

Chemical Kinetics

Chapter 13



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Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

Reaction rate is the change in the concentration of a reactant or a product with time (M/s).

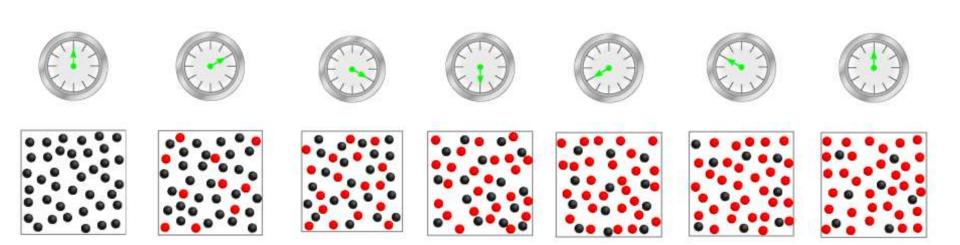
 $A \longrightarrow B$

rate =
$$\frac{\Delta[A]}{\Delta t}$$

rate = $\frac{\Delta[B]}{\Delta t}$

- $\Delta[A] = change in concentration of A over time period \Delta t$
- Δ [B] = change in concentration of B over time period Δt

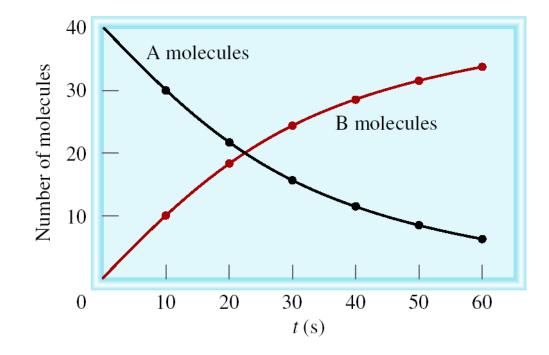
Because [A] decreases with time, Δ [A] is negative.



