

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

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

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

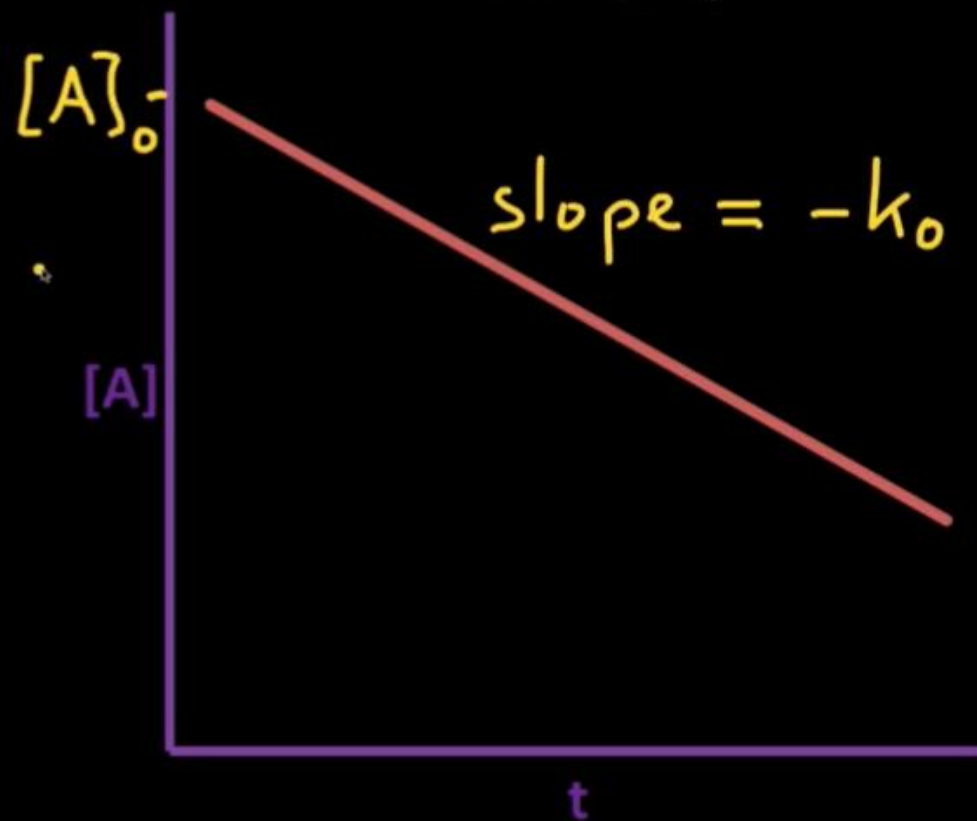
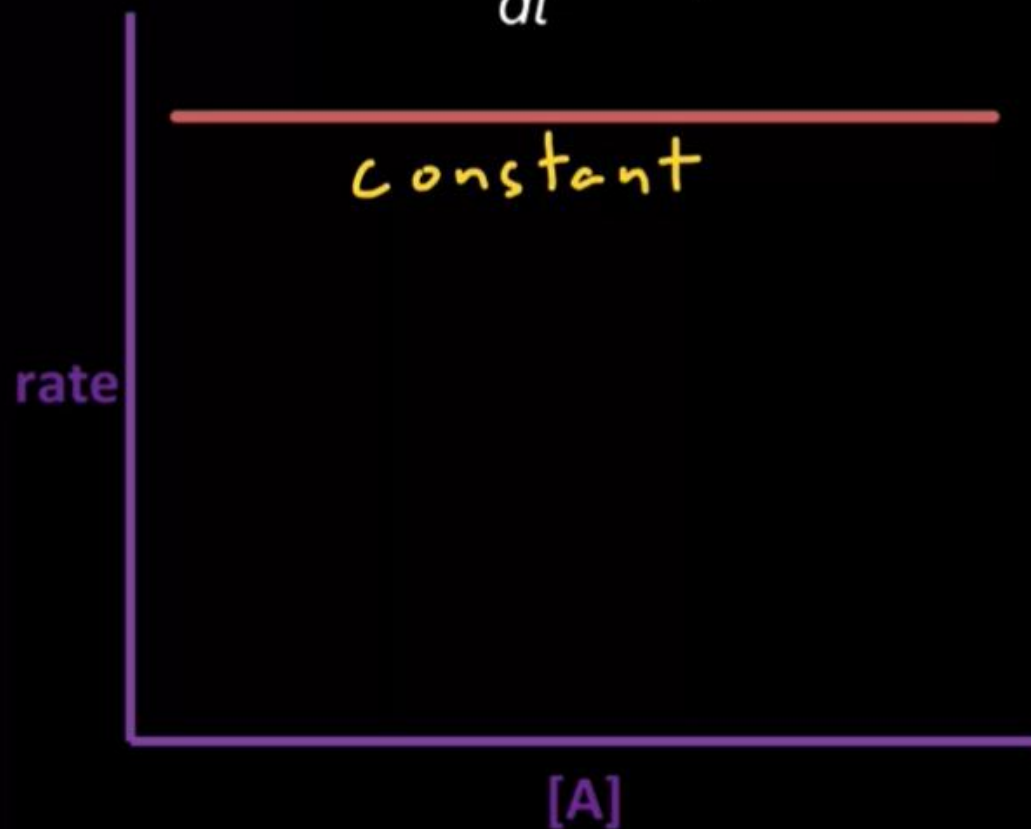
or $[A] = [A]_0 - k_0 t$

