

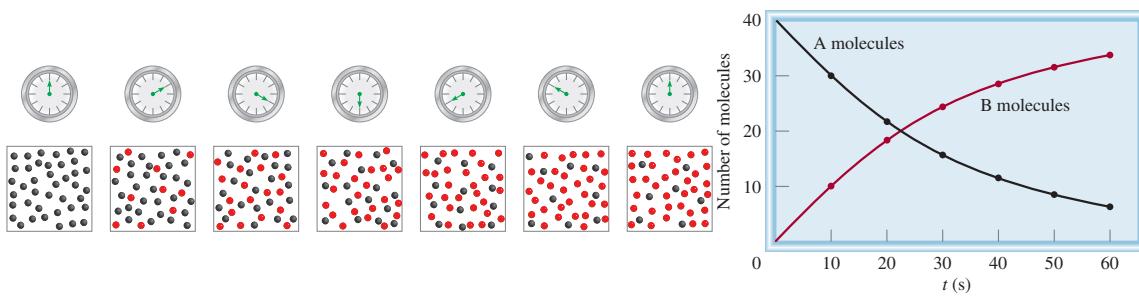
# Chemical Kinetics

*Branch of science concerned with the rates at which chemical reactions occur*

**Reactants → products**

**Reaction Rate:** rate at which products are formed and reactants are used up

Consider the rxn:  $\text{A} \rightarrow \text{B}$



## Reaction Rate

*The rate of a reaction is defined as the amount of products created (or reactants depleted) per unit time*



rate based on  
products

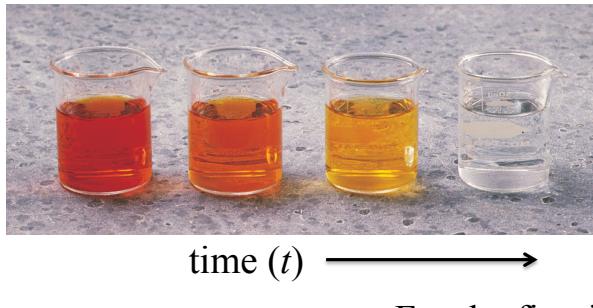
$$\text{rate} = \frac{[\text{B}]_{t_2} - [\text{B}]_{t_1}}{t_2 - t_1} = \frac{\Delta[\text{B}]}{\Delta t}$$

rate based on  
reactants

$$\text{rate} = -\frac{[\text{A}]_{t_2} - [\text{A}]_{t_1}}{t_2 - t_1} = -\frac{\Delta[\text{A}]}{\Delta t}$$

These rates represent *average* rates over the interval  $\Delta t$

# Reaction Rate Example



Measured reaction progress data

Time (s)	[Br <sub>2</sub> ] (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296

For the first interval

$$\begin{aligned}\text{rate} &= -\frac{[\text{Br}_2]_{50\text{s}} - [\text{Br}_2]_{0\text{s}}}{50\text{s} - 0\text{s}} \\ &= -\frac{0.0101M - 0.0120M}{50\text{s}} = 3.8 \times 10^{-5} M/\text{s}\end{aligned}$$

For the second

$$\text{rate} = -\frac{0.0101M - 0.0120M}{100\text{s} - 50\text{s}} = 3.3 \times 10^{-5} M/\text{s}$$

## Instantaneous Rate of reaction

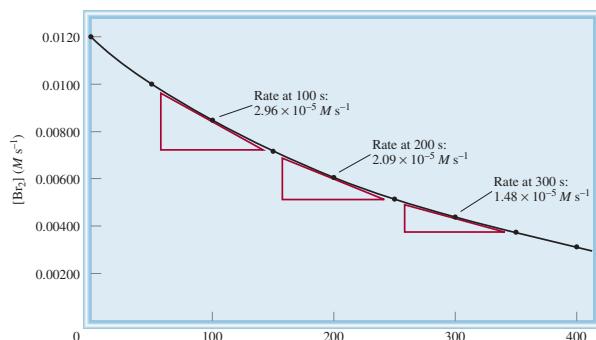
The **instantaneous rate of reaction** is the rate of the reaction in the limit that the time interval goes to zero - that is, it is the **slope** of the concentration versus time curve



$$\text{instantaneous rate} = -\lim_{\Delta t \rightarrow 0} \frac{[\text{Br}_2]_{t+\Delta t} - [\text{Br}_2]_t}{\Delta t} = -\frac{d[\text{Br}_2]}{dt}$$

Measured reaction progress data

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350.0	0.00353
400.0	0.00296



# Reaction Rates and Stoichiometry

The rates of production or depletion of products and reactants are related by the stoichiometry



