Reaction Mechanisms

A mechanism represents the sequence of bond-making and bond-breaking steps that occur during the conversion of reactants to products.

- Must be determined by experiment
- Must agree with overall stoichiometry
- The slowest step is the rate determining step
- Must agree with the experimentally determined rate law (determine the slowest step, add slowest step to all steps that occur before it)
- Reaction intermediate – product in one step but consumed in another
- Catalyst – goes in as a reactant, comes out as a product

ELEMENTARY STEP	MOLECULARITY	RATE EXPRESSION
A→ products	unimolecular	rate = k[A]
A + B → products	bimolecular	rate = k[A][B]
A + A → products	bimolecular	rate = k[A]^2
2 A + B → products*	termolecular*	rate = k[A]^2[B]

Stoichiometry (coefficients) may be used to predict rate expressions for elementary steps only, but not for overall reactions.

1. Nitrogen oxide is reduced by hydrogen to give water and nitrogen,

$$2\,H_2(g) + 2\,NO(g) \rightarrow N_2(g) + 2\,H_2O(g)$$

and one possible mechanism to account for this reaction is

$2\,NO(g) \rightarrow N_2O_2(g)$ bimolecular

$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ bimolecular

$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ bimolecular

What is the molecularity for each step? Show that the sum of these elementary steps yields the overall reaction.

$2\,NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

2. One mechanism for the destruction of ozone in the upper atmosphere is

$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$ *slow*

$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$ *fast*

a. What is the overall balanced equation for the reaction? $O_3(g) + O(g) \rightarrow 2O_2(g)$

b. Which species is a catalyst? $NO(g)$ - 1st appears as reactant then product

c. Which species is an intermediate?

$NO_2(g)$ - 1st made as product then used as a reactant

3. The balanced equation for the reaction of the gases of nitrogen dioxide and fluorine is

$$2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$$

The experimentally determined rate law is Rate = $k\ [NO_2]\ [F_2]$

A suggested mechanism for the reaction is

$NO_2 + F_2 \rightarrow NO_2F + \cancel{F}$ *Slow* rate = $k[NO_2]^1[F_2]^1$

$\cancel{F} + NO_2 \rightarrow NO_2F$ *Fast*

Is this an acceptable mechanism? Explain your reasoning.

Yes, the rate law of the slow step matches the experimentally determined rate law and the sum of the steps equals the overall rxn.

4. Consider the reaction between nitrogen dioxide and carbon monoxide:

$$NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g)$$

The rate law for this reaction is known to be:

$$\text{Rate} = k[NO_2]^2$$

The following mechanism is proposed.

Step 1: $NO_2\ (g) + NO_2\ (g) \rightarrow NO_3\ (g) + NO\ (g)$ rate = $k[NO_2]^2$

Step 2: $NO_3\ (g) + CO\ (g) \rightarrow NO_2\ (g) + CO_2\ (g)$ rate = $k[NO_3]^1[CO]^1$

Which step is the rate-determining step? Justify your answer.

Step #1 is the rate-determining step. b/c its rate law equals that of the known rate law of the overall rxn.