5. REACTION MECHANISMS

UNIT 2 – CHEMICAL KINETICS

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WHAT REALLY HAPPENS IN A REACTION?

Consider the following reaction:

$$4\ HBr_{(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} + 2Br_{2(g)}$$

- Reactions involving more than 2 or 3 colliding particles are called **termolecular** reactions. They seem very rare.
- **Unimolecular** and **bimolecular** reactions are more probable.

How is it possible that this reaction occurs then?

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BABY STEPS!

1. $HBr + O_2 \rightarrow HOOBr$	Slow
2. $HOOBr + HBr \rightarrow 2\ HOBr$	Fast
3. $HOBr + HBr \rightarrow H_2O + Br_2$	Fast
4. $HOBr + HBr \rightarrow H_2O + Br_2$	Fast
Net. $4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$	???

elementary step a step involving a one-, two-, or three-entity collision that cannot be explained by simpler reactions

Complex chemical reactions involving multiple reactant molecules are believed to occur in a series of elementary steps called a reaction mechanism.

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RATE DETERMINING STEP

The slowest step in the reaction mechanism is called the rate-determining step. This step dictates the rate of the reaction.

1.	$NO_2 + NO_2 \rightarrow NO_3 + NO$	(slow)
2.	$NO_3 + CO \rightarrow NO_2 + CO_2$	(fast)
NET:	$NO_2 + CO \rightarrow NO + CO_2$	

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RATE DETERMINING STEP

To increase the rate, you must increase the rate of this step.

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RATE DETERMINING STEP

The rate determining step must agree with the rate law for that reaction.

Table 1 Examples of Elementary Steps

Elementary step	Rate law equation
$A \rightarrow$ products	rate $= k[A]$
$A + A \rightarrow$ products	rate $= k[A]^2$
$A + B \rightarrow$ products	rate $= k[A][B]$

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FOR EXAMPLE

NET REACTION: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

RATE LAW: $\text{rate} = k[NO_2(g)]^2$

PROPOSED MECHANISM:

Step 1: $NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g)$

Step 2: $NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$

WHICH STEP IN THE PROPOSED MECHANISM IS THE RATE DETERMINING STEP?

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INTERMEDIATES

Substances that are produced in an early step of a reaction but consumed in a later step are called intermediate products, or **intermediates**.

1. $NO_2 + NO_2 \rightarrow NO_3 + NO$ (slow)
2. $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

NET: $NO_2 + CO \rightarrow NO + CO_2$

Intermediates are <u>not</u> part of the net reaction equation.

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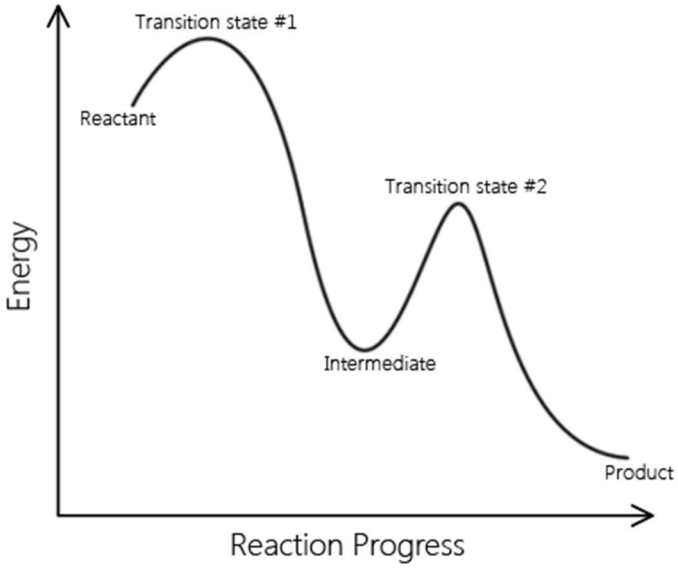
INTERMEDIATES



Intermediates produced in the first elementary step of a reaction mechanism act as reactants in the second elementary step of the reaction.

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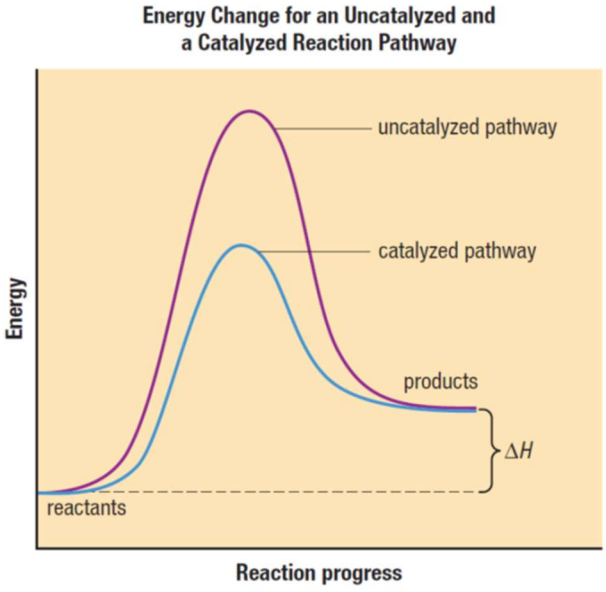
CATALYSTS

A catalyst provides a reaction pathway with a lower activation energy.

Found as a <u>reactant at the beginning</u> of a reaction mechanism and again as a <u>product at the end</u>.

Catalysts are not consumed in a reaction and are therefor **<u>not</u>** part of the net reaction equation.



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EXAMPLE #1

Step 1: A + B → C

Step 2: C + D → CD

Step 3: CD + E → ABE + D

Overall :

Catalyst(s):

Intermediate(s):

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EXAMPLE #2:

The rate law of a chemical reaction was found to be rate=k[NO] $[Cl_2]$. The following reaction mechanism was proposed:

Step 1: $NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$

Step 2: $NOCl_2(g) + NO(g) \rightarrow 2\ NOCl_2(g)$

Overall:

Intermediate(s):

Which step is the rate determining step? Why?

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SUMMARY

- Most chemical reactions occur in a series of elementary steps. The sequence of elementary steps making up a reaction is known as its reaction mechanism.
- A rate law equation can be written for each elementary step of a reaction, and the overall rate law equation for a reaction may be deduced from these.
- The slowest elementary step in a reaction mechanism is the rate-determining step.
- There are two requirements for a plausible reaction mechanism:
  1. The elementary steps must combine to give the correct overall balanced equation.
  2. The mechanism must agree with the experimentally determined rate law equation.

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