

Section 15.1 and 15.2

Introduction to Kinetics and Reactions Rates

Control of Solubility

In these sections...

Control of Reactivity:

- a. Thermodynamic control
- b. Kinetic control: Collision Theory

Describing Reaction Rates:

- a. Average rate
- b. Instantaneous rate
- c. Initial rate
- d. Relation to reaction stoichiometry

Control of Reactivity: Thermodynamics and Kinetics

Thermodynamics: are the products more stable (lower in energy) than the reactants?

Kinetics: does the reaction proceed at a significant rate?

For a reaction to occur, it must be favored by both thermodynamics and kinetics.

Thermodynamic Control: Enthalpy and Entropy

Enthalpy: (Bond strength) stronger bonds = lower enthalpy = more stable

Entropy: (Free motion of atoms) freer mobility = higher entropy = more stable

Formation of strong bonds and or more independent particles favor reactions.

For many systems these counteract and overall thermodynamic favorability depends on temperature.

Kinetic Control:

Activation Energy, Concentration and Temperature

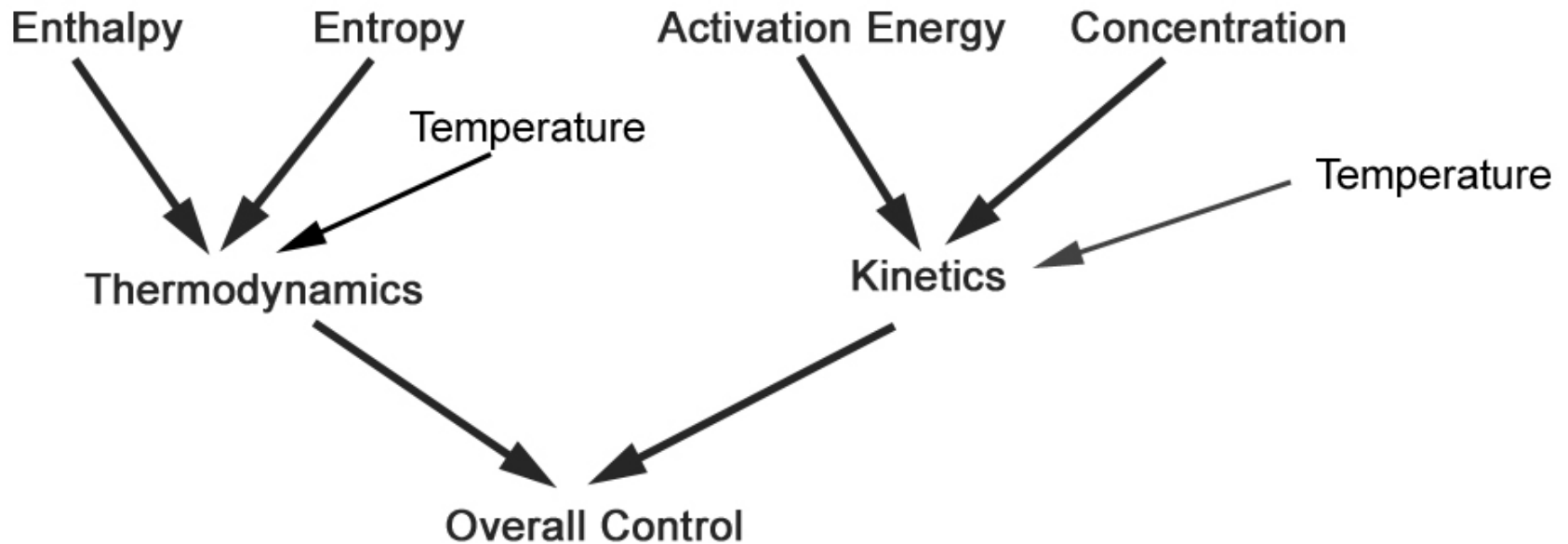
Activation Energy: the energy barrier reactants must overcome to react

Concentration: greater concentration usually increases the chances
reactants will meet and react

Temperature: higher temperature increases the number of collisions and
the fraction overcoming the activation energy

