

# Resulting tricks to empirically find rate laws

Consider  $A \rightarrow B$ :

0<sup>th</sup> Order:

$$[A](t) = -kt + [A]_0$$

1<sup>st</sup> Order:

$$\ln[A](t) = -kt + \ln[A]_0$$

2<sup>nd</sup> Order:

$$\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}$$

Linear regression  $y = mx + b$

Consider  $A + B \rightarrow C$ :

2nd Order:

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

BUT by

a) choosing  $[A]_0 = [B]_0$   
 $\Rightarrow [A] = [B] !$

$$-\frac{d[A]}{dt} = k[A]^2$$

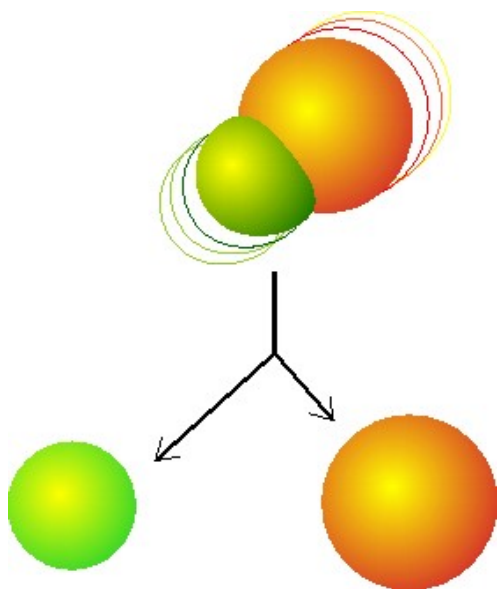
b) choosing  $[A]_0 \ll [B]_0 \Rightarrow [B] \approx \text{constant} !$

$\Rightarrow$

$$-\frac{d[A]}{dt} = k'[A]; \quad k' = k[B]_0$$

Pseudo-1<sup>st</sup> order

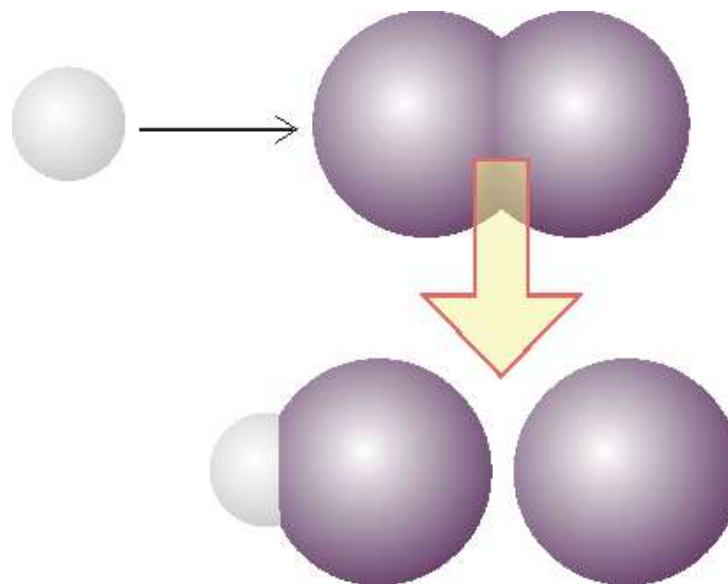
# For elementary reaction steps the rate law can be directly inferred



