REACTION MECHANISM

1) reaction / reactants
2) overall rate law
3) formulate a mechanism

* the "overall reaction" is the sum a sequence of "elementary" steps

$$6\,CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6\,O_2$$

without correct orientation, E_a ⇒ NO REACTION

"molecularity" 1 molecule ⇒ UNIMOLECULAR
$A \rightarrow$ products

2 molecules ⇒ bimolecular $A + B \rightarrow$ products rate $= k[A][B]$
$A + A \rightarrow$ products rate $= k[A]^2$

3 molecules ⇒ termolecular $2A + B \rightarrow$ products
→ rare ←

RATE for an ELEMENTARY STEP IS
∴ Coefficients DO become "orders of reaction"
for an ~~elementary~~ elementary step

RATE DETERMINING STEP (RDS)
→ slowest step in the mechanism
→ determines the overall kinetics

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2 molecules ⇒ bimolecular A + B → products rate = k[A][B]
A + A → products rate = k[A]²

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RATE for an ELEMENTARY STEP ∝ n
∴ Coefficients DO become "orders of reaction" for an ~~elementary~~ elementary step

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MECHANISM RULES

- the sum of the elementary steps must match the balanced equation overall reaction
- the RDS must match the experimentally determined rate law

* proposed intermediates must be detectable

$Cl_2 \rightleftharpoons 2\,\dot{Cl}$ (slow) — rate = $k_1[Cl_2]$

$\dot{Cl} + CHCl_3 \longrightarrow HCl + \dot{C}Cl_3$ (fast) — rate = $k_2[Cl][CHCl_3]$

$\dot{C}Cl_3 + \dot{Cl} \longrightarrow CCl_4$ (fast) — rate = $k_3[CCl_3][Cl]$

$Cl_2 + CHCl_3 \longrightarrow HCl + CCl_4$

observed rate law: rate = $k[Cl_2][CHCl_3]^0$

Cl, CCl_3 = INTERMEDIATES

* INTERMEDIATES SHOULD NOT APPEAR IN THE OVERALL RATE LAW

$A + B \longrightarrow C + D$ (slow) — rate = $k_1[A][B]$

$C + E \longrightarrow B + F$ (fast) — rate = $k_2[C][E]$

$A + E \longrightarrow D + F$ — rate = $k[A][B][E]^0$

C = intermediate ; B = catalyst [reforming]

$O_3 + NO_2 \longrightarrow \cancel{NO_3} + O_2$ (slow)

$\cancel{NO_3} + NO_2 \longrightarrow N_2O_5$ (fast)

$O_3 + 2NO_2 \longrightarrow N_2O_5 + O_2$ rate = $k[O_3][NO_2]$

FIRST STEP ≠ RDS

$2A + 2B \longrightarrow C + 2D$ overall rate law: rate = $k[A]^2[B]$

proposed

(1) $2A \rightleftharpoons \cancel{E}$ (fast)

(2) $\cancel{E} + B \longrightarrow \cancel{F} + D$ (slow) rate = $k_2[E][B]$

(3) $\cancel{F} + B \longrightarrow C + D$ (fast)

$2A + 2B \longrightarrow C + 2D$

EQ is reached before (2)

rate$_{FWD}$ = rate$_{REV}$

rate = $k_1[A]^2$ rate = $k_{-1}[E]$

$k_1[A]^2 = k_{-1}[E]$

$\frac{k_1}{k_{-1}}[A]^2 = [E]$

rate = $\left(k_2\left(\frac{k_1}{k_{-1}}\right)\right)[A]^2[B]$

rate = $k[A]^2[B]$