Control of Reactivity

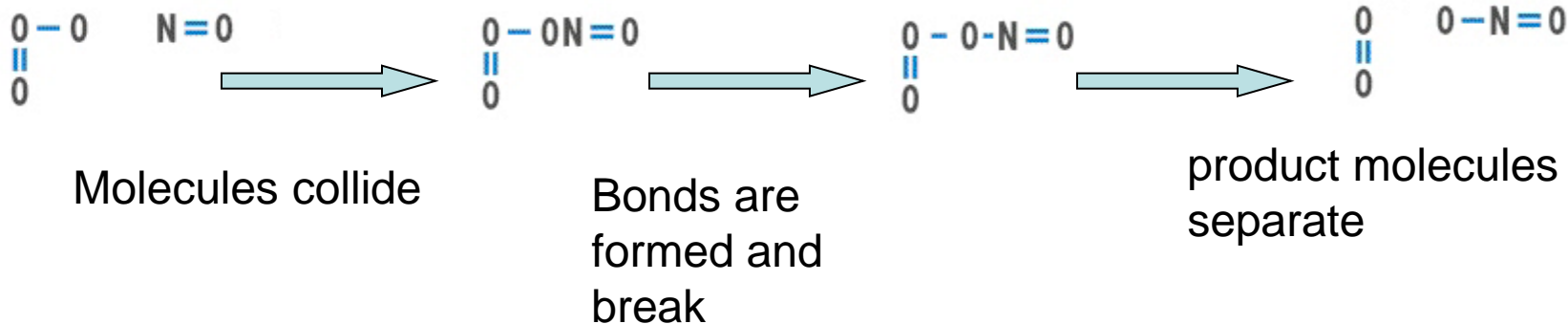
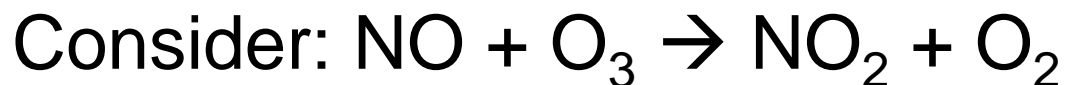
Control of Chemical Reactivity



Kinetic Control: Collision Theory

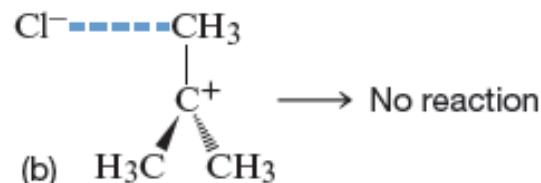
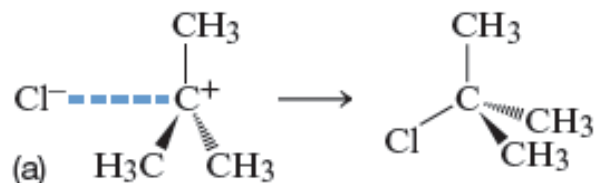
For a reaction to take place:

- Molecules must collide
- They must do so in the correct orientation
- They must collide with an energy greater than the “activation” energy



So, what controls the rate of a reaction?

- Number of collisions
- How often they collide with an orientation that allows new bonds to form

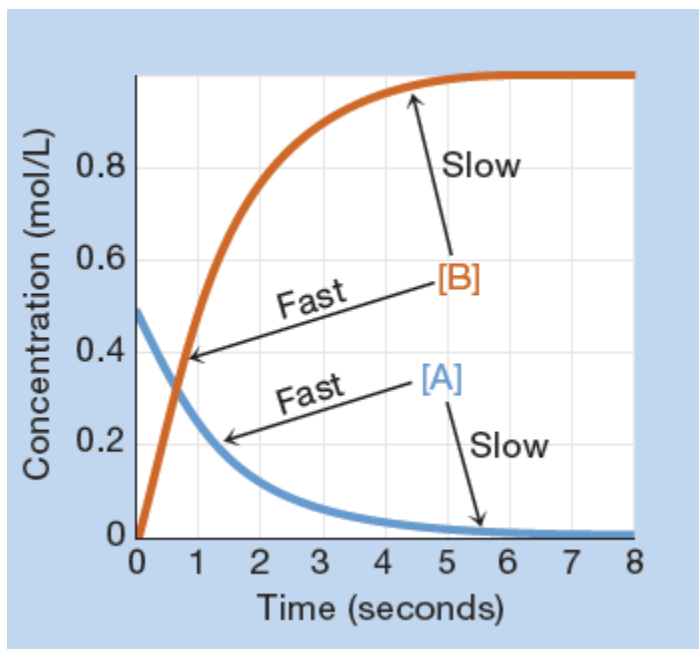


- The energy of the colliding reactant molecules

So, what controls the rate of a reaction?

$$rate = Ae^{-\frac{E_a}{RT}} [reactants]^{order}$$

Expressing the Rate of a Reaction: Graphically

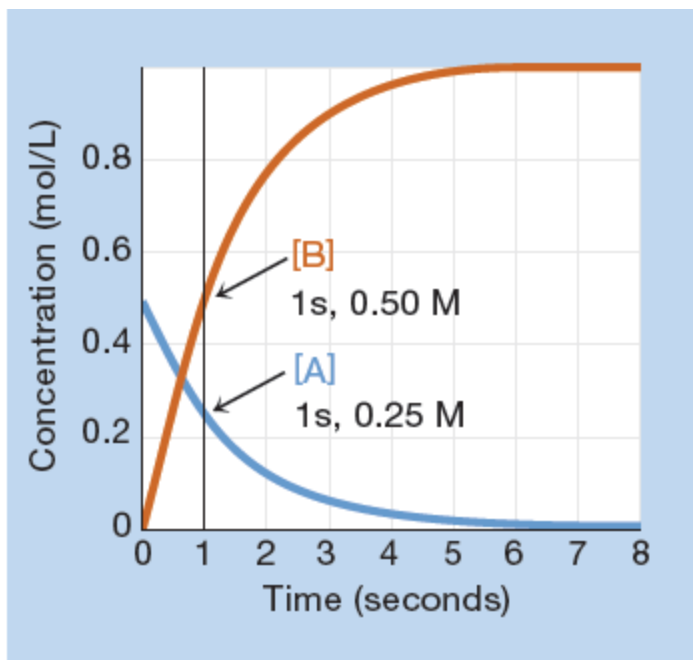


- Reactant concentration decreases
- Product concentration increases
- Steeper slope = faster reaction

Expressing the Rate of a Reaction: Numerically: Average Rate

$$\text{Rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}}$$

Reaction: $A \rightarrow 2 B$



After 1 second, $[A] = 0.25 \text{ M}$ and $[B] = 0.50 \text{ M}$.