Zero order integrated rate expression

Zero order

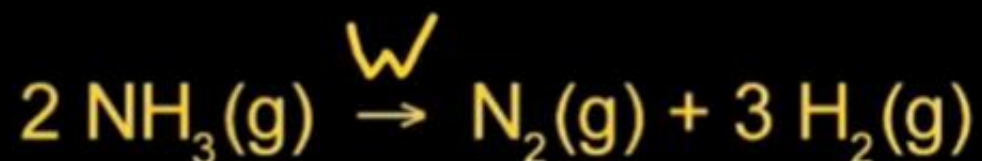
$$-\frac{d[A]}{dt} = k_o$$

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

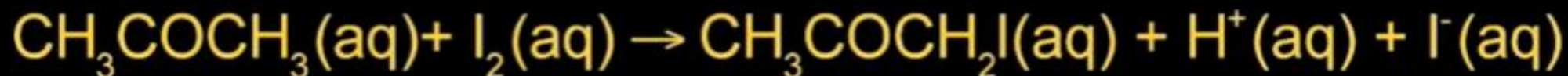


Zero order reactions are not common

i) gases on metals



ii) some solution reactions



iii) enzyme reactions

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

rearrange

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

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

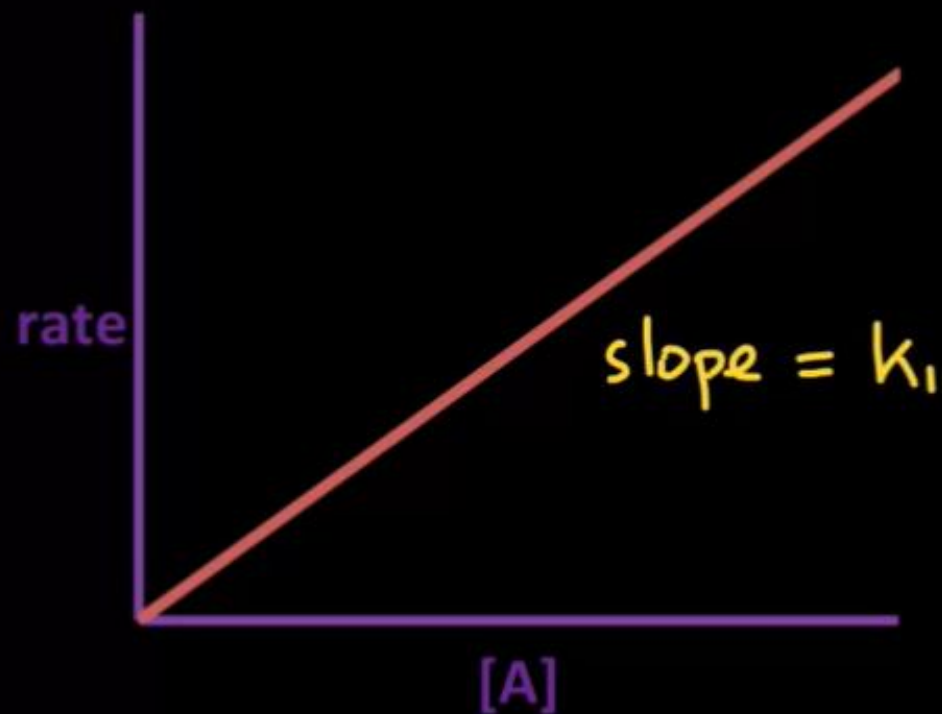
$$\ln [A] - \ln [A]_0 = -k_1 t$$

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

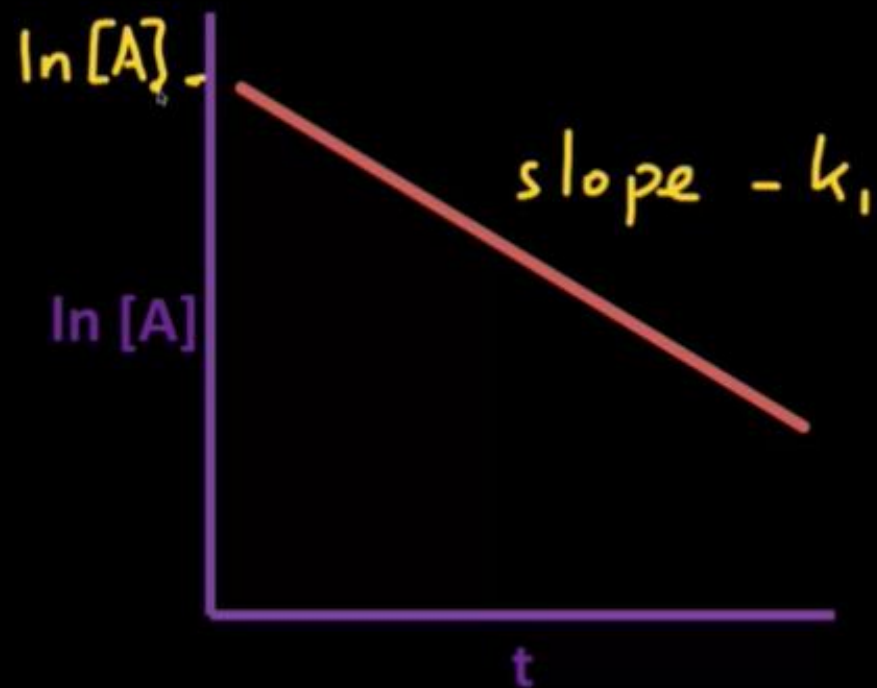
First order integrated rate expression

First order

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



