REACTION MECHANISMS

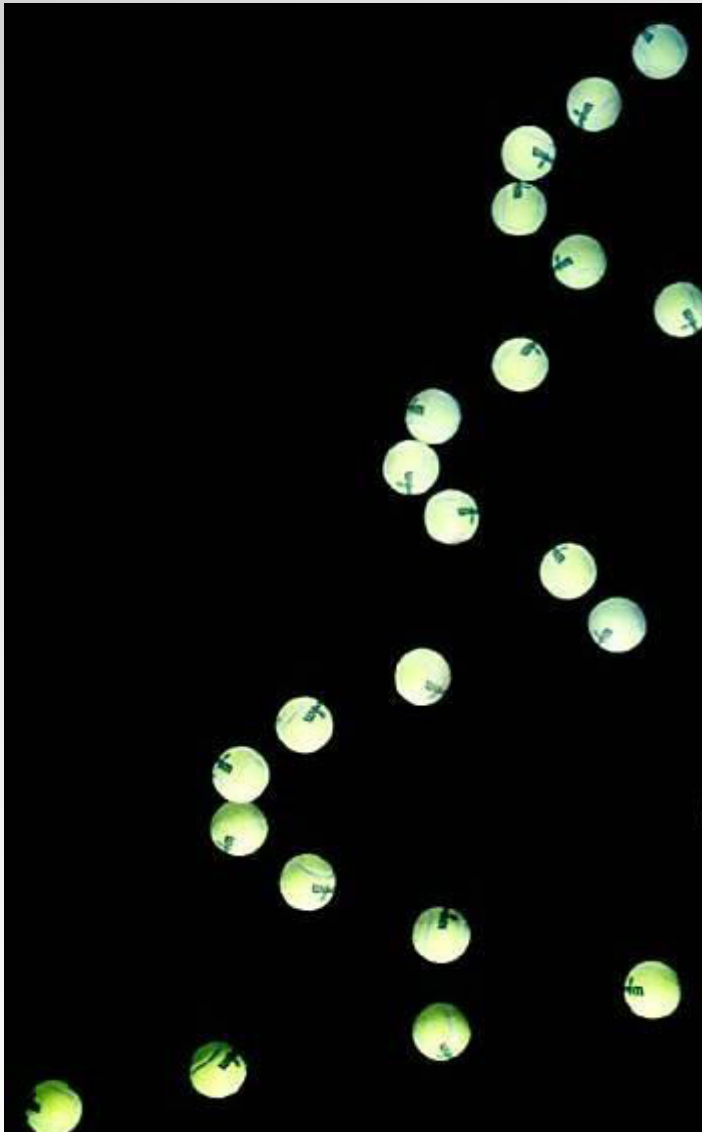
REACTION MECHANISMS

Which reaction do you think will proceed faster? Why?

$A + B + C \rightarrow ABC$

$A + B \rightarrow AB$

Reactions that require a greater number of particles to collide at the same time will decrease the chances of a successful reaction to occur.



REACTION MECHANISMS

Of all possible chemical reactions, how many would require three particles colliding?

Many reactions take place through multiple two-collision steps at a time, especially when more than two reactants are involved.

Overall: $4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$

Step 1: $HBr + O_2 \rightarrow HOOBr$

Step 2: $HOOBr + HBr \rightarrow 2\ HOBr$

Step 3: $(HOBr + HBr \rightarrow H_2O + Br_2)$ x2

REACTION MECHANISMS

Each step of the mechanism is known as an elementary process.

The complete series of elementary processes is known as the reaction mechanism of a chemical reaction.

You are not expected to come up with elementary processes!!

REACTION MECHANISMS

If each elementary process occurs at different rates, how fast is the overall reaction?