Rate of depletion of A =  $(1/2) \times$  rate of production of B

$$\frac{\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{\Delta[B]}{\Delta t}$$

In general:  $aA + b B \rightarrow c C + d D$

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

## Reaction Rates and Stoichiometry: Example

Consider the reaction



- (a) If  $N_2O_5(g)$  is formed at a rate of  $0.048 \text{ M/s}$ , what is the rate of depletion of  $NO_2(g)$

$$\frac{\Delta[NO_2]}{\Delta t} = -2 \frac{\Delta[N_2O_5]}{\Delta t} = -2 \times 0.048 \text{ M/s} = -0.096 \text{ M/s}$$

$NO_2$  is being depleted at a rate of  $0.096 \text{ M/s}$

- (b) What is the overall rate of the reaction

$$\text{rate} = \frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = 0.024 \text{ M/s}$$

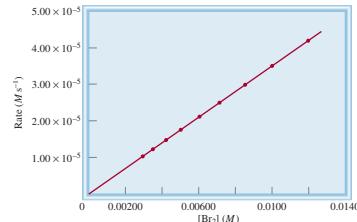
# Rate Laws

A **rate law** is an equation relating the rate of a reaction to the concentration of the reactants raised to some powers

Look back at decomposition of  $\text{Br}_2(aq)$



Time (s)	$[\text{Br}_2] (M)$	Instantaneous Rate ( $M \text{ s}^{-1}$ )	$k = \frac{\text{rate}}{[\text{Br}_2]} (\text{s}^{-1})$
0.0	0.0120	$4.20 \times 10^{-5}$	$3.50 \times 10^{-3}$
50.0	0.0101	$3.52 \times 10^{-5}$	$3.49 \times 10^{-3}$
100.0	0.00846	$2.96 \times 10^{-5}$	$3.50 \times 10^{-3}$
150.0	0.00710	$2.49 \times 10^{-5}$	$3.51 \times 10^{-3}$
200.0	0.00596	$2.09 \times 10^{-5}$	$3.51 \times 10^{-3}$
250.0	0.00500	$1.75 \times 10^{-5}$	$3.50 \times 10^{-3}$
300.0	0.00420	$1.48 \times 10^{-5}$	$3.52 \times 10^{-3}$
350.0	0.00353	$1.23 \times 10^{-5}$	$3.48 \times 10^{-3}$
400.0	0.00296	$1.04 \times 10^{-5}$	$3.51 \times 10^{-3}$



$$\text{rate} = -\frac{\Delta [\text{Br}_2]}{\Delta t} = k[\text{Br}_2]$$

$k$  is called the *rate constant*      Here  $k = 3.50 \times 10^{-3} \text{ s}^{-1}$

# Rate Laws

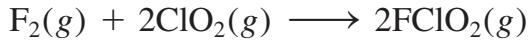
A **rate law** is an equation relating the rate of a reaction to the concentration of the reactants raised to some powers

In general for  $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$   
 $\text{rate} = k[\text{A}]^x[\text{B}]^y$

$x$  and  $y$  are experimentally determined and are not necessarily the same as the stoichiometric coefficients.

The sum of  $x + y$  here is called the **reaction order**

# Rate Laws: Example



Rate data for the reaction of  $\text{F}_2$  and  $\text{ClO}_2$

[ $\text{F}_2$ ] (M)	[ $\text{ClO}_2$ ] (M)	Initial Rate (M s <sup>-1</sup> )
1. 0.10	0.010	$1.2 \times 10^{-3}$
2. 0.10	0.040	$4.8 \times 10^{-3}$
3. 0.20	0.010	$2.4 \times 10^{-3}$

Doubling [ $\text{F}_2$ ] with [ $\text{ClO}_2$ ] constant doubles the rate

Quadrupling [ $\text{ClO}_2$ ] with [ $\text{F}_2$ ] constant quadruples the rate

Therefore, we can conclude that the rate law is

$$\text{rate} = k[\text{F}_2][\text{ClO}_2]$$

From the data, we find

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{F}_2][\text{ClO}_2]} \\ &= \frac{1.2 \times 10^{-3} \text{ M s}^{-1}}{(0.10 \text{ M})(0.010 \text{ M})} \\ &= 1.2 \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

Reaction is 1<sup>st</sup> order with respect to both  $\text{F}_2$  and  $\text{ClO}_2$  and 2<sup>nd</sup> order (1 + 1) overall

## Integrated Rate Laws

Using calculus, the rate laws can be transformed by the process of integration to give **integrated rate laws**, which tell us the concentrations of reactants at any time during the course of a reaction.