 $\longrightarrow B$

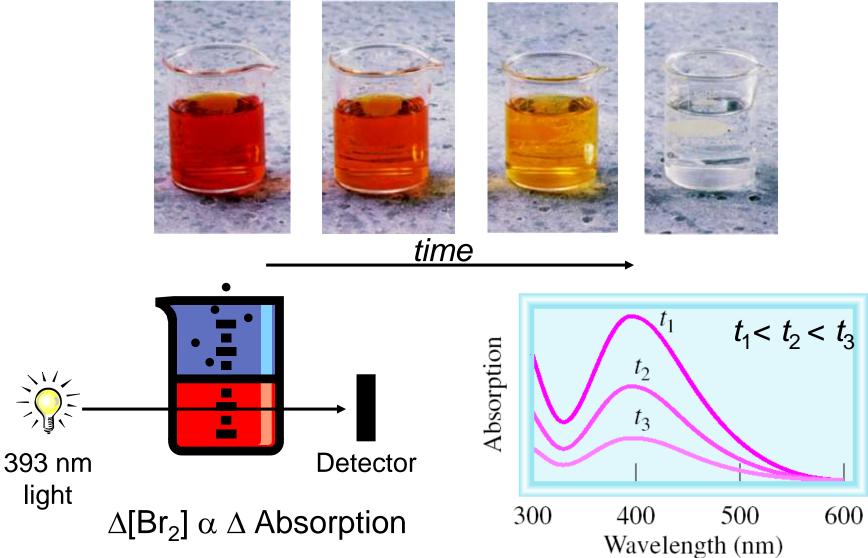
Α

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

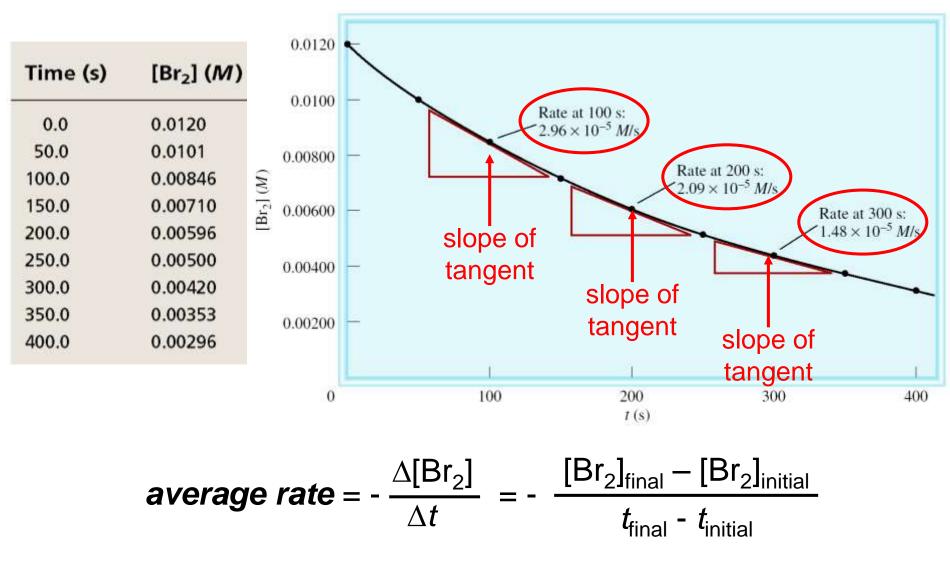


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$\frac{\text{red-brown}}{\text{Br}_2(aq)} + \text{HCOOH}(aq) \longrightarrow 2\text{Br}^-(aq) + 2\text{H}^+(aq) + \text{CO}_2(g)$

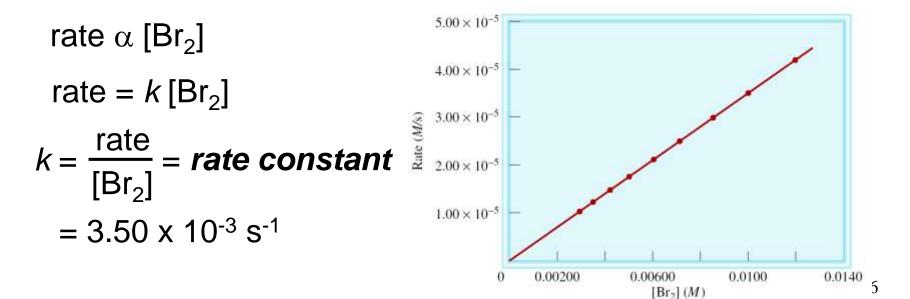


 $Br_2(aq) + HCOOH(aq) \longrightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$



instantaneous rate = rate for specific instance in time 5

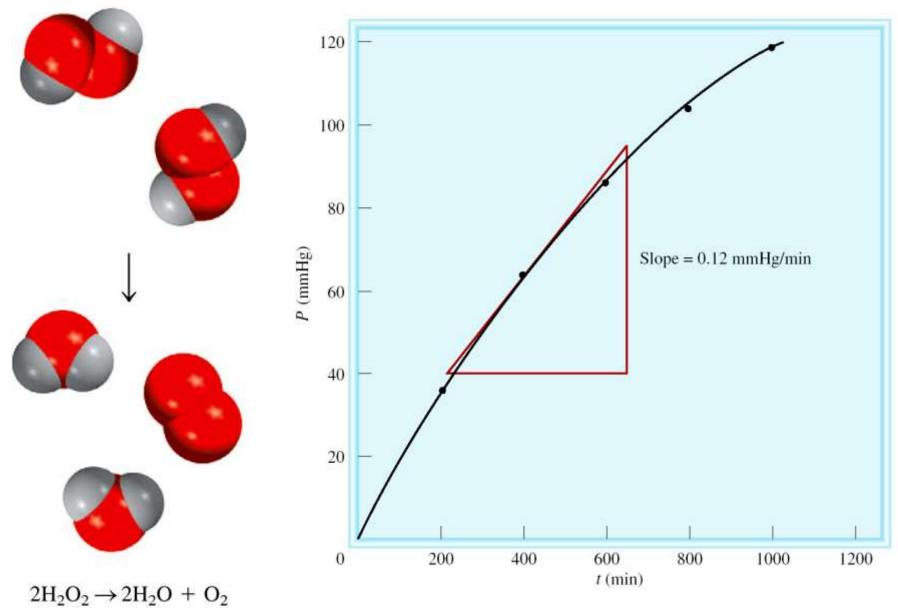
TABLE 13.1	Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C			
Time (s)	[Br ₂] (<i>M</i>)	Rate (M/s)	$k = \frac{\text{rate}}{[\text{Br}_2]} \text{ (s}^{-1}\text{)}$	
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}	
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}	
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}	
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}	
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}	
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}	
300.0	0.00420	1.48×10^{-5}	3.52×10^{-3}	
350.0	0.00353	1.23×10^{-5}	3.48×10^{-3}	
400.0	0.00296	1.04×10^{-5}	3.51×10^{-3}	





$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$				
PV = nRT				
$P = \frac{n}{V}RT = [O_2]RT$				
$[O_2] = \frac{1}{RT} P$				
$\Delta[O_2]$ 1 ΔP				
rate = $\frac{\Delta[O_2]}{\Delta t} = \frac{1}{RT} \frac{\Delta P}{\Delta t}$				

measure ΔP over time



Reaction Rates and Stoichiometry

 $2A \longrightarrow B$

Two moles of A disappear for each mole of B that is formed.