Step 1: $HBr + O_2 \rightarrow HOOBr$ slow

Step 2: $HOOBr + HBr \rightarrow 2\ HOBr$ fast

Step 3: $(HOBr + HBr \rightarrow H_2O + Br_2)$ x2 fast

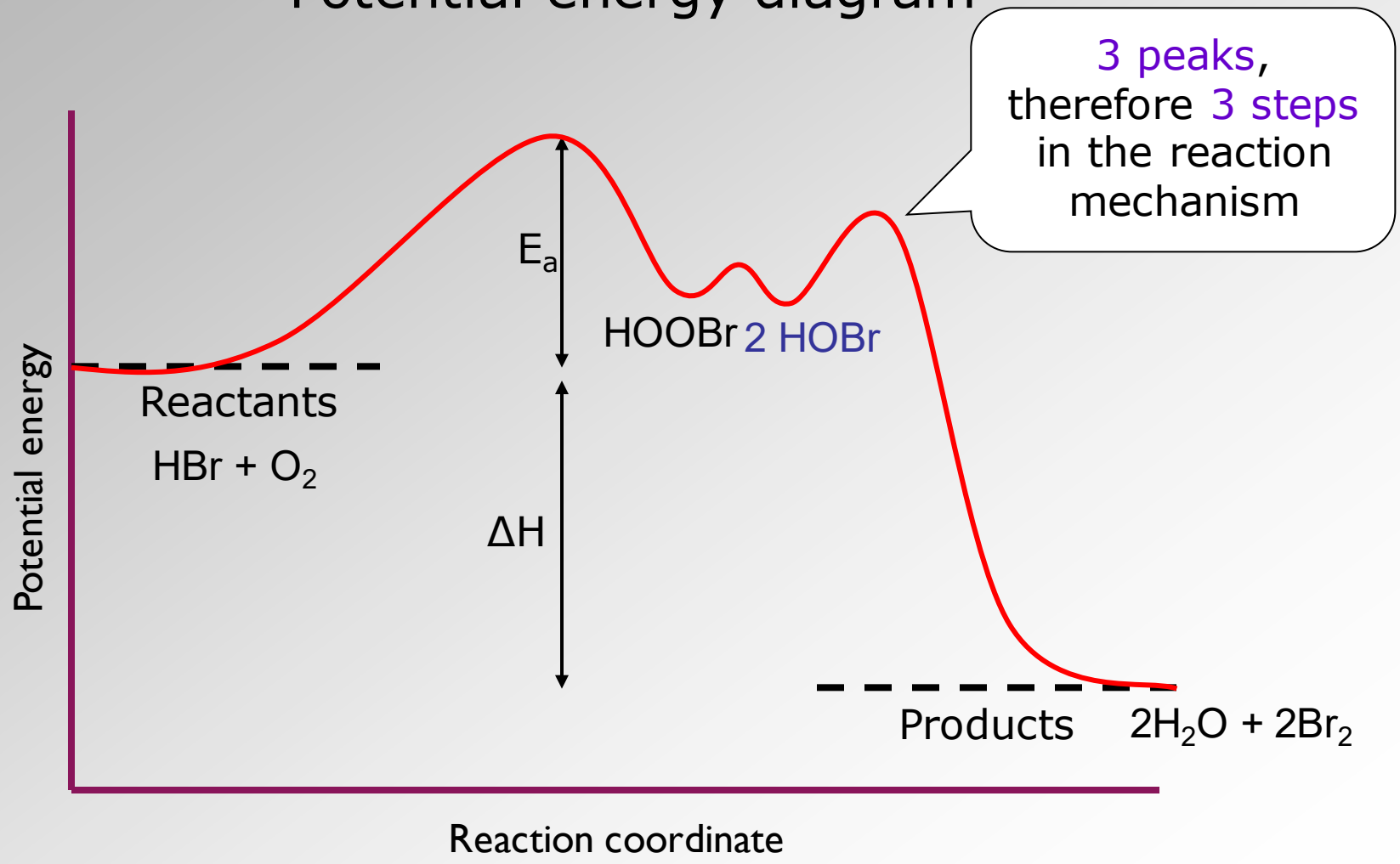
The overall reaction can only be as fast as the SLOWEST elementary process. So the rate of the reaction ($r=k[HBr]^x[O_2]^y$) is the same as the rate of the slowest step.