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



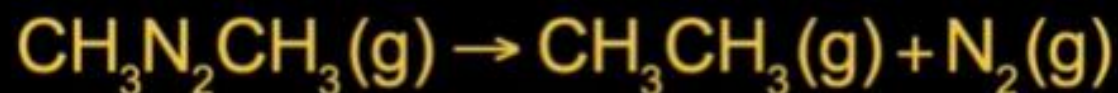
Examples of first order reactions

i) Radioactive decay

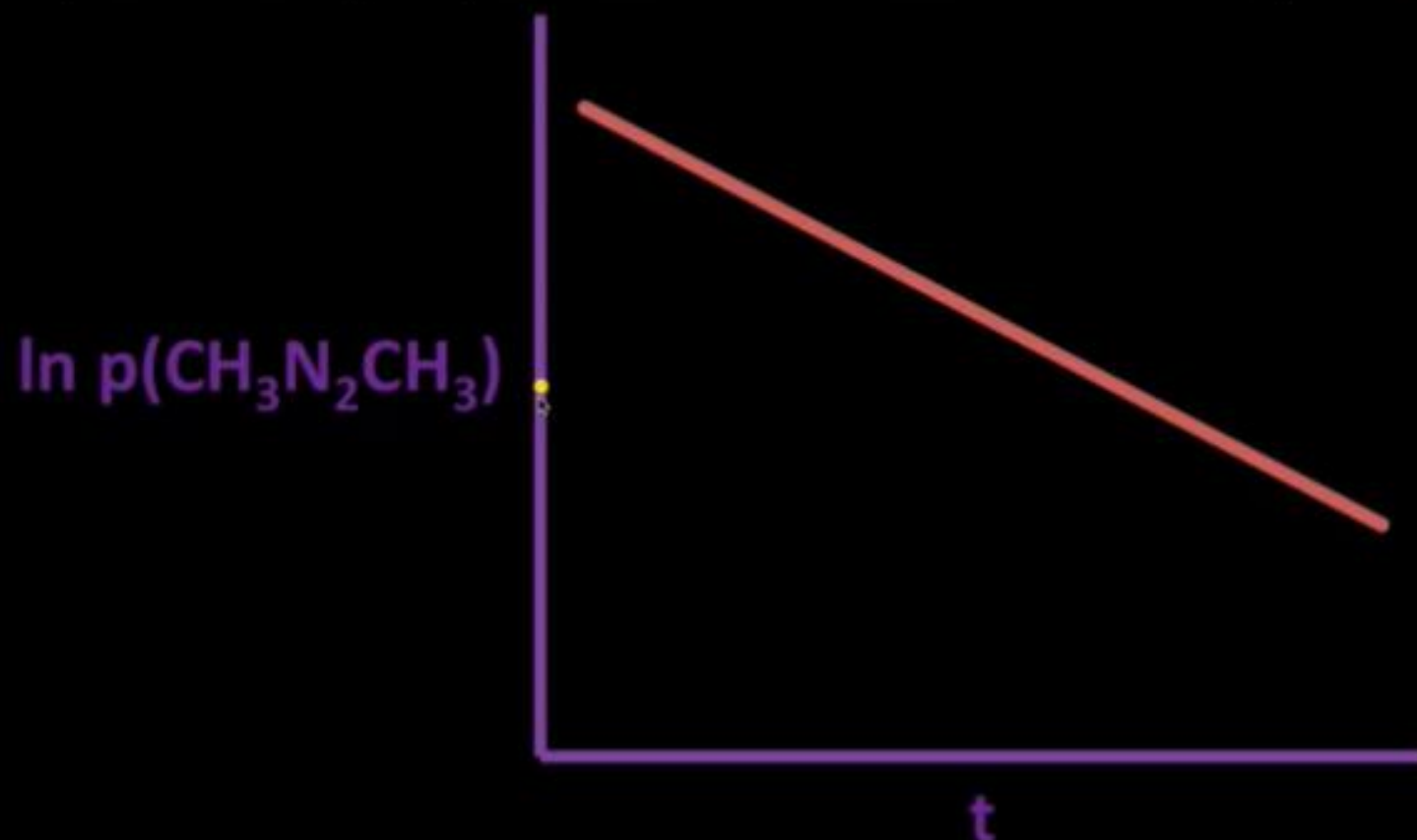


$$\frac{d {}_{88}^{226}\text{Ra}}{dt} = -k[{}_{88}^{226}\text{Ra}]$$

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

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

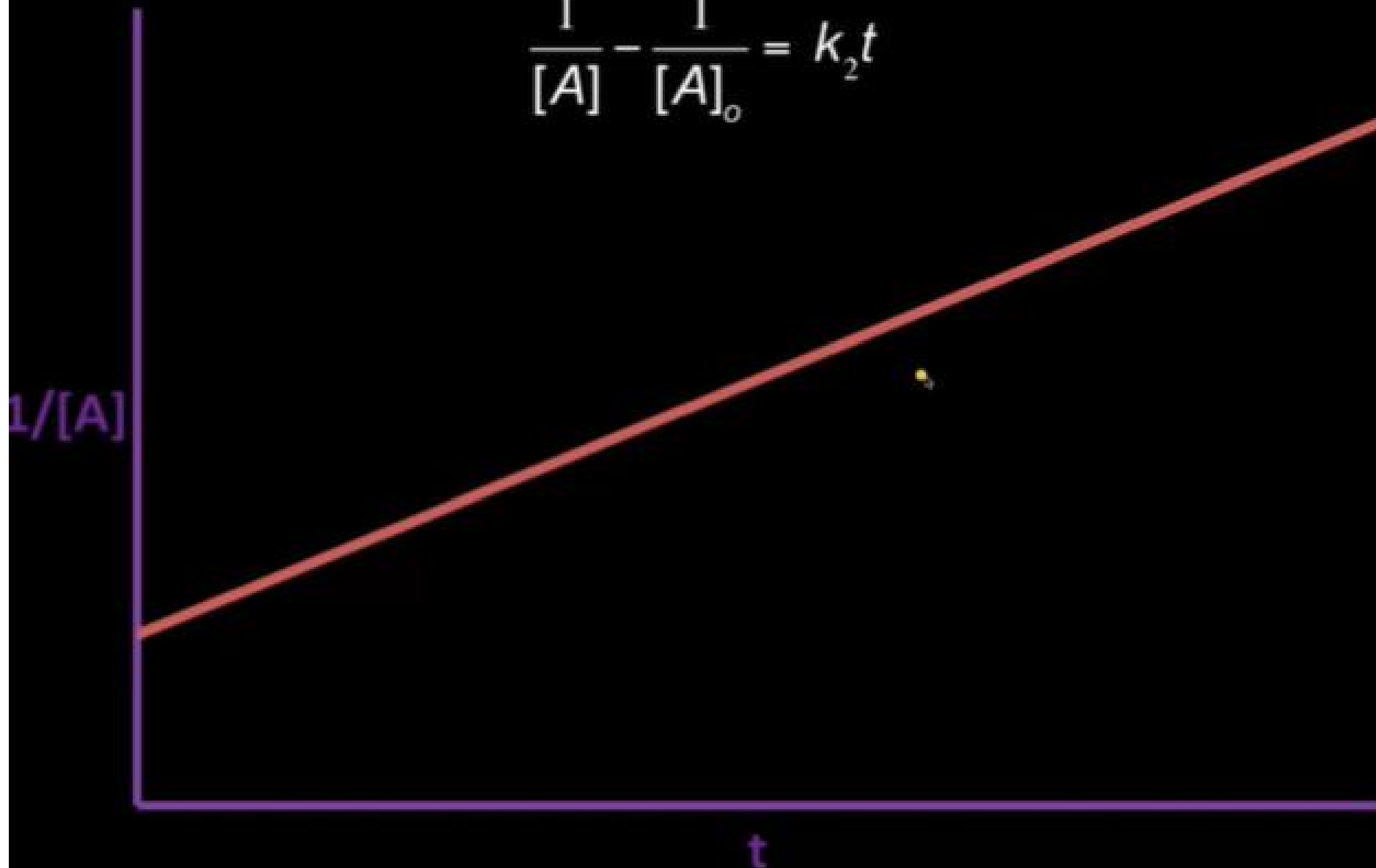
$$\tau_{1/2} = \frac{\ln 2}{k_1}$$

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

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

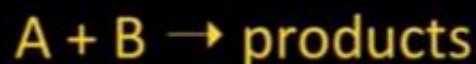
The best straight line will give you the order of reaction

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

$$= k_1' [A]$$

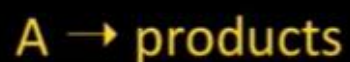
k_1' is a pseudo 1st order rate constant