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

$$aA + bB \longrightarrow cC + dD$$

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

Write the rate expression for the following reaction:

$$CH_4(g) + 2\Phi_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

rate =
$$-\frac{\Delta[CH_4]}{\Delta t} = -\frac{1}{2}\frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

The Rate Law

The *rate law* expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

 $aA + bB \longrightarrow cC + dD$ Rate = $k [A \not B \not b]$

Reaction is **xth order** in A Reaction is **yth order** in B Reaction is **(x +y)th order overall**

$\mathsf{F}_{2}\left(g\right) + 2\mathsf{CIO}_{2}\left(g\right) \longrightarrow 2\mathsf{FCIO}_{2}\left(g\right)$

TABLE 13.2	Rate Data for th	e Reaction Between F ₂ and ClO ₂
[F ₂] (M)	[CIO ₂] (M)	Initial Rate (M/s)
1. 0.10	0.010	1.2×10^{-3}
2. 0.10	0.040	$4.8 imes 10^{-3}$
3. 0.20	0.010	2.4×10^{-3}

rate = $k [F_2]^x [CIO_2]^y$

Double [F₂] with [CIO₂] constant

Rate doubles

x = 1

Quadruple [CIO₂] with [F₂] constant

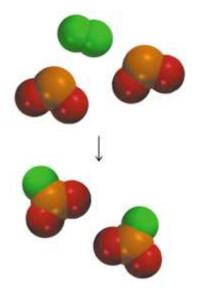
rate = $k [F_2][CIO_2]$

Rate quadruples

y = 1

Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



$$F_{2}(g) + 2O(O_{2}(g)) \longrightarrow 2FCO_{2}(g)$$

rate = $k [F_{2}][CO_{2}]^{1}$

Determine the rate law and calculate the rate constant for the following reaction from the following data: $S_2O_8^{2-}(aq) + 3I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$

Experiment	[S ₂ O ₈ ²⁻]	[I-]	Initial Rate (<i>M</i> /s)
1	0.08	0.034	2.2 x 10 ⁻⁴
2	0.08	0.017	1.1 x 10 ⁻⁴
3	0.16	0.017	2.2 x 10 ⁻⁴

rate =
$$k [S_2O_8^{2-}]^x [I^-]^y$$

 $y = 1$
 $x = 1$
rate = $k [S_2O_8^{2-}][I^-]$

Double [I⁻], rate doubles (experiment 1 & 2)

Double [S₂O₈²⁻], rate doubles (experiment 2 & 3)

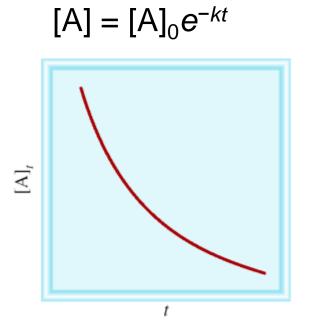
$$k = \frac{\text{rate}}{[S_2 O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4} \text{ M/s}}{(0.08 \text{ M})(0.034 \text{ M})} = 0.08/\text{M} \cdot \text{s}$$

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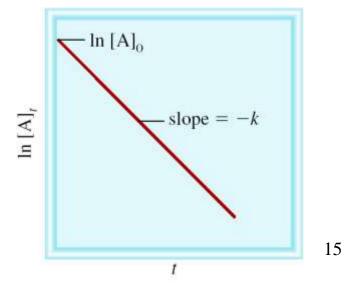
First-Order Reactions

$$A \longrightarrow \text{product} \quad \text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = k [A]$$

$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/s \text{ or } s^{-1} \qquad -\frac{\Delta[A]}{\Delta t} = k [A]$$
[A] is the concentration of A at any time t
[A]₀ is the concentration of A at time t=0

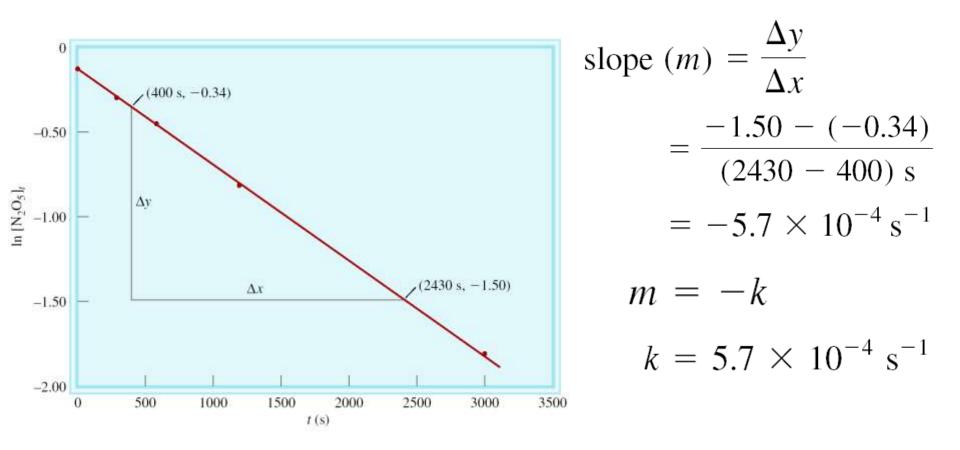


 $\ln[A] = \ln[A]_0 - kt$



Graphical Determination of k

$$2N_2O_5 \longrightarrow 4NO_2(g) + O_2(g)$$



The reaction $2A \longrightarrow B$ is first order in A with a rate constant of 2.8 x 10^{-2} s⁻¹ at 80°C. How long will it take for A to decrease from 0.88 *M* to 0.14 *M*?

