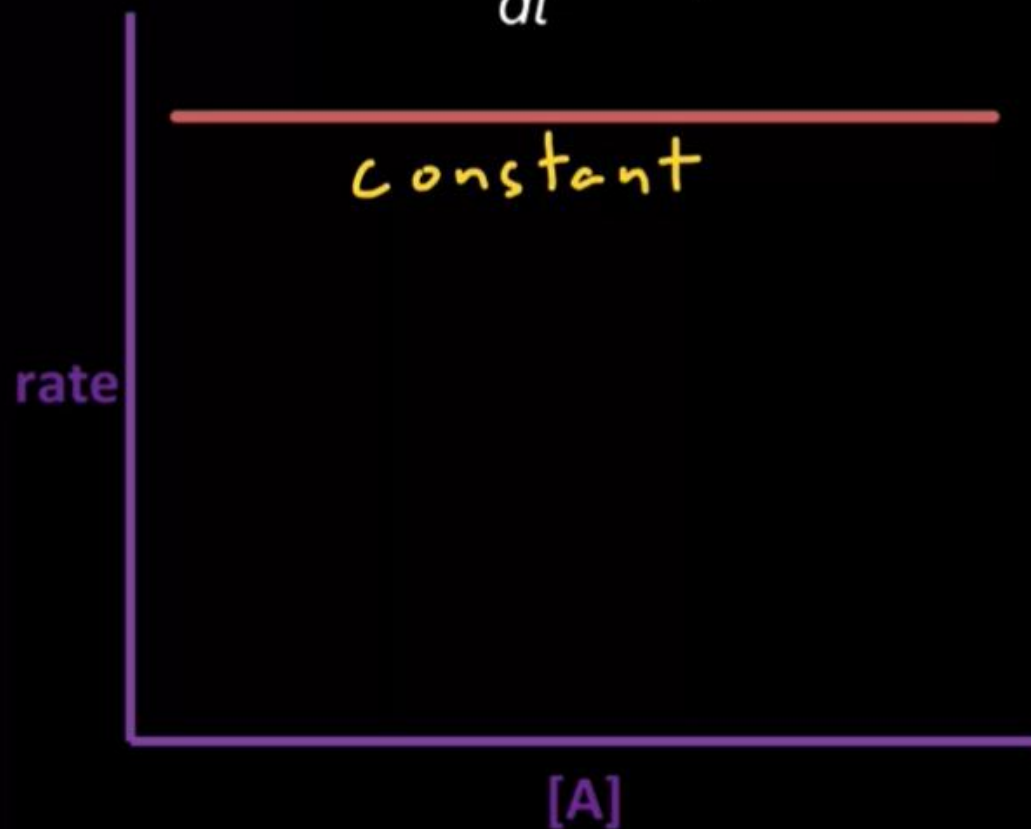
or $[A] = [A]_0 - k_0 t$

Zero order integrated rate expression

Zero order

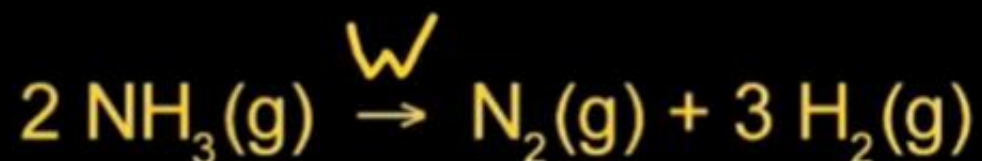
$$-\frac{d[A]}{dt} = k_o$$

$$[A] = [A]_o - k_o t$$

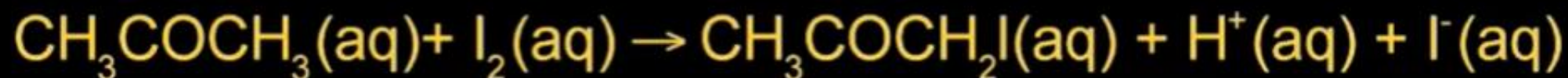


Zero order reactions are not common

i) gases on metals



ii) some solution reactions



iii) enzyme reactions

integrate $\frac{d[A]}{dt} = -k_1[A]$

rearrange

$$\frac{d[A]}{[A]} = -k_1 dt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k_1 \int_0^t dt$$

