

REACTION MECHANISM

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

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



without correct orientation, $E_a \Rightarrow$ NO REACTION

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

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

3 molecules \Rightarrow termolecular $2A+B \rightarrow$ products
 \rightarrow rare \leftarrow

RATE for an ELEMENTARY STEP $\propto n$

\therefore coefficients DO become "orders of reaction"
for an ~~elementary~~ elementary step

RATE DETERMINING STEP (RDS)

- \rightarrow slowest step in the mechanism
- \rightarrow determines the overall kinetics

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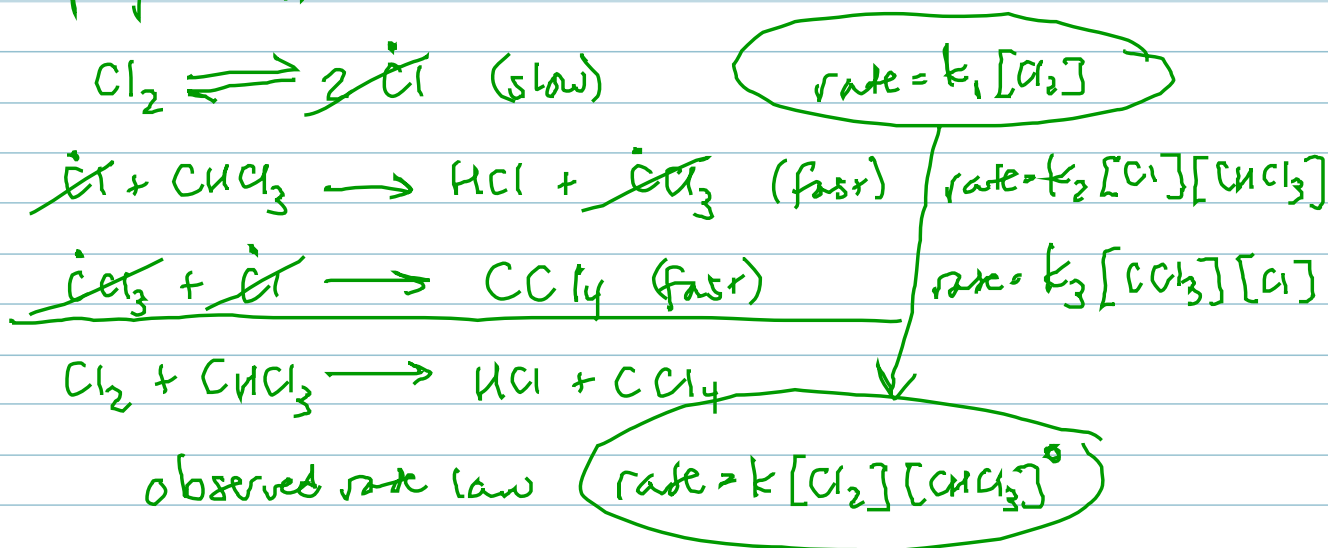
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MECHANISM RULES

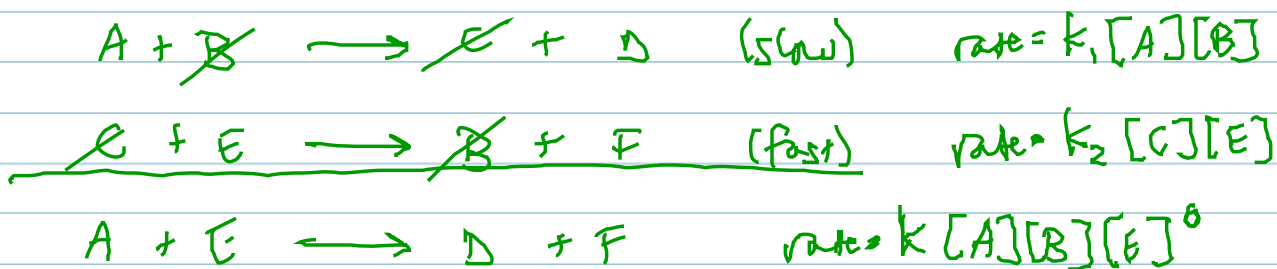
- the sum of the elementary steps must match the balanced equation overall reaction
- the RDS must match the experimentally determined rate law

* proposed intermediates must be detectable

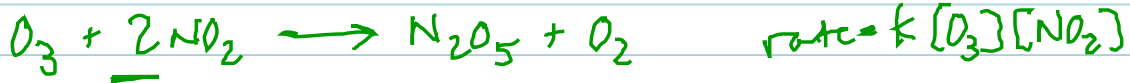
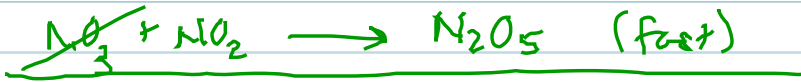


$\text{Cl}\cdot, \text{CCl}_3\cdot = \text{INTERMEDIATES}$

* INTERMEDIATES SHOULD NOT APPEAR IN THE OVERALL RATE LAW



$\text{C} = \text{intermediate}$; $\text{B} = \text{catalyst}$ [reforming]

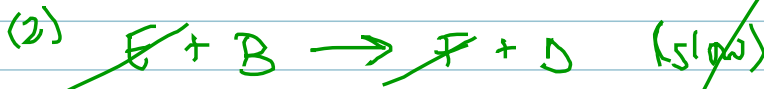
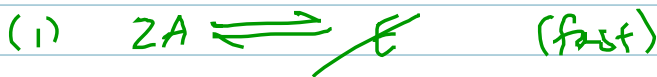


FIRST STEP \neq RDS



overall rate law $\text{rate} = k[A]^2[B]$

proposed



EQ is reached before (2)
rate FWD = rate REV

$$\text{rate} = k_2 [E][B]$$

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

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

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

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

$$\text{rate} = k [A]^2 [B]$$