 $ln[A] = ln[A]_0 - kt$ [A]_0 = 0.88 M
[A] = 0.14 M

$$kt = \ln[A]_{0} - \ln[A]$$
$$t = \frac{\ln[A]_{0} - \ln[A]}{k} = \frac{\ln \frac{[A]_{0}}{[A]}}{k} = \frac{\ln \frac{0.88 M}{0.14 M}}{2.8 \times 10^{-2} \text{ s}^{-1}} = 66 \text{ s}$$

First-Order Reactions

The *half-life*, $t_{\frac{1}{2}}$, is the time required for the concentration of a reactant to decrease to half of its initial concentration.

 $t_{\frac{1}{2}} = t$ when [A] = [A]_0/2

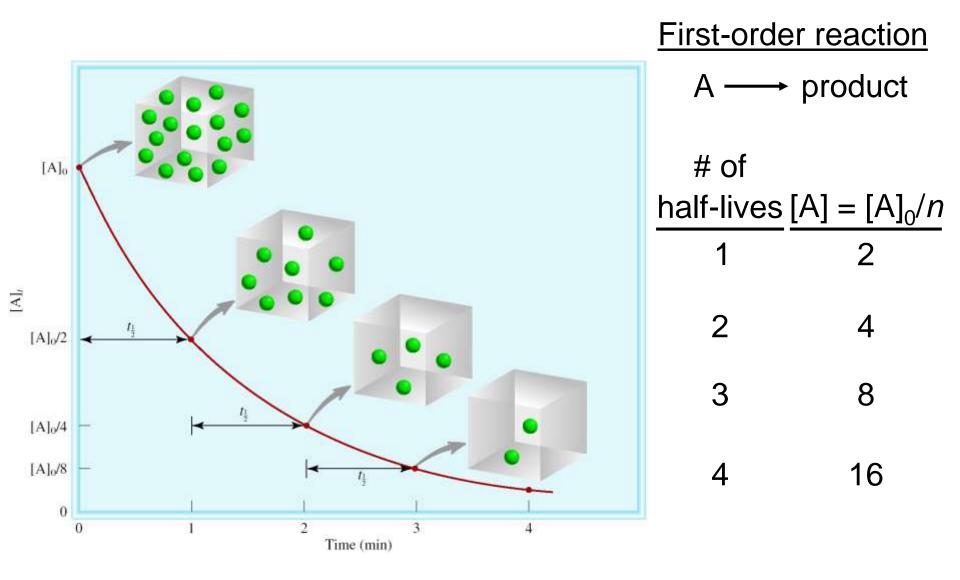
$$t_{\frac{1}{2}} = \frac{\ln \frac{[A]_{0}}{[A]_{0}/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

What is the half-life of N_2O_5 if it decomposes with a rate constant of 5.7 x 10⁻⁴ s⁻¹?

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4} \text{ s}^{-1}} = 1200 \text{ s} = 20 \text{ minutes}$$

How do you know decomposition is first order?

units of k (s⁻¹) ¹⁸



Second-Order Reactions

$$A \longrightarrow \text{product} \quad \text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = k [A]^2$$

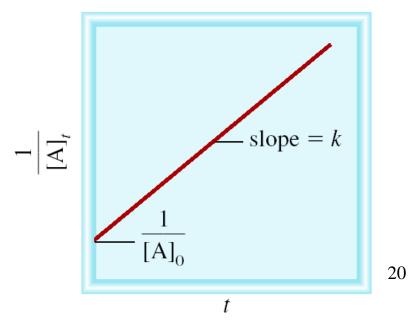
$$\text{rate} \quad M/s \quad \text{rate} \quad \Delta[A]$$

$$k = \frac{\text{fate}}{[A]^2} = \frac{N/S}{M^2} = 1/M \cdot s \qquad -\frac{\Delta[A]}{\Delta t} = k [A]^2$$

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

[A] is the concentration of A at any time t[A]₀ is the concentration of A at time t=0

$$t_{\frac{1}{2}} = t$$
 when [A] = [A]_0/2
 $t_{\frac{1}{2}} = \frac{1}{k[A]_0}$