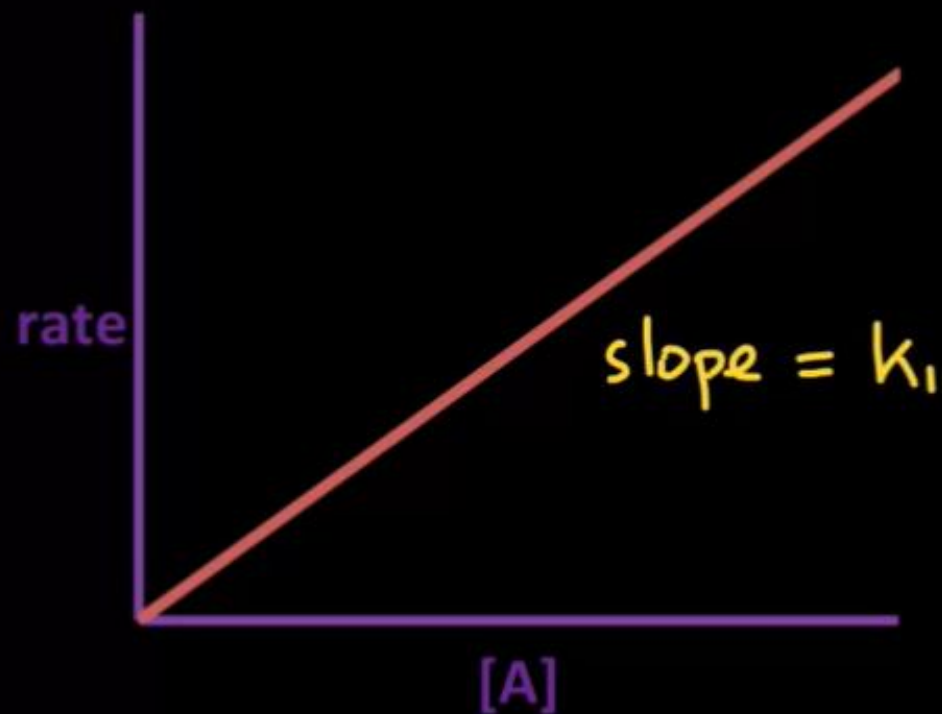
$$\ln [A] - \ln [A]_0 = -k_1 t$$

or $\ln \frac{[A]}{[A]_0} = -k_1 t$ $[A] = [A]_0 e^{-k_1 t}$

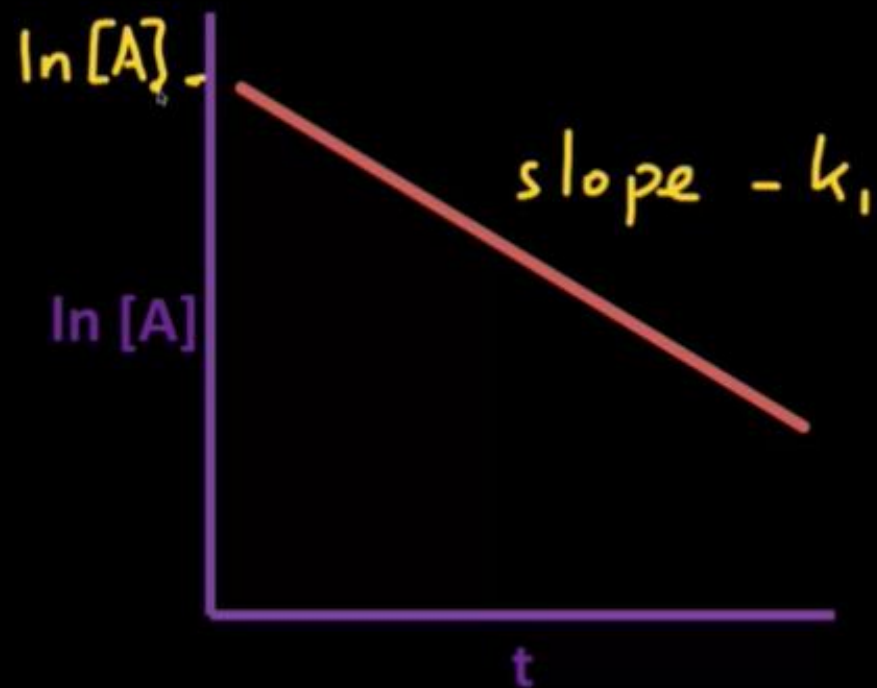
First order integrated rate expression

First order

$$\text{rate} = -\frac{d[A]}{dt} = k_1[A]$$



$$\ln[A] = \ln[A_0] - k_1 t$$



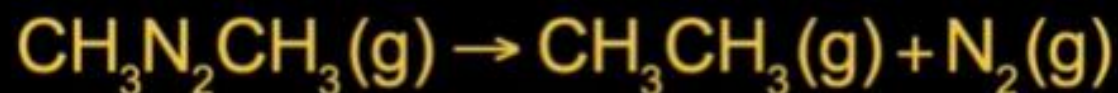