The exact form of these rate laws depend upon the order of the reaction

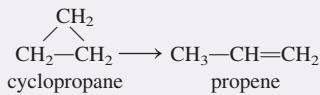
$$\textbf{First Order Reactions} \quad \text{rate} = -\frac{d[A]}{dt} = k[A]$$

$$\text{Rearranging: } \frac{1}{[A]} d[A] = -k dt \rightarrow \text{Integrating: } \int_{[A]_0}^{[A]_t} \frac{1}{[A]} d[A] = - \int_0^t k dt$$

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad [A]_t = [A]_0 e^{-kt}$$

# First-Order Rate Law: Example

The gas-phase conversion of cyclopropane to propene is a first-order reaction with a rate constant  $k = 6.7 \times 10^{-4} \text{ s}^{-1}$  at 500°C



- (a) If the initial concentration of cyclopropane was 0.25M, what is the concentration after 8.8 min?
- (b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from 0.25M to 0.15M?

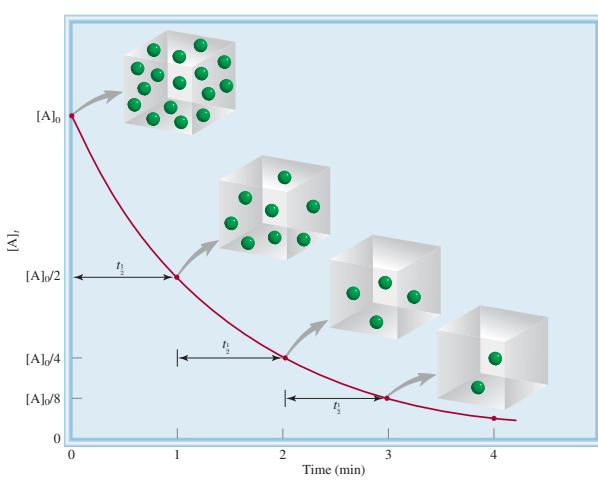
$$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$$

$$[\text{A}]_t = [\text{A}]_0 e^{-kt}$$

# First-Order Rate Law: Half-life

The **half-life ( $t_{1/2}$ )** of a reaction is the *time required for the concentration of a reactant to decrease to one-half of its original concentration*.

For a 1<sup>st</sup>-order reaction, the half-life is independent of concentration



$$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$$

$$\ln \frac{[\text{A}]_0/2}{[\text{A}]_0} = -kt_{1/2}$$

$$\ln (1/2) = -kt_{1/2}$$

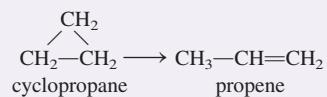
$$-\ln(2) = -kt_{1/2}$$



$$t_{1/2} = \frac{\ln(2)}{k} \approx \frac{0.693}{k}$$

## First-Order Rate Law: Example

The gas-phase conversion of cyclopropane to propene is a first-order reaction with a rate constant  $k = 6.7 \times 10^{-4} \text{ s}^{-1}$  at 500°C



What is the  $\frac{1}{2}$  life?

$$t_{1/2} = \frac{\ln(2)}{k} \approx \frac{0.693}{k}$$

## Integrated Rate Law for zero-order reactions

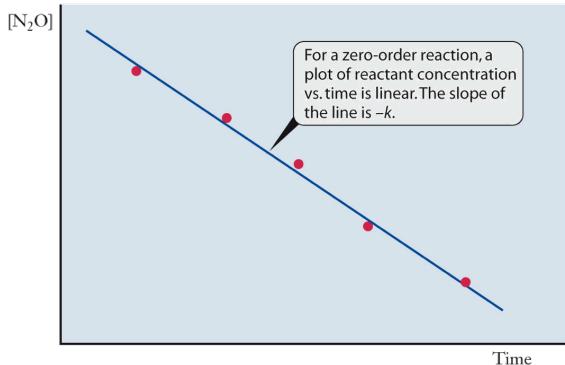
*Zero-Order Reactions:* A → product

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^0 = k$$

This is easily integrated to give

$$[A]_t = [A]_0 - kt$$

**Example:**  
decomposition of  
 $\text{N}_2\text{O}$  at a gold surface



## Integrated Rate Law for second-order reactions

**Second-Order Reactions:** A → product

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2$$

This is easily integrated

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = - \int_0^t k dt$$

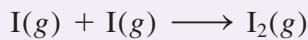
$\rightarrow$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$
$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

What is the  $\frac{1}{2}$ -life of a second order reaction?