Then determine reaction order by integration

Determination of Reaction Order

3) HALF-LIFE METHOD

For reaction of type



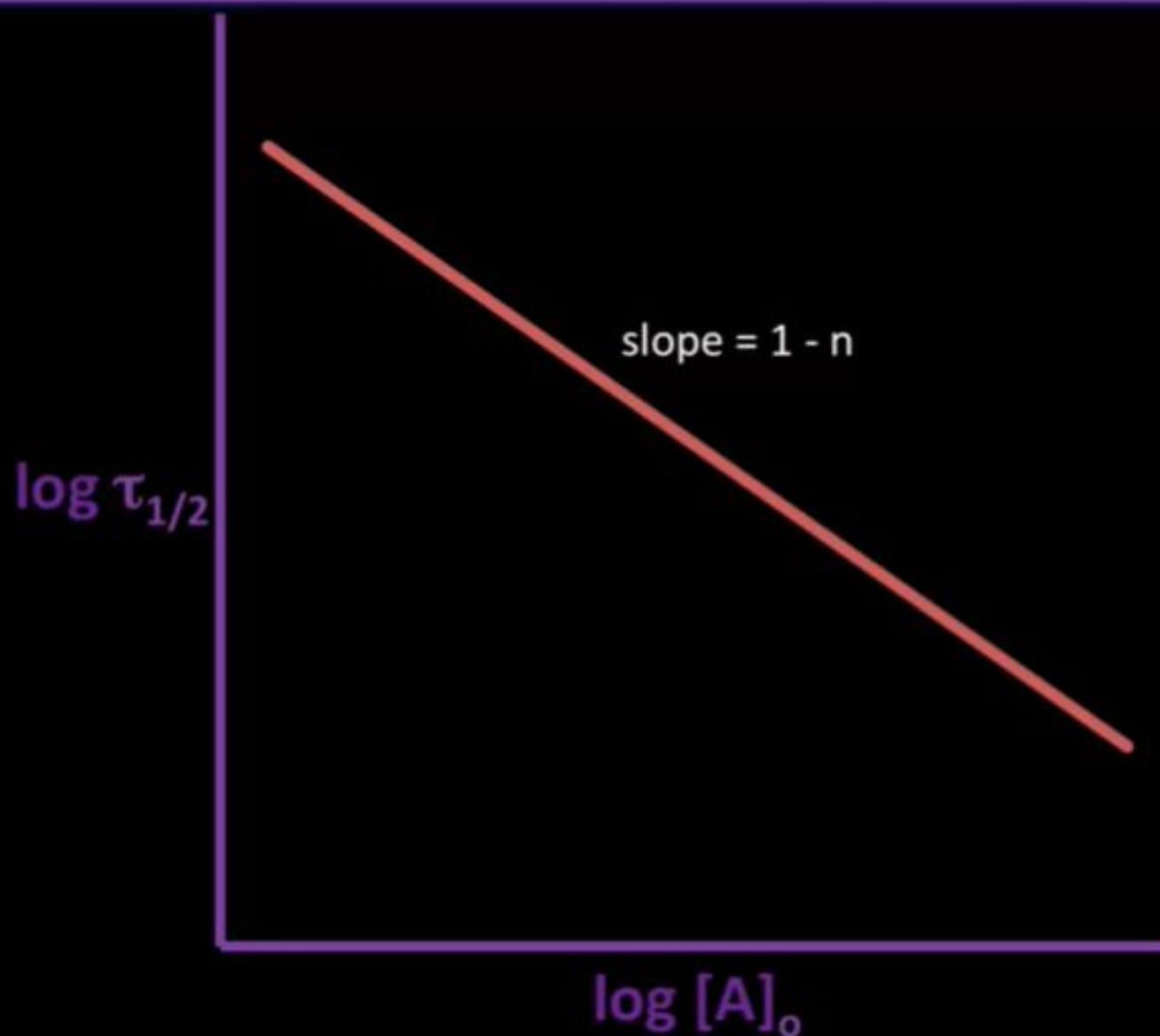
$$\tau_{1/2} \propto [A]_0^{1-n}$$
$$= C [A]_0^{1-n}$$

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 $t = 0$

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

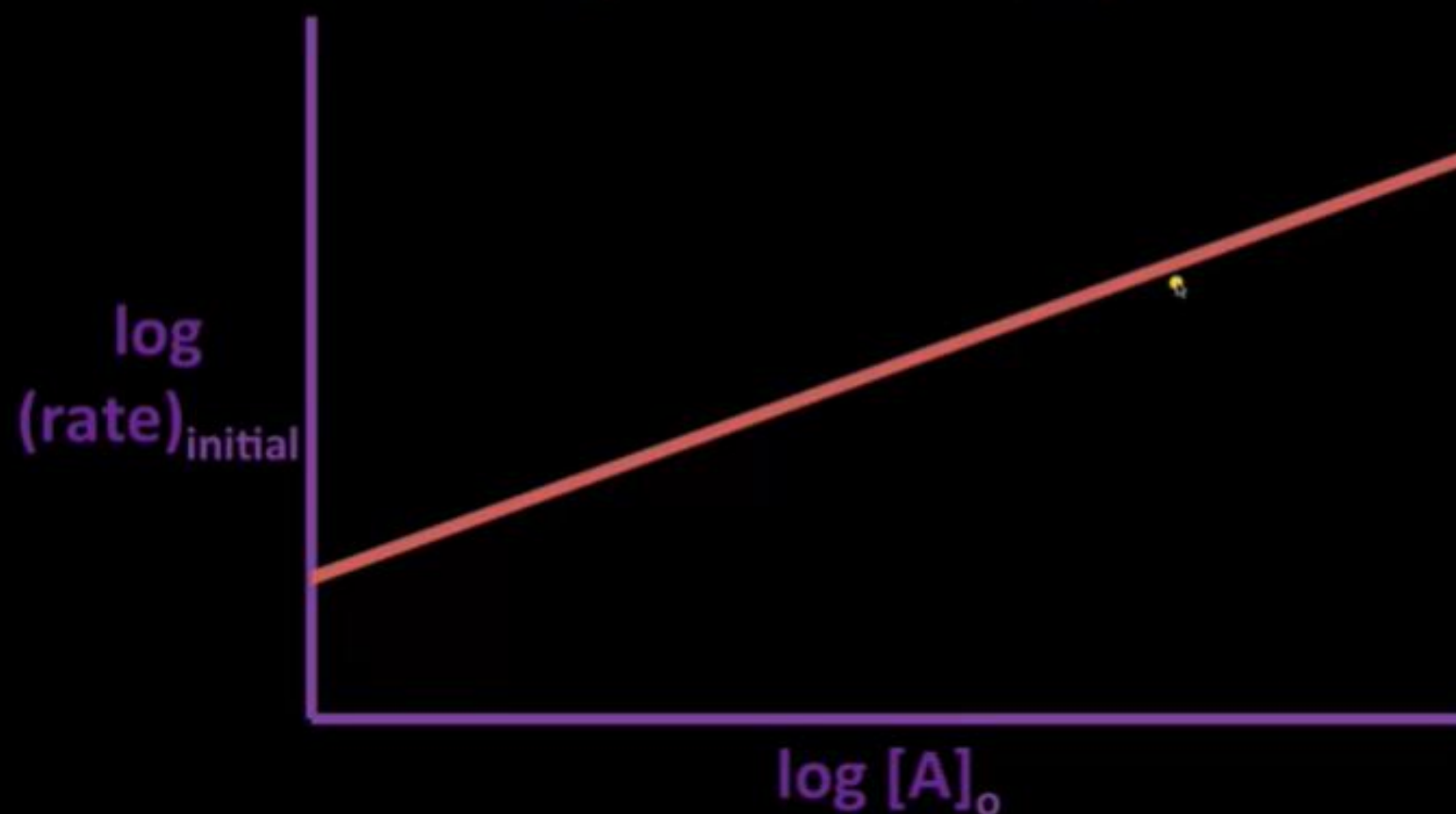
take logs

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

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

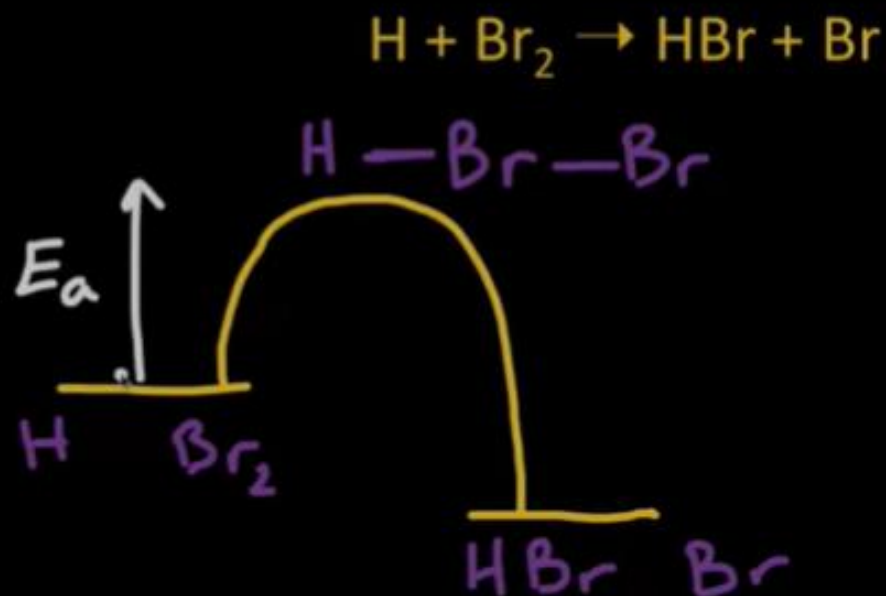
Measure small volume changes in a solution