Examples of first order reactions

i) Radioactive decay

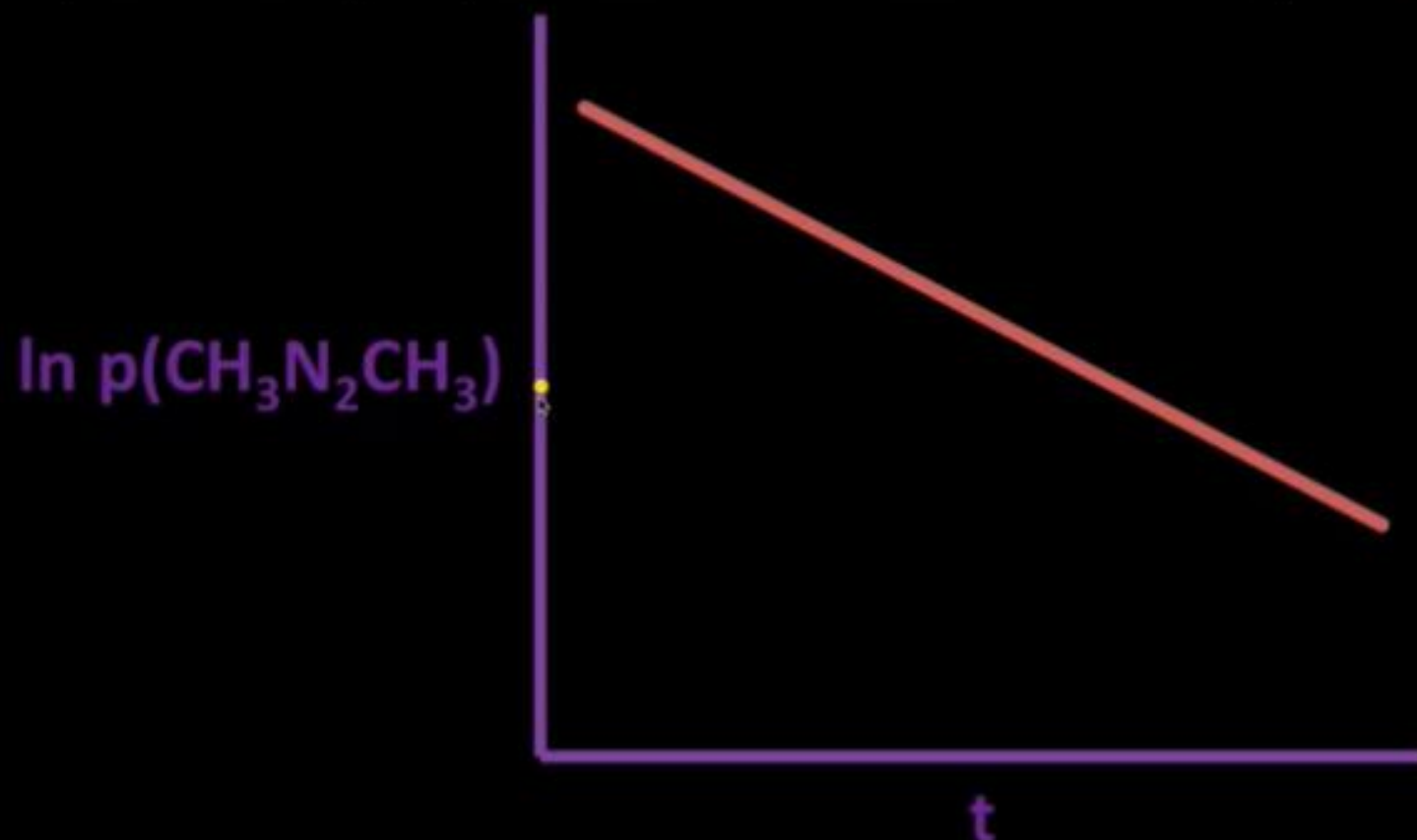


$$\frac{d {}_{88}^{226}\text{Ra}}{dt} = -k[{}_{88}^{226}\text{Ra}]$$

ii) Gas phase reactions



As pressure proportional to concentration plot $\ln p$ versus t



Half-life

Half-life is time $\tau_{1/2}$ for concentration of [A] to drop from $[A]_0$ to $[A]_0/2$