**unimolecular elementary step**



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



**bimolecular elementary step**

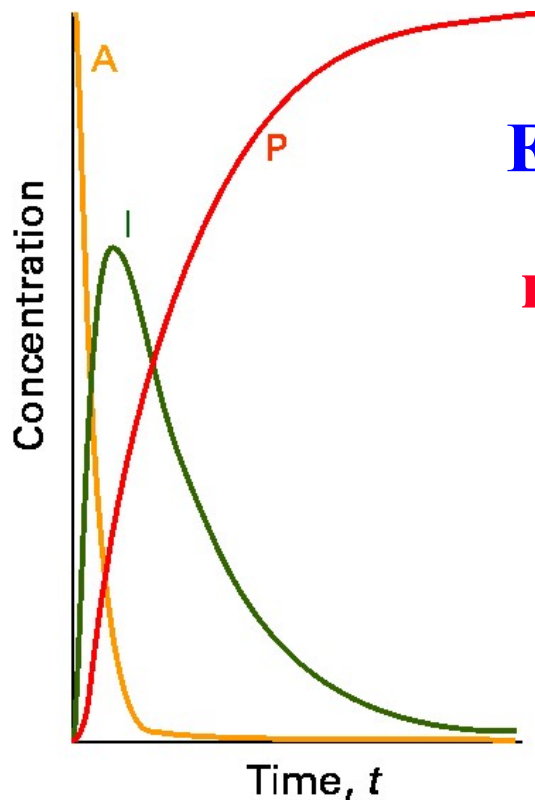
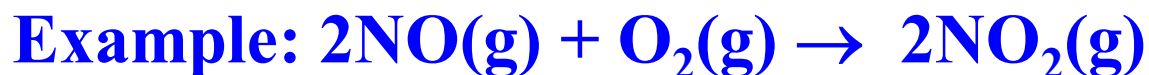


$$\text{Rate} = -\frac{d[A]}{dt} = k[A][B]$$

**Molecularity: Number of particles coming together to react in an elementary step**



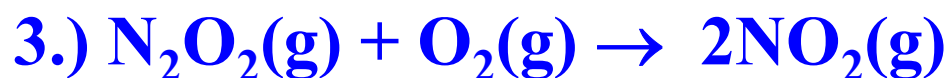
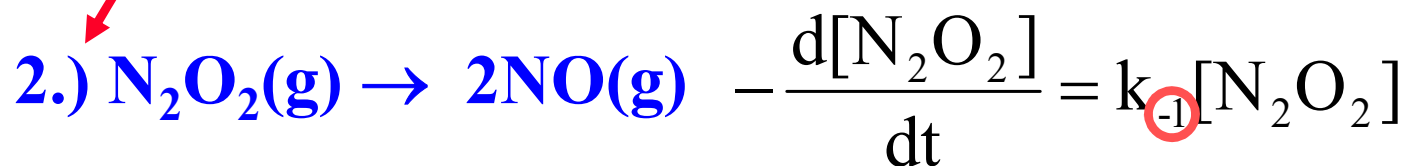
# An overall reaction often consists of consecutive elementary steps = mechanism



**Elementary steps:** 1.)  $2\text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}_2(\text{g})$

**reverse steps**

$$\frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}]^2$$



$$-\frac{d[\text{N}_2\text{O}_2]}{dt} = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

**and**  $-\frac{d[\text{N}_2\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$

$\Rightarrow$

$$\frac{d[\text{NO}_2]}{dt} = 2k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

**problem: intermediate**

**M**

# From steady-state approximation to rate law

$$\frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}]^2 \quad -\frac{d[\text{N}_2\text{O}_2]}{dt} = k_{-1}[\text{N}_2\text{O}_2] \quad -\frac{d[\text{N}_2\text{O}_2]}{dt} = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

**Overall:**  $\Sigma = \frac{d[\text{N}_2\text{O}_2]}{dt} = k_1[\text{NO}]^2 - k_{-1}[\text{N}_2\text{O}_2] - k_2[\text{N}_2\text{O}_2][\text{O}_2] = 0$

**Steady-state approximation =  
[intermediate] remains small and constant**

$$\Rightarrow [\text{N}_2\text{O}_2] = \frac{k_1[\text{NO}]^2}{k_{-1} + k_2[\text{O}_2]} \quad \text{and} \quad \frac{d[\text{NO}_2]}{dt} = 2k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

$$\Rightarrow \frac{d[\text{NO}_2]}{dt} = \frac{2k_1k_2[\text{NO}]^2[\text{O}_2]}{k_{-1} + k_2[\text{O}_2]} \quad \text{and} \quad k_{-1} \gg k_2[\text{O}_2] \quad (2^{\text{nd}} \text{ approximation})$$

$$\Rightarrow \frac{d[\text{NO}_2]}{dt} = \frac{2k_1k_2}{k_{-1}}[\text{NO}]^2[\text{O}_2] = k[\text{NO}]^2[\text{O}_2]$$

**Indeed observed  $\Rightarrow$  the proposed reaction mechanism is correct!**