Effect of temperature on reaction rate

Reaction cannot proceed directly to products
but **MUST** pass through some **transition state**

This transition state might involve the **lengthening** of a bond or
change in **bond angles** which **requires energy**



$$G = \frac{[A]}{[A] + [B]} G_0 + \frac{[B]}{[A] + [B]} G_\infty$$

$$([A] + [B]) G = [A] G_0 + [B] G_\infty$$

but $[A] + [B] = [A]_0$

+ $[B] = [A]_0 - [A]$

$$[A]_0 G = [A] G_0 + ([A]_0 - [A]) G_\infty$$

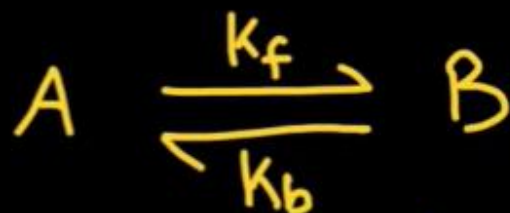
$$[A] = \left(\frac{G - G_\infty}{G_0 - G_\infty} \right) [A]_0$$

Effect of temperature on reaction rate

Reaction rates generally increase with temperature

Arrhenius Equation

consider



equilibrium constant

$$K = \frac{k_f}{k_b}$$

van't Hoff isochore relates K to T

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

$$\frac{d \ln k_f/k_b}{dT} = \frac{\Delta H}{RT^2}$$

More complex reactions

Reactions moving towards equilibrium

Consider



Assume all reactions are 1st order

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

Forward reaction: $\text{rate} = k_1[A]$

Back reaction: $\text{rate} = -k_{-1}[B]$

More complex reactions

$$\text{rate} = -\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

$$[B] = [A]_0 - [A]$$

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}([A]_0 - [A])$$

$$\frac{d[A]}{dt} = -(k_1 + k_{-1})[A] + k_{-1}[A]_0$$

This can be integrated to give:

$$[A] = [A]_0 \left\{ \frac{k_{-1} + k_1 \exp[-(k_1 + k_{-1})t]}{(k_1 + k_{-1})} \right\}$$

If there is no back reaction $k_{-1} = 0$

$$[A] = [A]_0 e^{-k_1 t}$$

simple 1st order reaction that goes to completion

More complex reactions

$$[A] = [A]_0 \left\{ \frac{k_{-1} + k_1 \exp\left[-(k_1 + k_{-1})t\right]}{(k_1 + k_{-1})} \right\}$$

At $t = \infty$ system reaches equilibrium

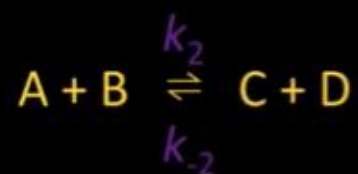
More complex reactions

$$[A]_{\infty} = \frac{k_{-1}}{k_1 + k_{-1}} [A]_0 \quad [B]_{\infty} = \frac{k_1}{k_1 + k_{-1}} [A]_0$$

$$K = \frac{[B]_e}{[A]_e} = \frac{[B]_{\infty}}{[A]_{\infty}} = \frac{k_1}{k_{-1}}$$

A simple relationship between rate constants and equilibrium constant

Also holds for simple bimolecular reactions

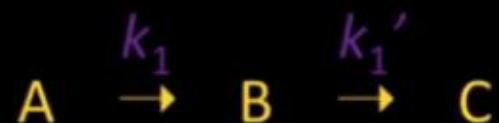


$$K = \frac{[C]_e [D]_e}{[A]_e [B]_e} = \frac{[C]_{\infty} [D]_{\infty}}{[A]_{\infty} [B]_{\infty}} = \frac{k_2}{k_{-2}}$$

Consecutive reactions

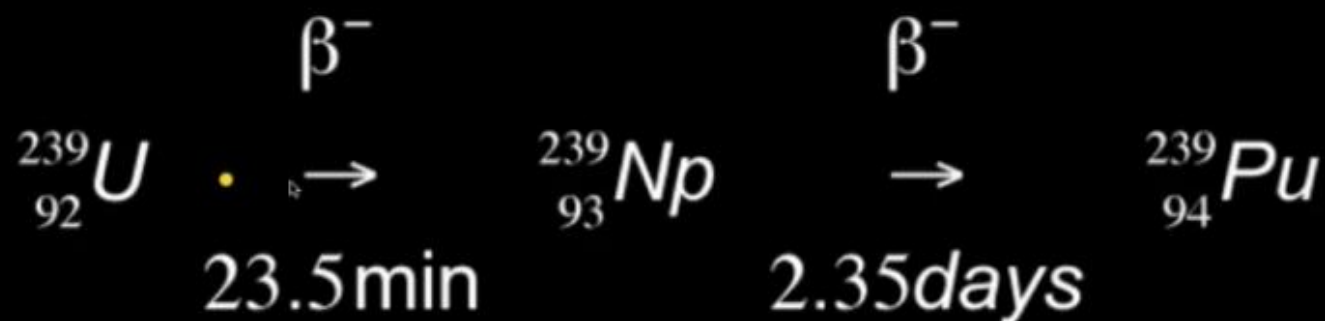
Many reactions proceed through several **consecutive** steps

e.g.



B is a **reaction intermediate**

e.g.



Consecutive reactions

e.g.



$$[A] = [A]_0 e^{-k_1 t}$$

[B] and [C] much more difficult to solve

$$[B] = [A]_0 \left\{ \frac{k_1}{k_1' - k_1} \right\} \left(e^{-k_1 t} - e^{-k_1' t} \right)$$

$$[C] = [A]_0 \left\{ 1 + \left(\frac{1}{k_1 - k_1'} \right) \left(k_1' e^{-k_1 t} - k_1 e^{-k_1' t} \right) \right\}$$