Using integrated rate expression $\ln \frac{[A]}{[A]_0} = -k_1 t$

$$\ln \frac{1}{2} = -k_1 \tau_{1/2}$$

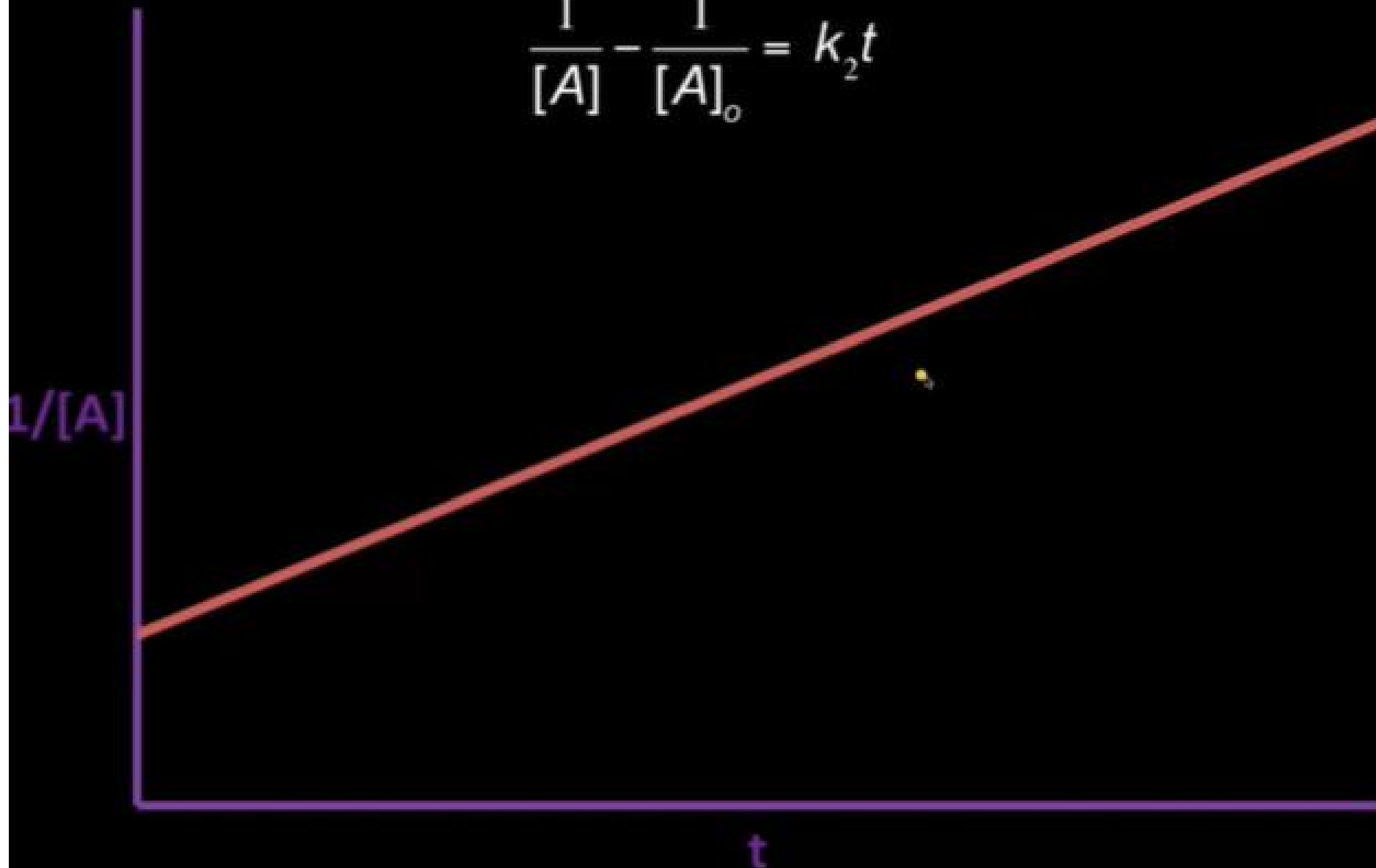
$$\tau_{1/2} = \frac{\ln 2}{k_1}$$

$$\ln \frac{(a-x_1)}{(a-x_2)} = k_1 (t_2 - t_1)$$

Interval formula

Second Order Reactions

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_2 t$$



Half-life for second order reactions

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_2 t$$

when $t = \tau_{1/2}$

$$[A] = \frac{[A]_0}{2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = k_2 \tau_{1/2}$$

$$\tau_{1/2} = \frac{1}{k_2 [A]_0}$$

2nd order reactions are the most common requiring two species to interact

Determination of Reaction Order

1) INTEGRATION METHOD

Determine the concentration of reactants at a series of times t

This can either be the amount x or the amount remaining $[A] = [A]_0 - x$

Then make a series of plots of the relevant functions

eg.	$[A]$ vs t	<u>order</u>
	$\ln [A]$ vs t	0
	$1/[A]$ vs t	1
		2

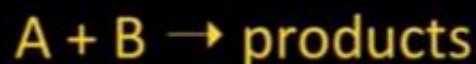
The best straight line will give you the order of reaction

Determination of Reaction Order

2) ISOLATION METHOD

Useful when reaction contains **more than one** reactant

e.g.



suppose

$$\text{rate} = -\frac{d[A]}{dt} = k_2[A][B]$$

have a large excess of B

$$[B]_0 \gg [A]_0$$

then concentration of B will hardly vary during the reaction

$$\therefore [B] \approx [B]_0 \quad \text{at all time}$$

Determination of Reaction Order

$$-\frac{d[A]}{dt} = k_2[A][B]$$

$$[B] \approx [B]_0$$

Then

$$-\frac{d[A]}{dt} = k_2 [B]_0 [A]$$

↖ constant

$$= k_1' [A]$$

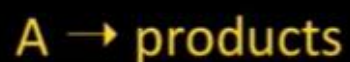
k_1' is a pseudo 1st order rate constant