This step is called the **rate-determining step**

REACTION MECHANISMS

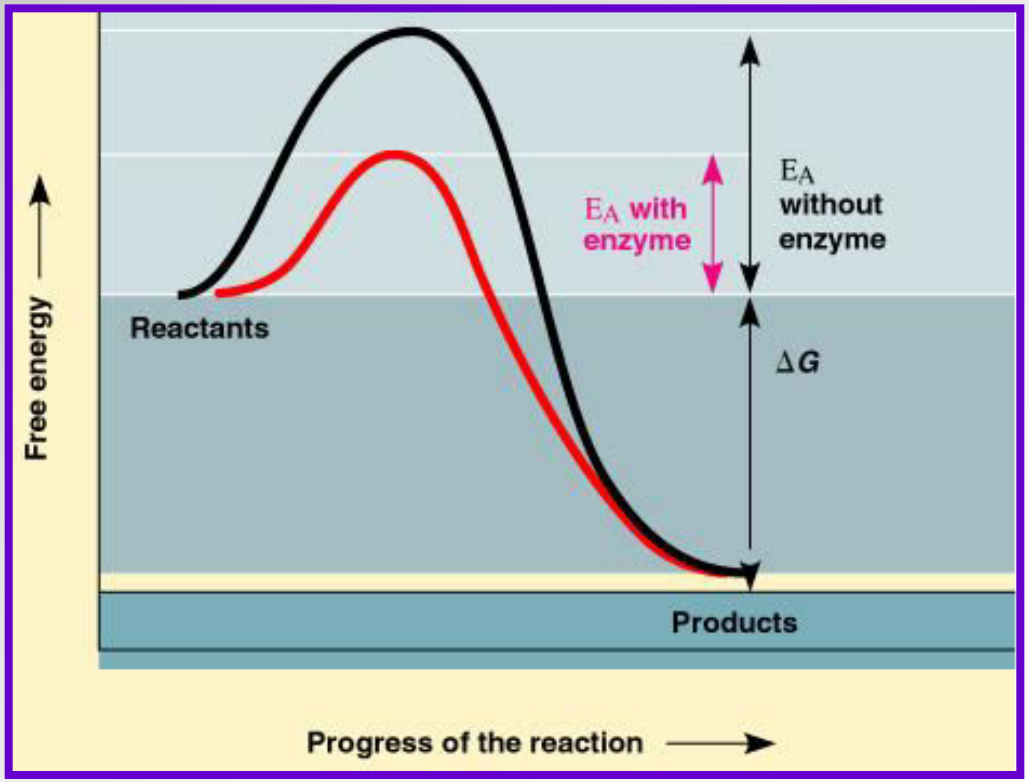
$4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$