### Example: 2<sup>nd</sup>-order reaction integrated rate law

Iodine atoms combine to form molecular iodine in the gas phase:

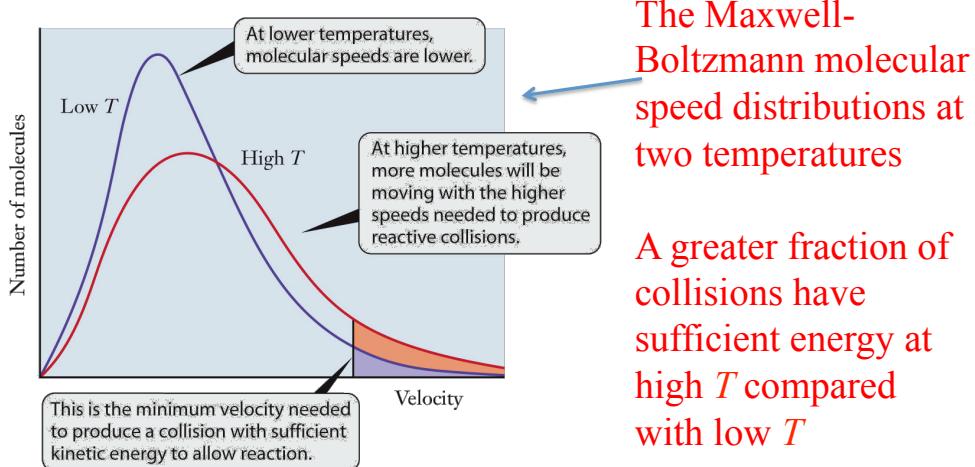


This reaction follows second-order kinetics with  $k = 7.0 \times 10^9 M^{-1} s^{-1}$  at 23°C.

- (a) If the initial concentration of I was 0.086 M, calculate the concentration after 2.0 min. (b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42 M.

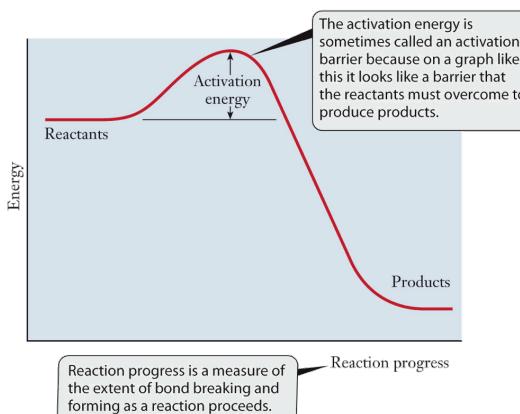
# Temperature dependence of rate constants

- To react, the energy of the collision needs to be sufficient to overcome the *activation energy* of the reaction
- In a gas phase reaction, generally only a small fraction of collisions have sufficient energy



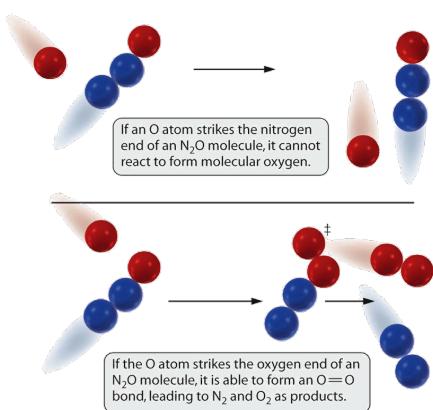
# Temperature dependence of rate constants

- Generally, rate constants will *increase* with temperature
- Reactions generally occur only when molecules collide: (either 2 reactants or a reactant and a non-reacting molecule)
- To react, the energy of the collision needs to be sufficient to overcome the *activation energy* of the reaction



## Temperature Effects on Molecules That React

- Collision geometry also plays an important role in determining if collisions are effective: **those improper geometry but sufficient kinetic energy are ineffective**



During an effective collision, both bond breaking and bond formation is occurring.

As bond rearrangement is occurring, an unstable intermediate species, called the ***activated complex*** and designated by  $\ddagger$ , exists in the reaction mixture.