Then determine reaction order by integration

Determination of Reaction Order

3) HALF-LIFE METHOD

For reaction of type



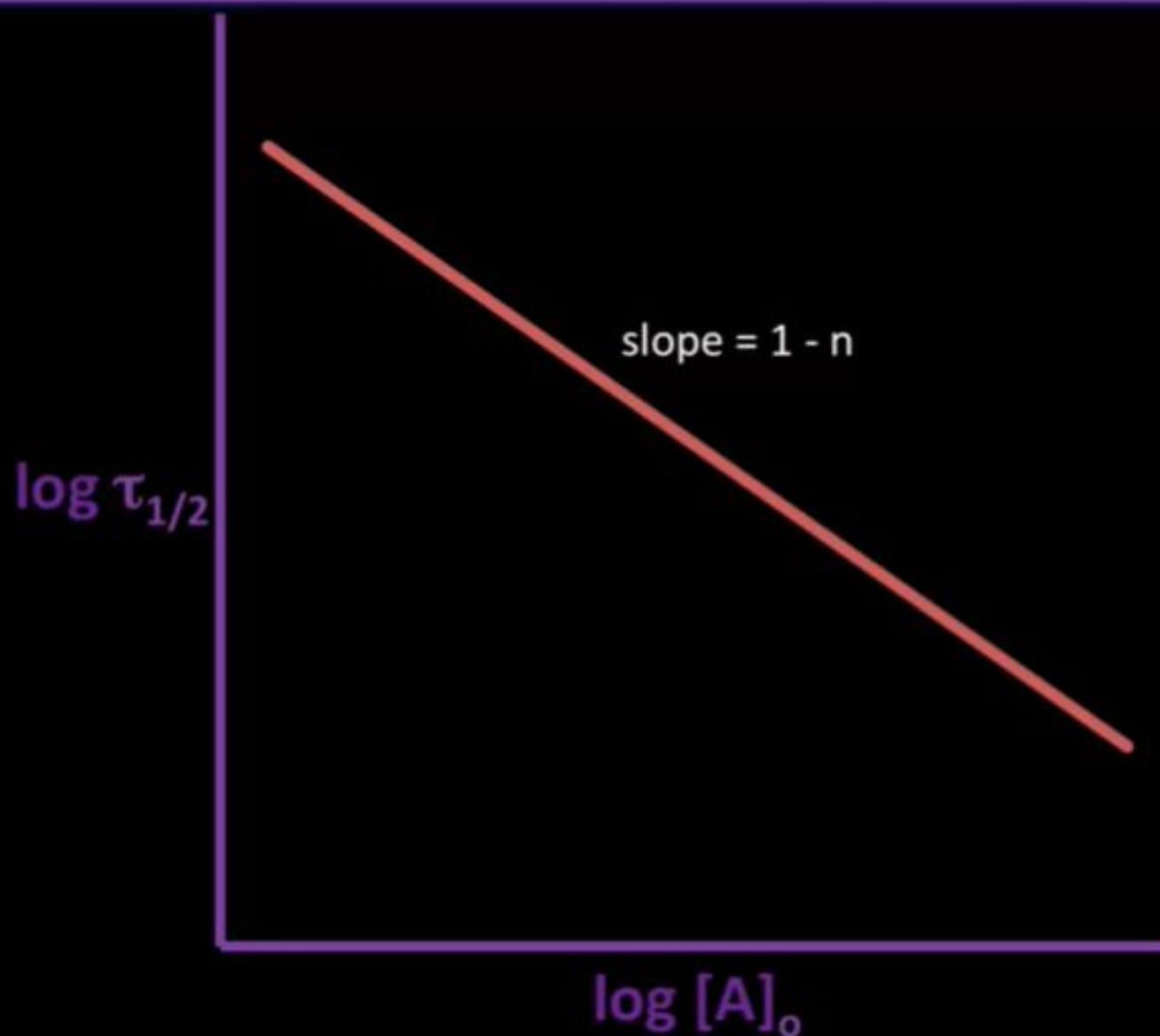
$$\tau_{1/2} \propto [A]_0^{1-n}$$
$$= C [A]_0^{1-n}$$

n - order of reaction

take logs

$$\log \tau_{1/2} = \log C + (1-n) \log [A]_0$$

Determination of Reaction Order

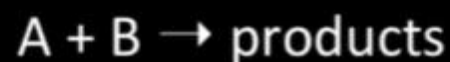


vary initial concentration $[A]_0$ and measure time for half-reaction

Determination of Reaction Order

4) INITIAL RATE (DIFFERENTIAL METHOD)

