Reaction Mechanisms

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   *sum steps = overall rxn* ✓
- 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
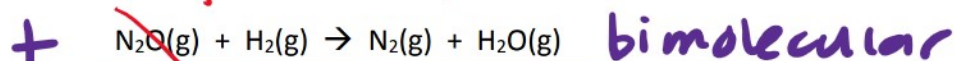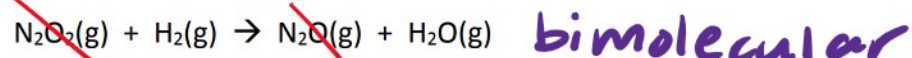- Catalyst – goes in as a reactant, comes out as a product   *NOT CONSUMED*

ELEMENTARY STEP	MOLECULARITY	RATE EXPRESSION
A → products	unimolecular 1	rate = $k[A]^1$
A + B → products	bimolecular 2	rate = $k[A][B]^1$
A + A → products *(2A)*	bimolecular 2	rate = $k[A]^2$
2 A + B → products*	termolecular* 3	rate = $k[A]^2[B]^1$

★ **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.

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

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

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

$$O_3 (g) + NO (g) \rightarrow NO_2 (g) + O_2 (g) \qquad \textit{slow}$$
$$NO_2 (g) + O (g) \rightarrow NO (g) + O_2 (g) \qquad \textit{fast}$$
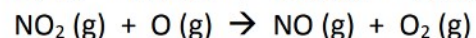
— rate determining step

a. What is the overall balanced equation for the reaction?

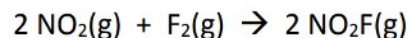b. Which species is a catalyst?

c. Which species is an intermediate?

a) $O_3 (g) + O (g) \rightarrow 2 O_2 (g)$

b) Catalyst - 1st appears as a reactant, then later as a product

NO = catalyst

c) intermediate - 1st appears as a product, then later as a reactant

NO₂ = intermediate

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 [NO₂] [F₂] ←

A suggested mechanism for the reaction is

A suggested mechanism for the reaction is

NO$_2$ + F$_2$ → NO$_2$F + F   Slow $rate = k[NO_2]^1[F_2]^1$

F + NO$_2$ → NO$_2$F   Fast
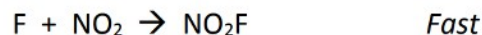
Is this an acceptable mechanism? Explain your reasoning.

$2 NO_2 + F_2 \rightarrow 2 NO_2F$ ✓ criteria #1
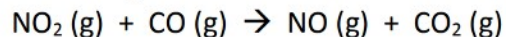sum of steps
equal the overall
rxn

criteria #2
rate of slow step matches the overall rxn ✓
rate law

yes, both criteria are met.

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:

Rate = $k[NO_2]^2$ ✓

The following mechanism is proposed.

Step 1: $NO_2 (g) + NO_2 (g) \rightarrow NO_3 (g) + NO (g)$

Step 2: $NO_3 (g) + CO (g) \rightarrow NO_2 (g) + CO_2 (g)$
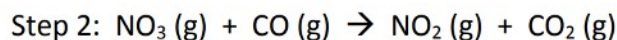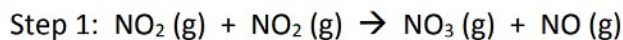
Which step is the rate-determining step? Justify your answer.

Step 1 = Slow

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

$2NO_2$

Fast Step 2: $NO_3 (g) + CO (g) \rightarrow NO_2 (g) + CO_2 (g)$
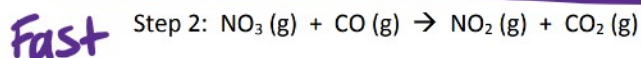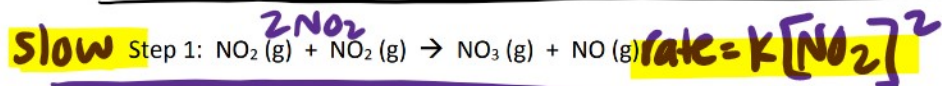
Step 1 is rate determining
 b/c step 1's rate law
matches the overall rate
 law of the rxn.

Step 2 = Slow

Fast Step 1: $NO_2 (g) + NO_2 (g) \rightarrow NO_3 (g) + NO (g)$

slow Step 2: $NO_3 (g) + CO (g) \rightarrow NO_2 (g) + CO_2 (g)$

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

rate = $k[NO_2]^1[CO]^1$ ✗