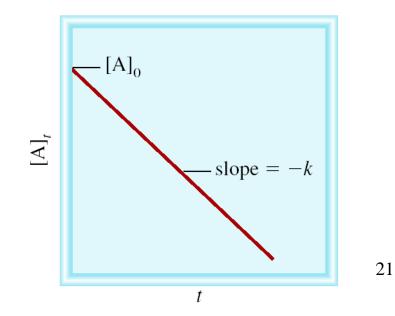
Zero-Order Reactions

$$A \longrightarrow \text{product} \quad \text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{rate} = k [A]^0 = k$$
$$k = \frac{\text{rate}}{[A]^0} = M/s \quad -\frac{\Delta[A]}{\Delta t} = k$$

$$[\mathsf{A}] = [\mathsf{A}]_0 - kt$$

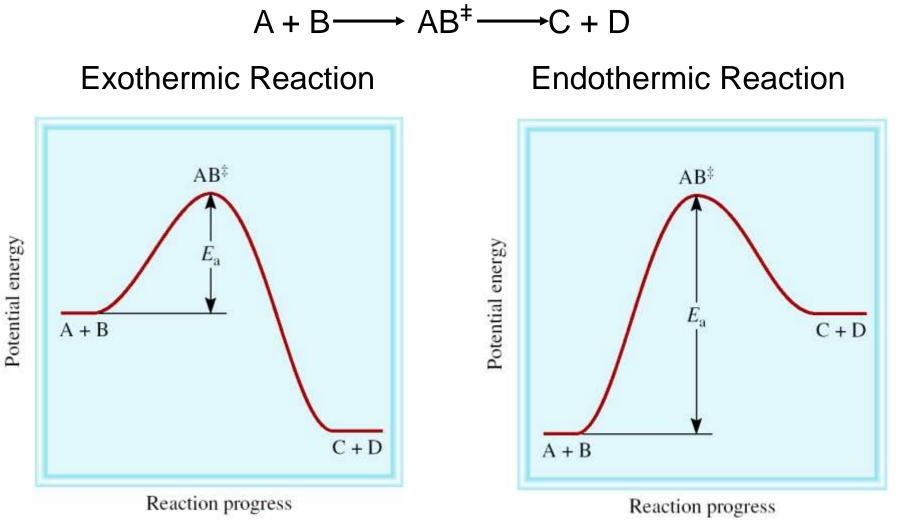
[A] is the concentration of A at any time t[A]₀ is the concentration of A at time t = 0

$$t_{\frac{1}{2}} = t$$
 when $[A] = [A]_0/2$
 $t_{\frac{1}{2}} = \frac{[A]_0}{2k}$



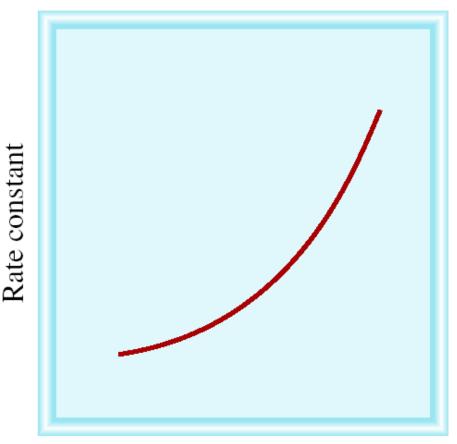
Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$
1	rate = k [A]	ln[A] = ln[A] ₀ - <i>kt</i>	$t_{\frac{1}{2}} = \frac{\ln 2}{k}$
2	rate = $k [A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$



The *activation energy* (E_a) is the minimum amount of energy required to initiate a chemical reaction.

Temperature Dependence of the Rate Constant



Temperature

 $k = A \cdot e^{(-E_a/RT)}$

(Arrhenius equation)

 E_a is the activation energy (J/mol) *R* is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

Alternate format:

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$

Alternate Form of the Arrhenius Equation

At two temperatures, T_1 and T_2

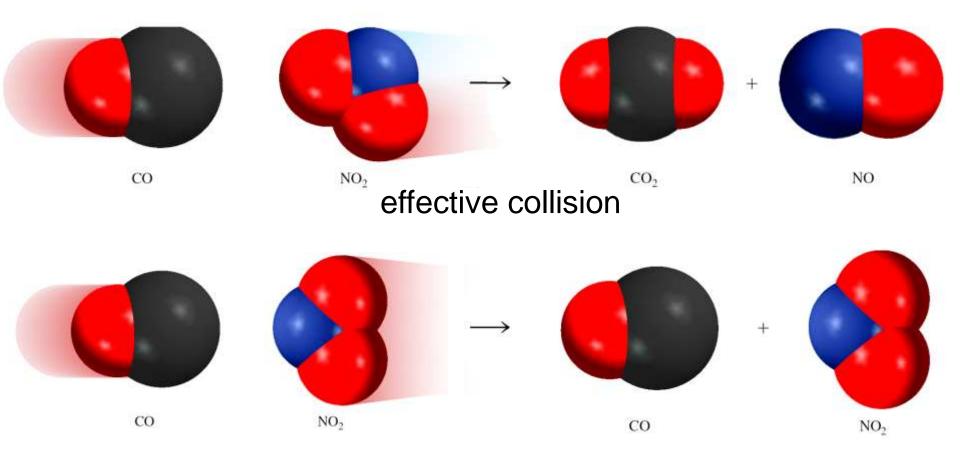
$$\ln\frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