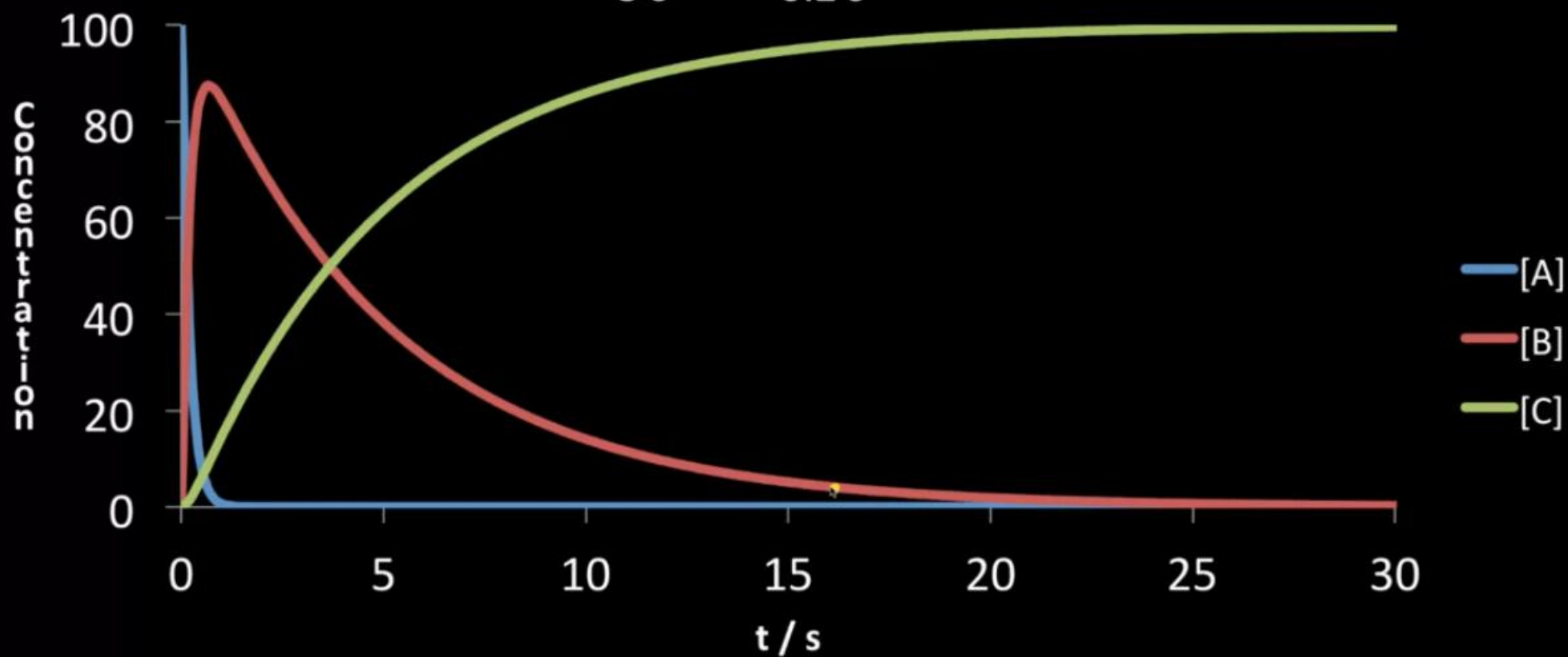
$$\frac{d[A]}{dt} = -k_1[A]$$

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

$$\frac{d[C]}{dt} = k_1'[B]$$

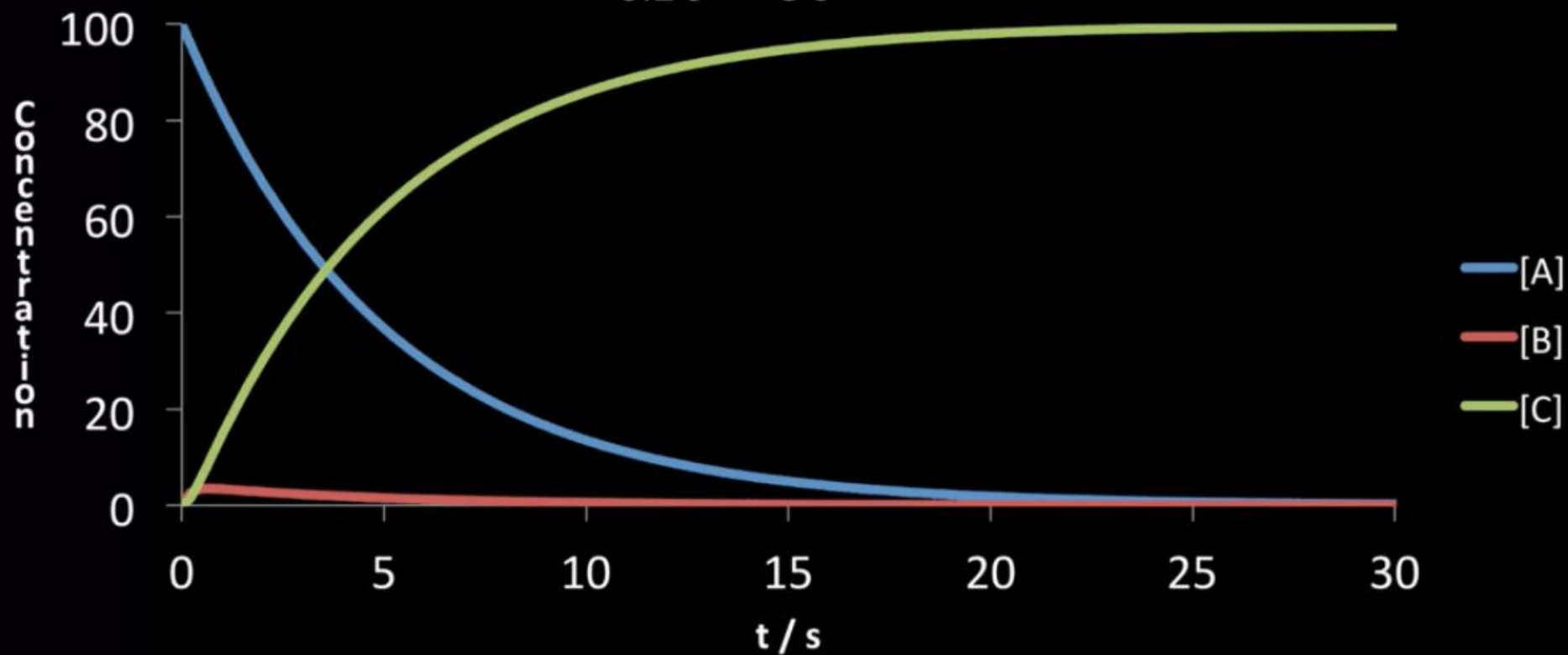
Consecutive reactions

$[A]_0 = 100$

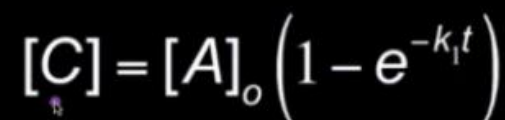
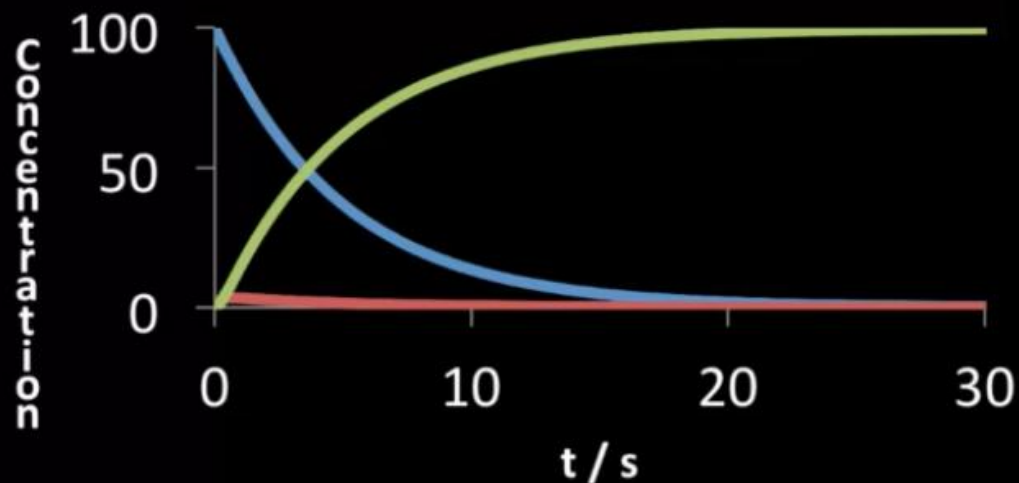
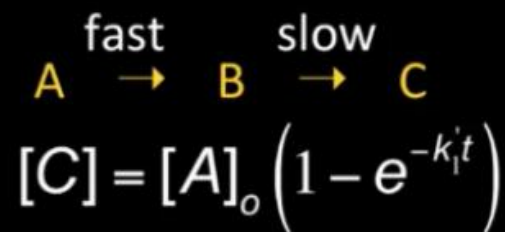
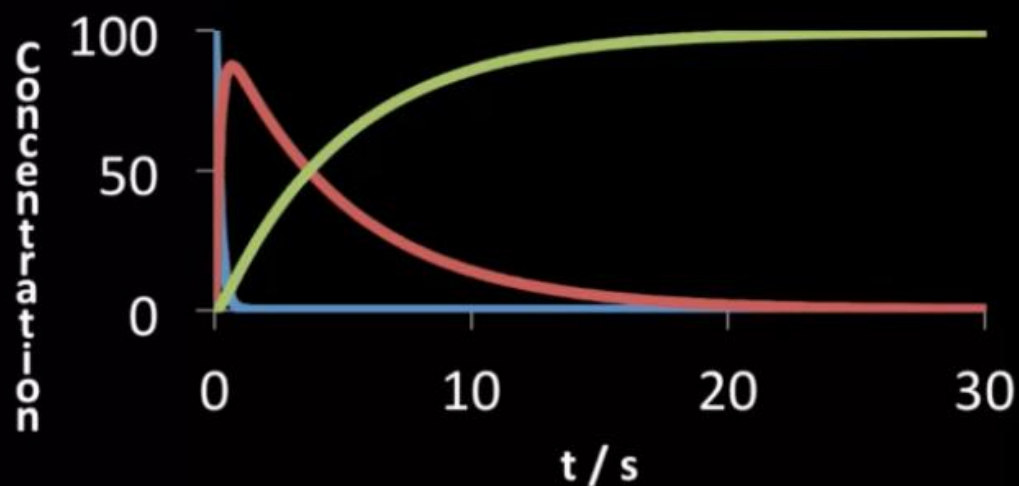


Consecutive reactions

$[A]_0 = 100$



Consecutive reactions



$$[C] = [A]_0 \left\{ 1 + \left(\frac{1}{k_1 - k_2} \right) \left(k_1 e^{-k_2 t} - k_2 e^{-k_1 t} \right) \right\}$$

Consecutive reactions

Only the slow step is important

RATE-DETERMINING STEP

Steady-state approximation

$$\textcircled{1} \frac{d[A]}{dt} = -k_1[A]$$

$$\textcircled{2} \frac{d[B]}{dt} = k_1[A] - k_1'[B] = 0$$

$$\textcircled{3} \frac{d[C]}{dt} = k_1'[B]$$



$$\textcircled{1} \text{ gives } [A] = [A]_0 e^{-k_1 t} \quad \textcircled{4}$$

$$\textcircled{2} \text{ gives } [B] = \frac{k_1}{k_1'} [A] = \frac{k_1}{k_1'} [A]_0 e^{-k_1 t} \quad \textcircled{5}$$

$\textcircled{3}$ and $\textcircled{5}$

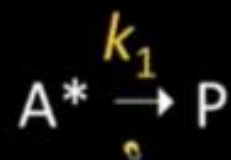
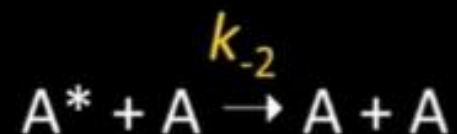
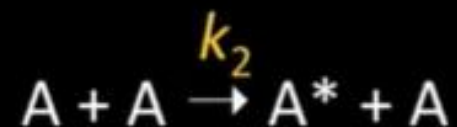
$$\frac{d[C]}{dt} = k_1 [A]_0 e^{-k_1 t}$$

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

$$[C] = \cancel{k_1} [A]_0 (1 - e^{-k_1 t}) \frac{1}{\cancel{k_1}}$$