Potential energy diagram



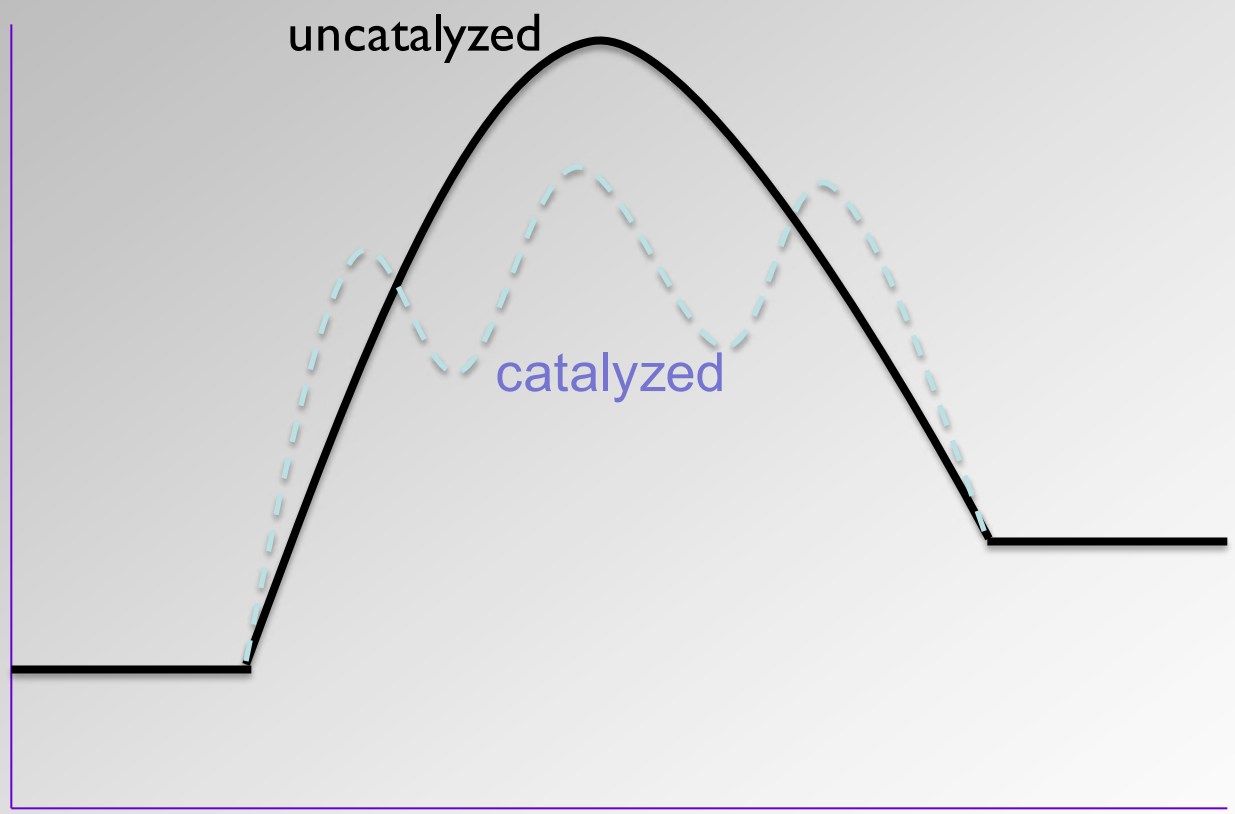
REACTION MECHANISMS

- catalysts increase reaction rate without being used up in the reaction
- all catalysts reduce activation energy for a reaction
- many catalysts also change the mechanism by which the reaction occurs