Consider



$$\text{rate} = k_2 [A]^a [B]^b$$

at $t = 0$

$$(\text{rate})_{\text{initial}} = k_2 [A]_0^a [B]_0^b$$

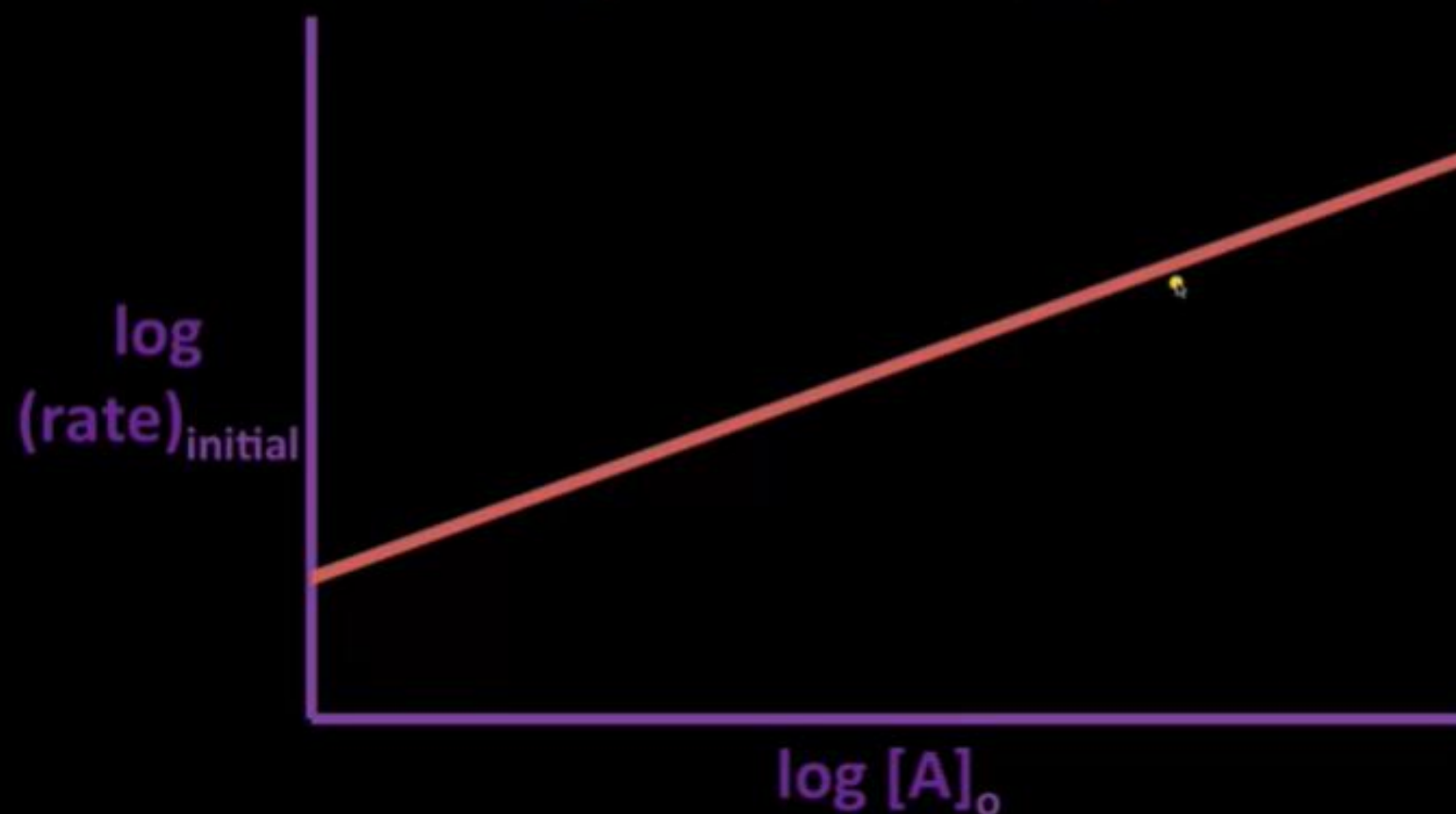
take logs

$$\log(\text{rate})_{\text{initial}} = \log k_2 + a \log [A]_0 + b \log [B]_0$$

Determination of Reaction Order

$$\log(\text{rate})_{\text{initial}} = \log k_2 + a \log [A]_0 + b \log [B]_0$$

keep $[B]_0$ constant, vary $[A]_0$



Repeat for b keeping $[A]_0$ constant

Experimental Determination of Rates

1) CHEMICAL DETERMINATION OF CONCENTRATIONS

e.g. titration. Useful when reactants or products contain a functional group (especially acids and bases)

2) PRESSURE CHANGES

Useful only when there is a pressure change



pressure increases upon reaction

Experimental Determination of Rates

3) SPECTROSCOPY

If NO pressure change BUT one component varies
its spectral characteristics



$\text{Br}_2(\text{g})$ absorbs visible light

4) POLARIMETRY

Measure optical rotation

e.g. hydrolysis of sucrose

Experimental Determination of Rates

5) ELECTROCHEMICAL METHODS

Useful when number or nature of ions in solution changes



measure conductance of solution

6) DILATOMETRY

Measure small volume changes in a solution

