

Reaction Rates

- A little review from our thermodynamics unit



•Above diagram from World of Chemistry p. 538

- Reactions happen when bonds are broken and atoms recombine to form new molecules
- There is a minimum energy required for bonds to be broken, so not all colliding particles react.
- More collisions and higher-energy collisions increase the chance that a bond can be broken – leading to a faster reaction
- Catalysts work differently – by creating a lower energy reaction pathway

Collision Theory

In order for a reaction to occur...

- 1 Reactants must collide
- 2 Collision must be at the correct orientation
- 3 Collision must have minimum amount of energy for bonds to break

Only a small number of collisions meet the requirements and result in a reaction

1. Reactants Must Collide

In order for two molecules to react, they must come in contact with one another



There's no way they'll ever react if they don't run into one another!

2. Collision with Incorrect Orientation

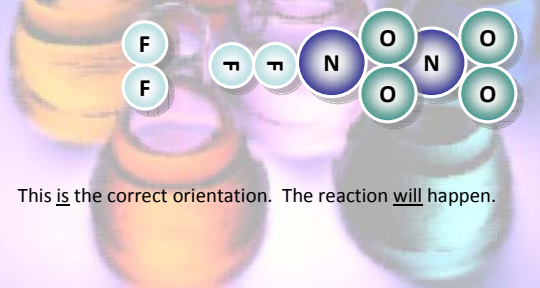
For a collision to result in a chemical reaction, it must occur with the correct orientation



This is not the correct orientation. The reaction will not happen.

2. Collision with Correct Orientation

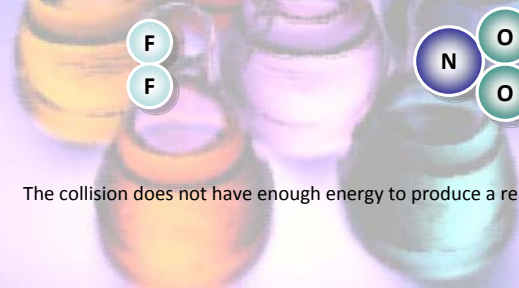
For a collision to result in a chemical reaction, it must occur with the correct orientation



This is the correct orientation. The reaction will happen.

3. Collision with Not Enough Energy

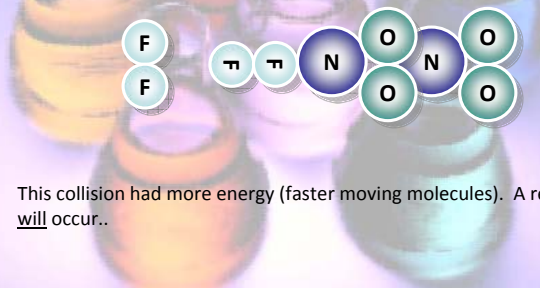
For a collision to result in a chemical reaction, it must occur with the minimum energy for reaction



The collision does not have enough energy to produce a reaction

3. Collision with Enough Energy

For a collision to result in a chemical reaction, it must occur with the minimum energy for reaction



This collision had more energy (faster moving molecules). A reaction will occur..

Factors Affecting Reaction Rate

1. Temperature
2. Concentration
3. Surface Area
4. Catalysts

Reaction Rates

- Effect of Concentration on Reaction Rates
 - Increasing the concentration of a reactant can increase the rate of reaction OR it might actually have little effect on the rate of reaction
 - For any reaction to happen, the particles must collide!

Reaction Rates

- An example (from <http://www.chemguide.co.uk/>) where changing concentration affects the rate of reaction
- “Suppose that at any one time 1 in a million particles have enough energy to equal or exceed the activation energy. If you had 100 million particles, 100 of them would react. If you had 200 million particles in the same volume, 200 of them would now react. The rate of reaction has doubled by doubling the concentration.”

Reaction Rates

- When doesn't changing the concentration affect the rate of reaction?
 - When a catalyst is already making the reaction happen as fast as possible
 - Certain multi-step reactions
 - Consider the following 2-step reaction:
 - $A \rightarrow X + Y$ (very slow)
 - $X + B \rightarrow Z + Q$ (very fast)
 - The overall rate will be determined by the slow step – in this case it will all depend on how fast A splits into X and Y
 - If you increase the concentration of B, it may speed up the 2nd step, but the overall reaction will still be waiting for the first step to finish.
 - So for this reaction we say that step 1 is the “rate determining step”

Reaction Rates

- Rate equations
 - Orders of reaction are found experimentally
 - To do this, you manipulate the concentrations to see how the rates are affected
 - Rates are measured in M/s (change in Molarity per second)

Reaction Rates

- Rate order
- Consider a hypothetical reaction:
 $aA + bB \rightarrow cC + dD$
- The rate law takes the form:
 $\text{rate} = k[A]^x[B]^y$ (k is called the "rate constant")
The brackets mean concentration (molarity)
x and y are found experimentally

Rate Law and Order

Example 1:

Hypothetical reaction $A + B + C \rightarrow D$

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.05	1.52×10^{-5}
2	0.1	0.3	0.05	1.52×10^{-5}
3	0.2	0.3	0.05	3.04×10^{-5}
4	0.2	0.3	0.1	6.08×10^{-5}

What happens to rate when [A] doubles?