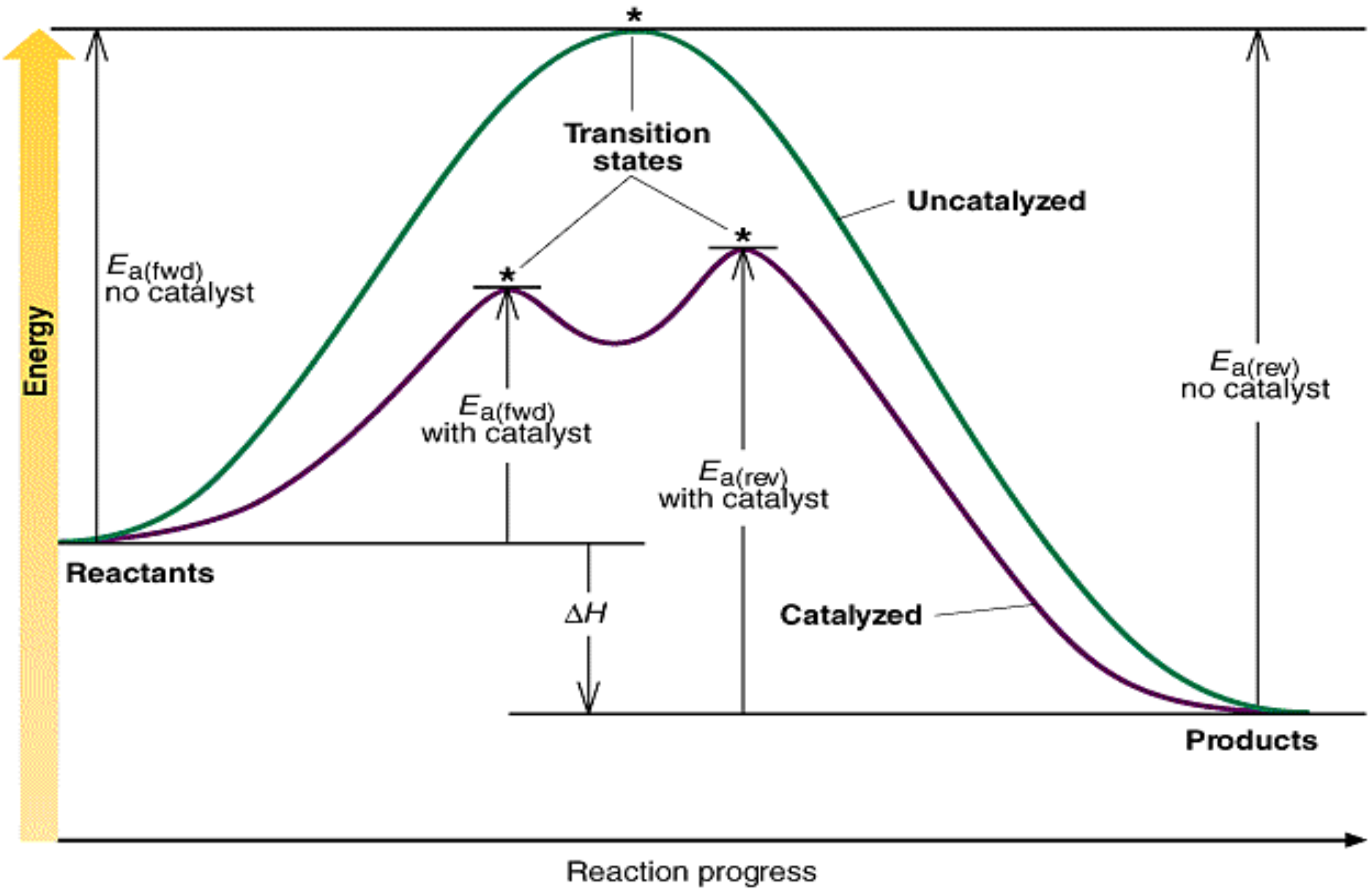


REACTION MECHANISMS

$$CH_2O_{2(aq)} \rightarrow CO_{(g)} + H_2O_{(l)}$$



REACTION MECHANISMS



REACTION MECHANISMS

Rate Law for Elementary Processes

- ONLY FOR ELEMENTARY PROCESSES, the exponents of the rate law is the same as the coefficients of the balanced elementary process equation

  i.e. $A + 2B \rightarrow AB_2$ $\qquad\qquad$ $r=k[A]^1[B]^2$

- if only given the overall equation, then rate experiments must be conducted

REACTION MECHANISMS

Rate Law for Elementary Processes

EXAMPLE 1

$$2\,NO_2Cl \rightarrow 2\,NO_2 + Cl_2$$

Elementary processes

i) $NO_2Cl \rightarrow NO_2 + Cl$ rate = $k[NO_2Cl]$

ii) $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$ rate = $k[NO_2Cl][Cl]$

REACTION MECHANISMS

Rate Law for Elementary Processes

EXAMPLE 2

$$2\,NO_2 \rightarrow 2\,NO + O_2$$

Elementary processes

i) $2\,NO_2 \rightarrow NO_3 + NO$ rate = $k[NO_2]^2$

ii) $NO_3 \rightarrow NO + O_2$ rate = $k[NO_3]$

REACTION MECHANISMS

Predicting Mechanisms

1. For a proposed mechanism to be acceptable, the rate law of the rate-determining step should be the same as the rate law for the overall reaction

2. overall reaction rate is determined by the rate determining step

This means that the rate law for the rate-determining step is directly related to the rate law for the overall reaction.

REACTION MECHANISMS

Predicting Mechanisms

EXAMPLE 1b

$2\ NO_2Cl \rightarrow 2\ NO_2 + Cl_2$

rate = $k[NO_2Cl]$
Experimentally-determined
1st order reaction

i) $NO_2Cl \rightarrow NO_2 + Cl$ **(slow)**

rate = $k[NO_2Cl]$
(predicted)

ii) $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$ **(fast)**

Since this mechanism yields a rate law that matches the experimental one, it should be correct.

REACTION MECHANISMS

Predicting Mechanisms

EXAMPLE 2b

$2\ NO_2 \rightarrow 2\ NO + O_2$

rate = $k[NO_2]^2$
Experimentally-determined
2nd order reaction

i) $2\ NO_2 \rightarrow NO_3 + NO$ **(slow)**

rate = $k[NO_2]^2$
(predicted)

ii) $NO_3 \rightarrow NO + O_2$ **(fast)**

Since this mechanism yields a rate law that matches the experimental one, it should be correct.

REACTION MECHANISMS

Predicting Mechanisms

- proposed mechanisms that match experimental rate laws DO NOT PROVE the mechanism is correct
  - *additional experimentation is required*
- other proposals may need to be examined

REACTION MECHANISMS

Predicting Mechanisms

The reaction of ozone, O_3, with nitric oxide, NO, forms nitrogen dioxide and oxygen gas. It is believed to be a one step mechanism to produce smog.

Determine the rate law.

$NO + O_3 \rightarrow NO_2 + O_2$ **rate = $k[NO][O_3]$**

REACTION MECHANISMS

Predicting Mechanisms

$$2\ N_2O_{5(g)} \rightarrow 2\ N_2O_{4(g)} + O_{2(g)}$$

a) Determine the rate equation if this was a one step reaction.

rate = $k[N_2O_5]^2$

b) Actual rate equation: rate = $k[N_2O_5]$

Propose the reactants for the rate determining step.

N_2O_5 → some reaction intermediates

REACTION MECHANISMS

Predicting Mechanisms

$$X + 2\,Y + 2\,Z \rightarrow XY_2Z_2$$

i) doubling [X] = no effect

ii) doubling [Y] = 4 x rate

iii) doubling [Z] = 2 x rate

a) What is the rate law? **rate = $k[Y]^2[Z]$**

b) Propose the reactants of the rate determining step?

$2Y + Z \rightarrow$ some product(s)

REACTION MECHANISMS