Importance of Molecular Orientation

 $CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$



ineffective collision

Reaction Mechanisms

The overall progress of a chemical reaction can be represented at the molecular level by a series of simple *elementary steps* or *elementary reactions*.

The sequence of **elementary steps** that leads to product formation is the *reaction mechanism*.

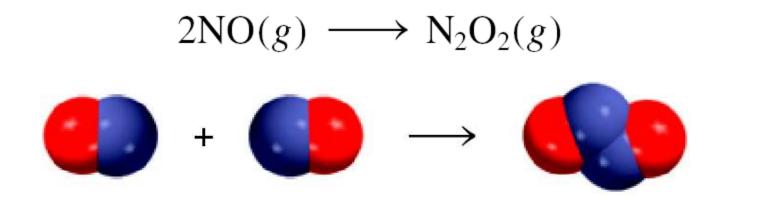
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

 N_2O_2 is detected during the reaction!

Elementary step:NO + NO \longrightarrow N_2O_2 + Elementary step: $N_2O_2 + O_2 \longrightarrow 2NO_2$ Overall reaction: $2NO + O_2 \longrightarrow 2NO_2$

 $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Mechanism:

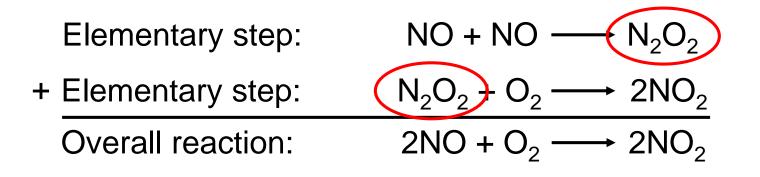


 $N_2O_2(g) + O_2(g) \longrightarrow 2NO_2(g)$



Intermediates are species that appear in a reaction mechanism **but not** in the overall balanced equation.

An **intermediate** is always formed in an early elementary step and consumed in a later elementary step.



The *molecularity of a reaction* is the number of molecules reacting in an elementary step.

- Unimolecular reaction elementary step with 1 molecule
- **Bimolecular reaction** elementary step with 2 molecules
- Termolecular reaction elementary step with 3 molecules

Rate Laws and Elementary Steps

Unimolecular reaction $A \longrightarrow \text{products}$ rate = k [A] Bimolecular reaction $A + B \longrightarrow \text{products}$ rate = k [A][B]

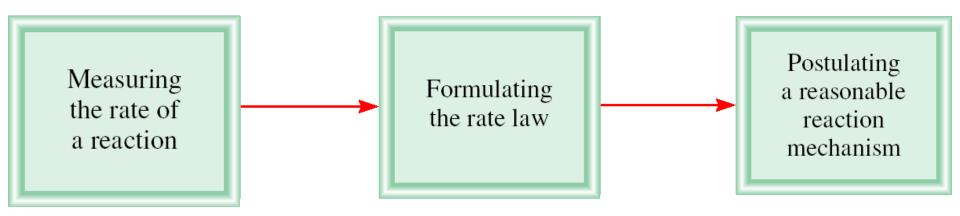
Bimolecular reaction $A + A \longrightarrow \text{products}$ rate = $k [A]^2$

Writing plausible reaction mechanisms:

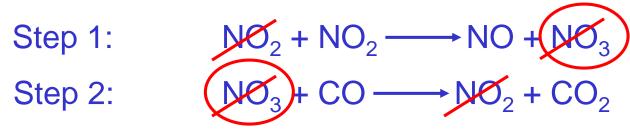
- The sum of the elementary steps **must** give the overall balanced equation for the reaction.
- The rate-determining step should predict the same rate law that is determined experimentally.

The *rate-determining step* is the **slowest** step in the sequence of steps leading to product formation.