Steady-state approximation

Example – First Order Reactions



Steady-state approximation

rate of formation of products

$$\frac{d[P]}{dt} = k_1 [A^*] \quad (1)$$

use SSA

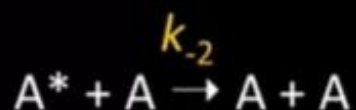
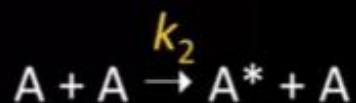
$$\frac{d[A^*]}{dt} = k_2 [A]^2 - k_{-2} [A^*][A] - k_1 [A^*] = 0 \quad (2)$$

rearrange

$$[A^*] = \frac{k_2 [A]^2}{k_1 + k_{-2} [A]} \quad (3)$$

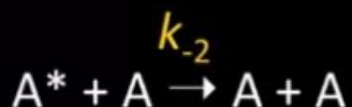
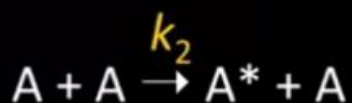
(3) in (1)

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_1 + k_{-2} [A]}$$



Steady-state approximation

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_1 + k_{-2} [A]}$$



$$k_{-2} \gg k_1, \quad \frac{d[P]}{dt} = \frac{k_1 k_2}{k_{-2}} [A]$$

1st order
kinetics

known as the Lindemann mechanism

At very low pressure

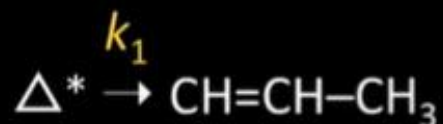
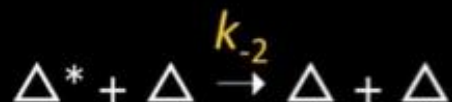
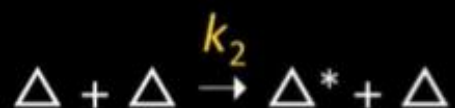
$$k_{-2} [A] \ll k_1$$

$$\frac{d[P]}{dt} = k_2 [A]^2$$

2nd order
kinetics

Lindemann mechanism

Example – isomerisation of cyclopropane



at high pressure

$$\text{rate} = \frac{k_1 k_2 [\Delta]}{k_{-2}}$$

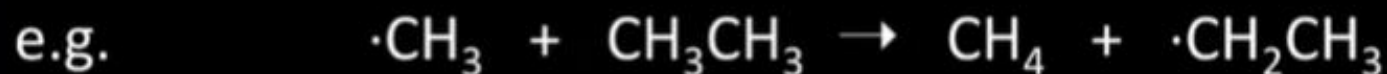
at low pressure

$$\text{rate} = k_2 [\Delta]^2$$

Complex reactions

Chain reactions

e.g. gas phase reactions that proceed via **free radicals**
(molecules with missing atoms)