What happens to rate when [B] triples?

What happens to rate when [C] doubles?

Rate Law and Order

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.05	1.52×10^{-5}
2	0.1	0.3	0.05	1.52×10^{-5}
3	0.2	0.3	0.05	3.04×10^{-5}
4	0.2	0.3	0.1	6.08×10^{-5}

➤ What happens to rate when [A] doubles?

➤ Rate doubles

➤ So from $\text{rate} \approx [A]^x$ then $[2]^x = 2$, $x = ?$

➤ $x=1$

➤ So this reaction is said to be first order with respect to A

➤ We say $[A]^1$

Rate Law and Order

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.05	1.52×10^{-5}
2	0.1	0.3	0.05	1.52×10^{-5}
3	0.2	0.3	0.05	3.04×10^{-5}
4	0.2	0.3	0.1	6.08×10^{-5}

➤ What happens to rate when [B] triples?

➤ Rate stays the same!

➤ So from $\text{rate} \approx [B]^y$ then $[3]^y = 1$, $y = ?$

➤ $y=0$

➤ So this reaction is said to be zero order with respect to B (this means [B] drops out of our rate equation $[B]^0$)

Rate Law and Order

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.05	1.52×10^{-5}
2	0.1	0.3	0.05	1.52×10^{-5}
3	0.2	0.3	0.05	3.04×10^{-5}
4	0.2	0.3	0.1	6.08×10^{-5}

➤ What happens to rate when [C] doubles?

➤ Rate doubles

➤ So from $\text{rate} \approx [C]^z$ then $[2]^z = 2$, $z = ?$

➤ $z=1$

➤ So this reaction is said to be first order with respect to C

➤ We say $[C]^1$

Rate Law and Order

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.05	1.52×10^{-5}
2	0.1	0.3	0.05	1.52×10^{-5}
3	0.2	0.3	0.05	3.04×10^{-5}
4	0.2	0.3	0.1	6.08×10^{-5}

Summary:

Rate = $k[A]^1 [B]^0 [C]^1$, but $[B]^0 = 1$ so it drops out

Thus Rate = $k[A]^1 [C]^1$

the overall rate order is 2 (sum of A, B, C orders)

Solve for k:

Using data from trial 1:

$$k = \frac{\text{rate}}{[A]^1 [C]^1}$$

$$k = \frac{1.52 \times 10^{-5}}{[0.1][0.05]} = 0.00304 \frac{1}{\text{M} \cdot \text{sec}}$$

Rate Law and Order

Example 2

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.1	0.01
2	0.1	0.1	0.2	0.01
3	0.1	0.2	0.1	0.02
4	0.2	0.2	0.1	0.08

What happens to rate when [A] doubles?

What happens to rate when [B] doubles?

What happens to rate when [C] doubles?

Rate Law and Order

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.1	0.01
2	0.1	0.1	0.2	0.01
3	0.1	0.2	0.1	0.02
4	0.2	0.2	0.1	0.08

➤ What happens to rate when [A] doubles?

➤ Rate quadruples (factor of 4)

➤ So from $\text{rate} \approx [A]^x$ then $[2]^x = 4$, $x = ?$

➤ $x=2$

➤ So this reaction is said to be second order with respect to A

➤ We say $[A]^2$

Rate Law and Order

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.1	0.01
2	0.1	0.1	0.2	0.01
3	0.1	0.2	0.1	0.02
4	0.2	0.2	0.1	0.08

- What happens to rate when [B] doubles?
 - Rate doubles (factor of 2)
 - So from $\text{rate} \approx [\text{B}]^y$ then $[2]^y = 2$, $y = ?$
 - $y=1$
 - So this reaction is said to be first order with respect to B
 - We say $[\text{B}]^1$

Rate Law and Order

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.1	0.01
2	0.1	0.1	0.2	0.01
3	0.1	0.2	0.1	0.02
4	0.2	0.2	0.1	0.08

- What happens to rate when [C] doubles?
 - Rate does not change (factor of 1)
 - So from $\text{rate} \approx [\text{C}]^z$ then $[2]^z = 1$, $z = ?$
 - $z=0$
 - So this reaction is said to be zero order with respect to C
 - We say $[\text{C}]^0$ (this means [C] will drop out of our rate equation)

Rate Law and Order

Trial	[A]	[B]	[C]	Rate (M/sec)
1	0.1	0.1	0.1	0.01
2	0.1	0.1	0.2	0.01
3	0.1	0.2	0.1	0.02
4	0.2	0.2	0.1	0.08

Summary:

Rate = $k[\text{A}]^2 [\text{B}]^1 [\text{C}]^0$, but $[\text{C}]^0 = 1$ so it drops out

Thus Rate = $k[\text{A}]^2 [\text{B}]^1$

The overall rate order is 3.

Solve for k:

$$k = \frac{\text{rate}}{[\text{A}]^2 [\text{B}]^1}$$

Using data from trial 3:

$$k = \frac{0.02}{[0.1]^2 [0.2]} = 10 \frac{1}{\text{M}^2 \cdot \text{sec}}$$

Rate Law and Order

[Iodine Clock Reaction Simulation](http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/kinetics2/kinetics.swf)

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