Sequence of Steps in Studying a Reaction Mechanism



The experimental rate law for the reaction between NO₂ and CO to produce NO and CO₂ is rate = $k[NO_2]^2$. The reaction is believed to occur via two steps:



What is the equation for the overall reaction?

$$NO_2 + CO \longrightarrow NO + CO_2$$

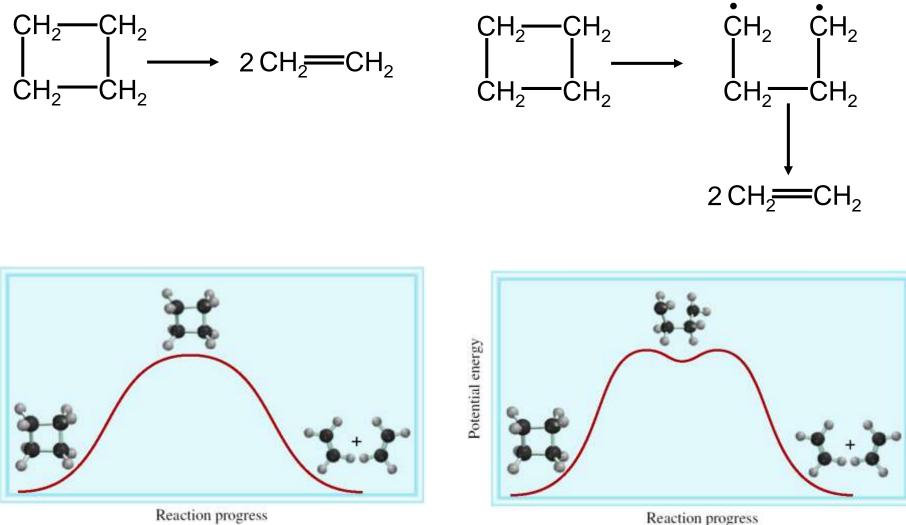
What is the intermediate?

 NO_3

What can you say about the relative rates of steps 1 and 2?

rate = $k[NO_2]^2$ is the rate law for step 1 so step 1 must be slower than step 2

Chemistry In Action: Femtochemistry



Reaction progress

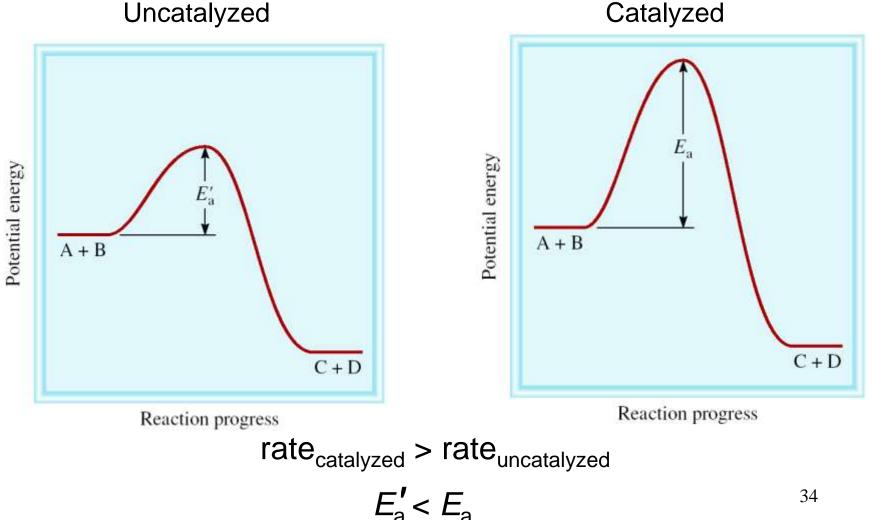
Potential energy

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A *catalyst* is a substance that increases the rate of a chemical reaction without itself being consumed.

$$k = A \cdot e^{(-E_a/RT)}$$

Uncatalyzed



 $E_a \downarrow$

k

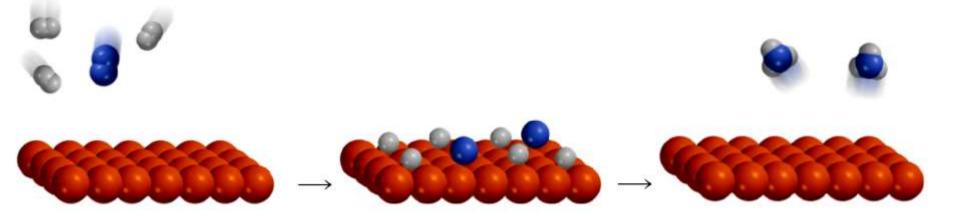
In *heterogeneous catalysis*, the reactants and the catalysts are in different phases.