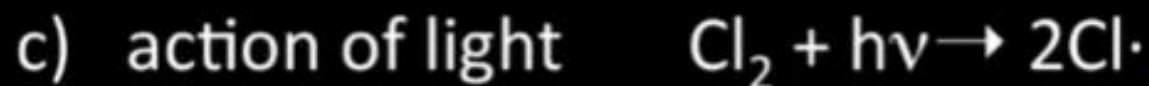
Complex reactions

Four important steps

1) Initiation production of free-radicals



b) Lindemann process (more complex molecules)



Complex reactions

Four important steps

2) Propagation

Attack of molecules by free-radicals with transfer of free radical



3) Inhibition



A free radical attacks a product slowing the reaction

Complex reactions

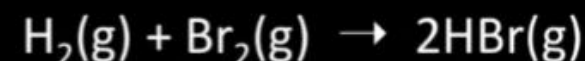
Four important steps

4) Termination

- a) dimerisation e.g. $\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3$
- b) reaction with walls of vessel
- c) addition of radical scavenger such as NO

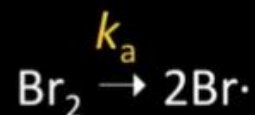
Example of complex reaction

$$\frac{d[\text{HBr}]}{dt} = \frac{k'[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k''([\text{HBr}] / [\text{Br}_2])}$$

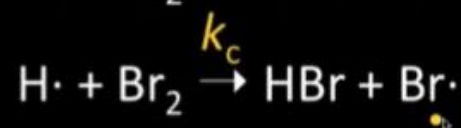
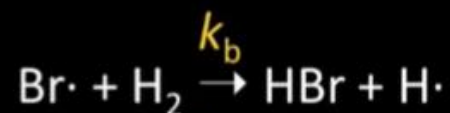


Need a mechanism

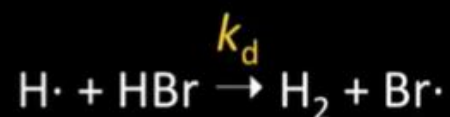
Initiation:



Propagation:



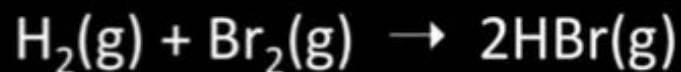
Inhibition:



Termination:



Example of complex reaction



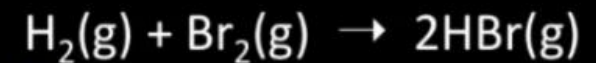
By experiment

$$\frac{d[\text{HBr}]}{dt} = \frac{k'[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k''([\text{HBr}] / [\text{Br}_2])}$$

Example of complex reaction

$$\frac{d[HBr]}{dt} = \frac{k'[H_2][Br_2]^{1/2}}{1 + k''([HBr]/[Br_2])}$$

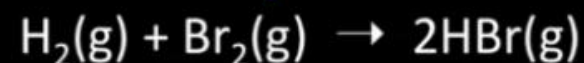
$$\textcircled{1} \quad k_b[Br\cdot][H_2] - k_c[H\cdot][Br_2] - k_d[H\cdot][HBr] = 0$$



$$\textcircled{2} \quad 2k_a[Br_2] - k_b[Br\cdot][H_2] + k_c[H\cdot][Br_2] + k_d[H\cdot][HBr] - 2k_e[Br\cdot]^2 = 0$$

Example of complex reaction

$$\frac{d[\text{HBr}]}{dt} = \frac{k'[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k''([\text{HBr}]/[\text{Br}_2])}$$



$$\textcircled{3} \quad [\text{Br}\cdot] = \left\{ \frac{k_a}{k_e} [\text{Br}_2] \right\}^{1/2}$$

Place in original equation

$$\frac{d[\text{HBr}]}{dt} = k_b[\text{Br}\cdot][\text{H}_2] + k_c[\text{H}\cdot][\text{Br}_2] - k_d[\text{H}\cdot][\text{HBr}]$$

$$\textcircled{4} \quad [\text{H}\cdot] = \frac{k_b \left(\frac{k_a}{k_e} \right)^{1/2} [\text{H}_2][\text{Br}_2]^{1/2}}{k_c[\text{Br}_2] + k_d[\text{HBr}]}$$

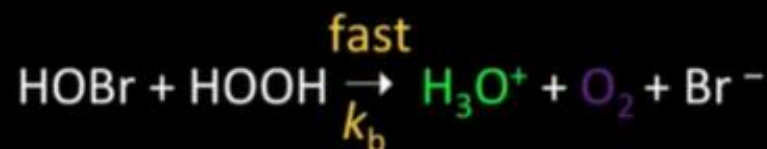
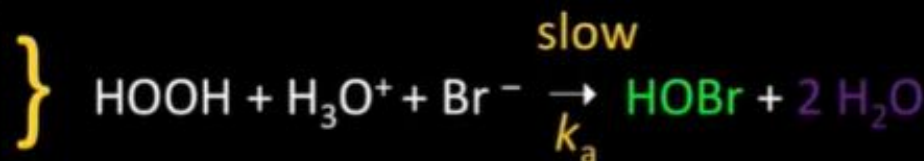
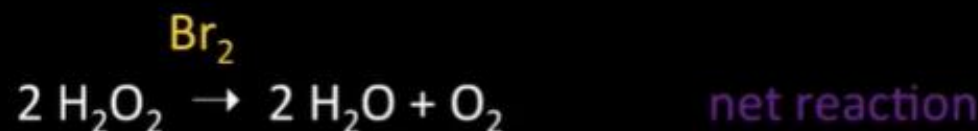
$$k' = 2k_b \left(\frac{k_a}{k_e} \right)^{1/2}$$

$$k'' = \frac{k_d}{k_c}$$

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_b \left(\frac{k_a}{k_e} \right)^{1/2} [\text{H}_2][\text{Br}_2]^{1/2}}{1 + \frac{k_d}{k_c} ([\text{HBr}]/[\text{Br}_2])}$$

Catalysis

Example of homogeneous catalysis



Catalysis

Examples of heterogeneous catalysis

W



$$E_a = 162 \text{ kJ mol}^{-1}$$

$$= 350 \text{ kJ mol}^{-1}$$

without catalyst

Au



$$E_a = 105 \text{ kJ mol}^{-1}$$

$$= 184 \text{ kJ mol}^{-1}$$

without catalyst

Catalysis

If E_a reduced from 76 kJ mol^{-1} to 57 kJ mol^{-1}

$$k = e^{\frac{-E_a}{RT}}$$

$$\frac{k_{\text{catalyst}}}{k_{\text{no catalyst}}} = \frac{e^{\frac{-57 \text{ kJ mol}^{-1}}{2.5 \text{ kJ mol}^{-1}}}}{e^{\frac{-76 \text{ kJ mol}^{-1}}{2.5 \text{ kJ mol}^{-1}}}} \approx 2000$$