Kinetics 15.4

Reaction Mechanisms
Catalysis

Reaction Mechanisms

Most reactions do not happen in one step.

e.g.

$2\ NO_{(g)} + O_{2(g)} \rightarrow 2\ NO_{2(g)}$

Occurs in two elementary steps

Reaction Mechanism:

$2\ NO_{(g)} \rightarrow \cancel{N_2O_{2(g)}}$

$\cancel{N_2O_{2(g)}} + O_{2(g)} \rightarrow 2\ NO_{2(g)}$

$2\ NO_{(g)} + O_{2(g)} \rightarrow 2\ NO_{2(g)}$

Reaction Mechanisms are the series of steps that sum to the overall reaction.

Reaction Mechanisms

Reaction Intermediate

- A substance that is produced and then consumed during the overall reaction.

Produced: $2\ NO_{(g)} \rightarrow \cancel{N_2O_{2(g)}}$

Consumed: $\cancel{N_2O_{2(g)}} + O_{2(g)} \rightarrow 2\ NO_{2(g)}$

$2\ NO_{(g)} + O_{2(g)} \rightarrow 2\ NO_{2(g)}$

N_2O_2 is a reaction intermediate

Determining a Rate Law

- The rate law for an overall reaction can only be found experimentally.

e.g. Consider this overall reaction.

$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$

$\text{Rate} = k\,[NO_2]^2\,[CO]^0$

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

Determining a Rate Law

Overall Reaction: $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$

But, rate laws for elementary steps are predictable!

Step 1. $2\ NO_{2(g)} \rightarrow NO_{(g)} + NO_{3(g)}$

Rate = $k_1\,[NO_2]^2$ ← Same rate law as the overall reaction!

Step 2. $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$

Rate = $k_2\,[NO_3][CO]$

For any elementary step…

$aA + bB \rightarrow dD + eE$ **Rate = $k[A]^a[B]^b$**

Determining a Rate Law

Overall Reaction: $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$

Step 1. $2\ NO_{2(g)} \rightarrow NO_{(g)} + NO_{3(g)}$ **[Slow]**

Rate = $k_1\,[NO_2]^2$

Step 2. $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$ **[Fast]**

Rate = $k_2\,[NO_3][CO]$

NO_3 is consumed as soon as it is produced.

Adding CO does not increase the rate, making it zero order in the overall reaction.

The rate of the overall reaction is always equal to the rate of the slowest elementary step.

Determining a Rate Law

1) Chemists determine the rate law through experimentation.

2) They use the rate law to figure out what the elementary steps are.
   - The rate law tells them what the slowest step is.
   - Then they try to figure out what the fast steps are.

Catalysis

- A catalyst increases the rate of a chemical reactions by providing a mechanism with a lower activation energy.
- Catalysts are not produced or consumed in the reaction.
- They are there before the reaction starts, and they return when the reaction is complete.

Catalysis

The destruction of ozone.

Cl reacts with O_3

$$Cl_{(g)} + O_{3(g)} \rightarrow O_{2(g)} + ClO_{(g)}$$

$$ClO_{(g)} + O_{(g)} \rightarrow O_{2(g)} + Cl_{(g)}$$

Cl is back to react with another O_3

$$O_{3(g)} + O_{(g)} \rightarrow 2\ O_{2(g)}$$

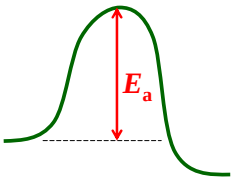
$$O_{3(g)} + O_{(g)} \xrightarrow{Cl} 2\ O_{2(g)}$$

Each $Cl_{(g)}$ atom will destroy about 100 ozone molecules before it reacts with something else and leaves with stratosphere.

Catalysis and Activation Energy

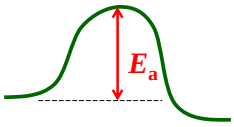
$O_{3(g)} + O_{(g)} \rightarrow 2\ O_{2(g)}$

no catalyst



$O_{3(g)} + Cl_{(g)} \rightarrow ClO_{(g)} + O_{2(g)}$

with a catalyst

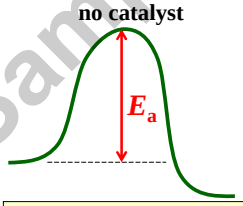


A catalyst provides a mechanism with a lower activation energy, thereby increasing the reaction rate.

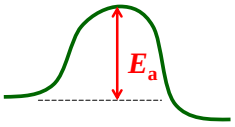
Catalysis and Equilibrium

A catalyst lowers the activation energy for the forward and the reverse reactions.

no catalyst



with a catalyst



K_{eq} for a reaction is the same at the same temperature, with of without the catalyst.

Catalysis

Homogeneous Catalyst

- The catalyst is in the same phase as the reactants.

e.g. The destruction of ozone. (Cl, O_3, and O are all gases)

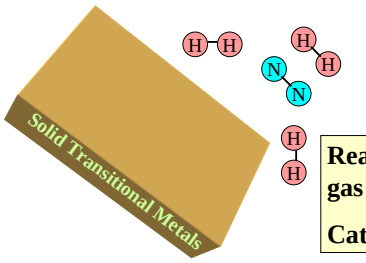
Heterogeneous Catalyst

- The catalyst is in a different phase than the reactants.

e.g. Synthesis of ammonia. (solid and gas)

Heterogeneous Catalysis

$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$

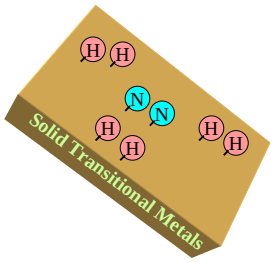


Reactants are in the gas phase.

Catalyst is a solid.

Heterogeneous Catalysis

$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$



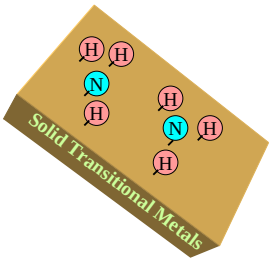
Reactants slam into the surface.

Bonds within each gas molecule break.

Bonds form between the metal and the individual atoms.

Heterogeneous Catalysis

$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$

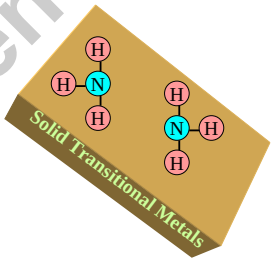


Migration

• Atoms move around on the surface of the metal.

Heterogeneous Catalysis

$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$

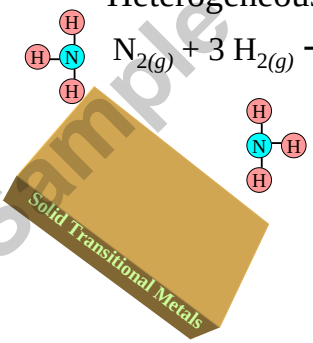


Reaction

• Nitrogen atoms form bonds with hydrogen atoms.

Heterogeneous Catalysis

$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$



Desorption

• Products enter the gas phase.