- Haber synthesis of ammonia
- Ostwald process for the production of nitric acid
- Catalytic converters

In *homogeneous catalysis*, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
- Base catalysis

Haber Process



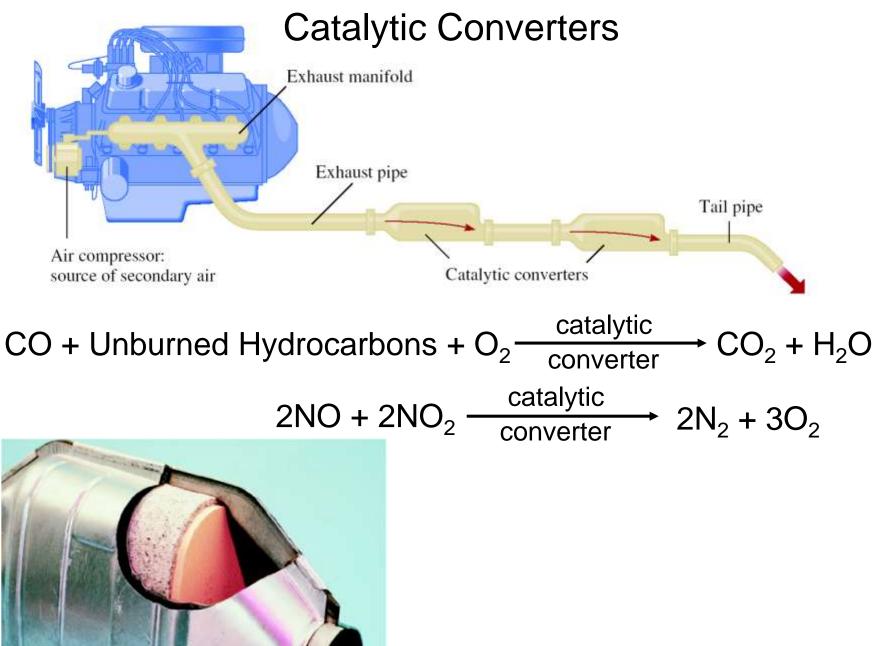
$$N_2(g) + 3H_2(g) \xrightarrow{Fe/Al_2O_3/K_2O} 2NH_3(g)$$

Ostwald Process

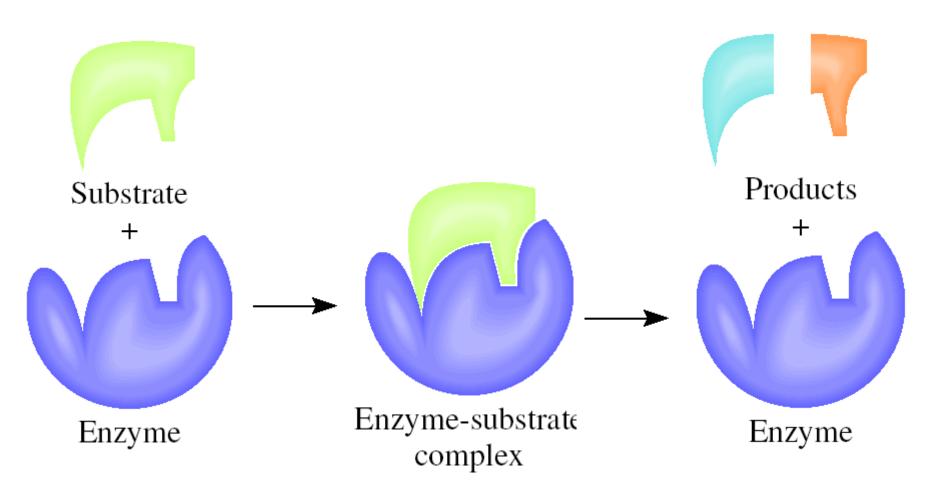
 $4NH_{3}(g) + 5O_{2}(g) \xrightarrow{\text{Pt catalyst}} 4NO(g) + 6H_{2}O(g)$ $2NO(g) + O_{2}(g) \longrightarrow 2NO_{2}(g)$ $2NO_{2}(g) + H_{2}O(l) \longrightarrow HNO_{2}(aq) + HNO_{3}(aq)$



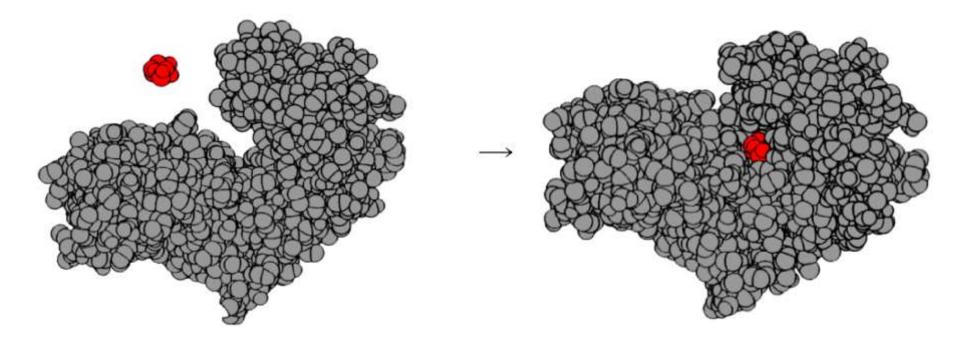
Pt-Rh catalysts used in Ostwald process



Enzyme Catalysis



Binding of Glucose to Hexokinase



Enzyme Kinetics