After 1 second:

- $[A]$ dropped from 0.50 M to 0.25 M
- $[B]$ increased from 0 M to 0.50 M

$$\text{rate of appearance of B} = \frac{\Delta[B]}{\Delta t} = \frac{(0.50 \text{ M} - 0 \text{ M})}{(1.0 \text{ s} - 0 \text{ s})} = 0.50 \text{ M/s}$$

$$\text{rate of disappearance of A} = -\frac{\Delta[A]}{\Delta t} = -\frac{(0.25 \text{ M} - 0.50 \text{ M})}{(1.0 \text{ s} - 0 \text{ s})} = 0.25 \text{ M/s}$$

Rates and Stoichiometry

In general for a reaction: $a A + b B \rightarrow c C + d D$

$$\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Relative rate of each species is proportional to its stoichiometric coefficient.

Rates and Stoichiometry



Experimental data:

t (min)	$[\text{H}_2\text{O}_2]$ (mol/L)
0	0.0912
434	0.0566
868	0.0351
1302	0.0218

What are the rates of change of H_2O_2 and O_2 during the first 434 minutes?

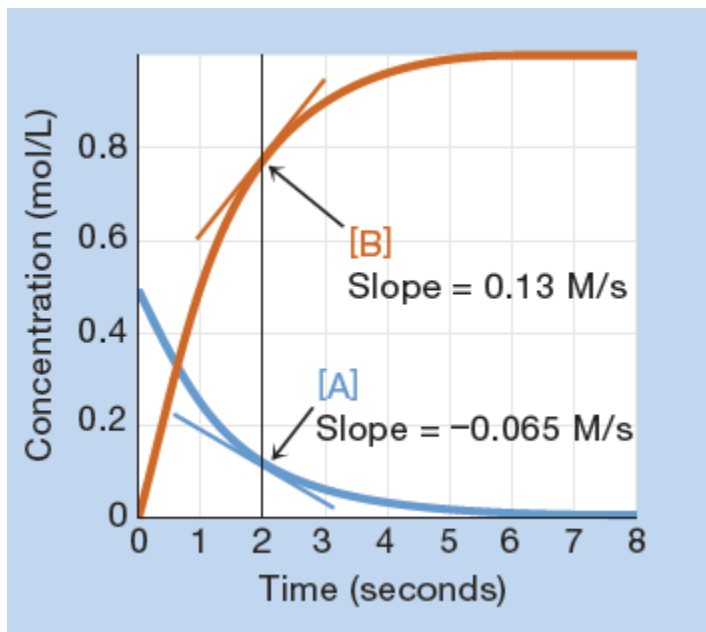
Rate of disappearance of H_2O_2 :

Rate of appearance of O_2 :

Expressing the Rate of a Reaction: Numerically: Instantaneous Rate

$$\text{Rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}}$$

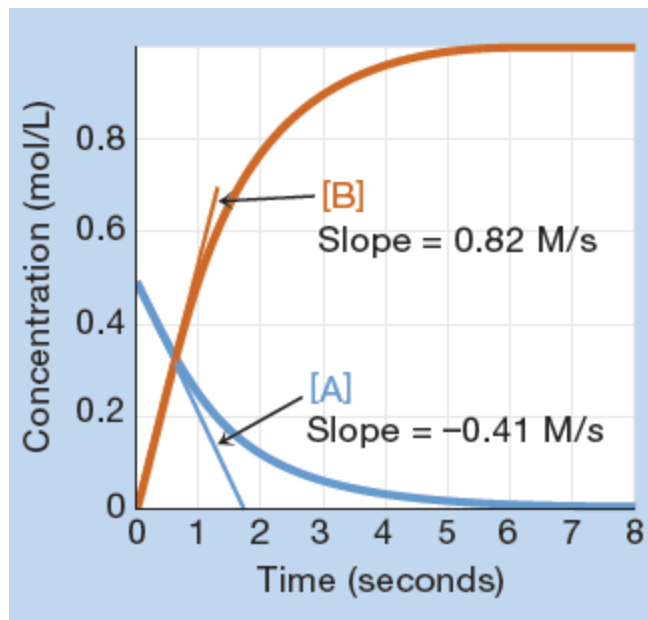
Reaction: $A \rightarrow 2 B$



Instantaneous rate =
slope of the concentration-time curve at
any particular time

Expressing the Rate of a Reaction: Numerically: Initial Rate

$$\text{Rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}}$$



Initial rate = Instantaneous rate at time = 0