## Arrhenius Law for $T$ -dependence of $k$

- The ***Arrhenius equation*** describes the temperature dependence of the rate constant,  $k$ .

$$k = A e^{-E_a/RT}$$

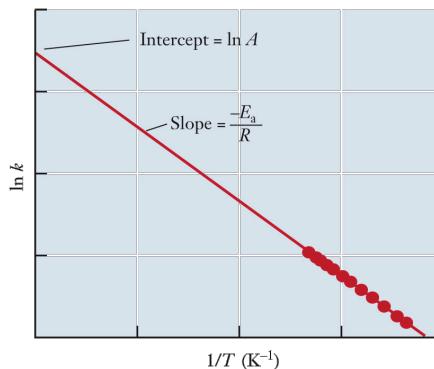
- $E_a$  is the ***activation energy***,  $R$  is the universal gas law constant,  $T$  is the absolute temperature, and  $A$  is the proportionality constant called the ***frequency factor*** or ***preexponential factor***.

$$(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$$

# Arrhenius Behavior

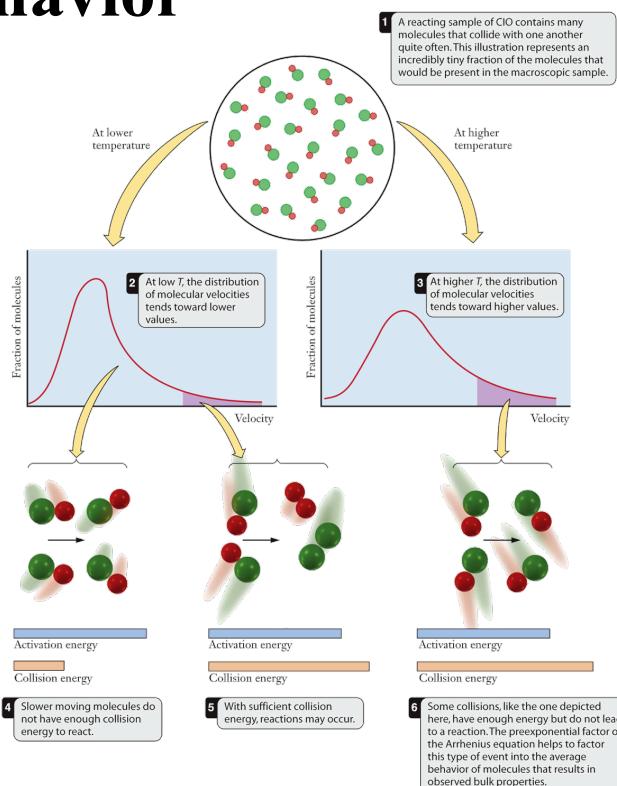
- The Arrhenius equation can be used to experimentally determine the activation energy for a reaction.
  - A plot of  $\ln k$  versus  $1/T$  for a reaction at different temperatures yields a linear plot. The slope of the line equals  $-E_a/R$ .

$$\ln k = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln A$$



# Arrhenius Behavior

- The connection between temperature, collision energy, and reaction rate.



# Arrhenius Law Example

The rate constant for the reaction



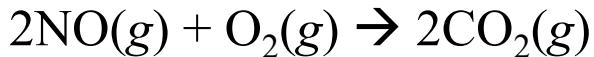
measured to be 0.011 and  $0.789 \text{ M}^{-1/2} \text{ s}^{-1}$  at 700K and 810K, respectively. Based on these data calculate the activation energy.

$$\ln k = \frac{-E_a}{R} \left( \frac{1}{T} \right) + \ln A$$

What is the activation energy of this reaction???

# Reaction Mechanisms

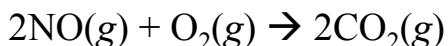
- The balanced chemical reaction does not tell us necessarily exactly how the reaction takes place.  
Example:



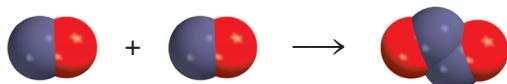
- From experiment we know that the rxn does not take place by 2NO and 1 O<sub>2</sub> colliding simultaneously because N<sub>2</sub>O<sub>2</sub> is detected
- So how does the reaction proceed?

## Elementary Steps make up a Reaction Mechanism

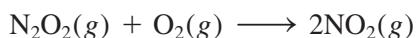
- A **reaction mechanism** is the sum of several **elementary steps** that lead to product formation –that is, *a series of simple reactions that represent the progress of the overall reaction at the molecular level.*
- Example: A possible reaction mechanism for



### Step 1

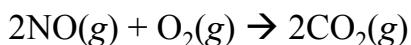


### Step 2



## Elementary Steps make up a Reaction Mechanism

- A **reaction mechanism** is the sum of several **elementary steps** that lead to product formation –that is, *a series of simple reactions that represent the progress of the overall reaction at the molecular level.*
- Example: A possible reaction mechanism for



*The overall reaction is a sum of elementary steps*



$\text{N}_2\text{O}_2$  is part of the mechanism, but not the overall reaction – it is called a **reaction intermediate**