

- Factors that Influence Reaction Rate
- Expressing the Reaction Rate
 - Average, Instantaneous, Initial Reaction rates
 - Rate & Concentration
- The Rate Law and its Components
 - Determining the Initial Rate
 - Reaction Order Terminology
 - Determining Reaction Orders
 - Determining the Rate Constant

- Integrated Rate Laws: Concentration Changes Over Time
 - First, Second, and Zero-Order Reactions
 - Reaction Order
 - Reaction Half-Life
- The Effect of Temperature on Reaction Rate
- Explaining the Effects of Concentration and Temperature
 - Collision Theory
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- Reaction Mechanisms: Steps in the Overall reaction
 - Elementary Reactions
 - The Rate-Determining Step
 - The Mechanism and the Rate Law
- Catalysis: Speeding up a Chemical Reaction
 - Homogeneous Catalysis
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Chemical Kinetics

- Chemical Kinetics is the study of:
 - Chemical Reaction Rates
 - The changes in chemical concentration of reactants as a function of time
- Chemical reactions range from:
Very Fast to Very Slow
- Under a given set of conditions each reaction has its own rate
- Factors that influence reaction rate:
 - Concentration
 - Physical state (surface area)
 - Temperature (frequency & energy of particle collisions)

Chemical Kinetics

■ Factors That Influence Reaction Rate

➤ Concentration

- ◆ Molecules must Collide to React
- ◆ Reaction rate is proportional to the concentration of the reactants

Rate \propto Collision Frequency \propto Concentration

➤ Physical State

- ◆ Molecules must Mix to Collide
- ◆ The more finely divided a solid or liquid reactant:
 - The greater its surface area per unit volume
 - The more contact it makes with the other reactants
 - The faster the reaction occurs

Chemical Kinetics

➤ Temperature

- ◆ Molecules must collide with enough energy to react
- ◆ At a higher temperature, more collisions occur in a given time
- ◆ Raising the temperature increases the reaction rate by increasing the number and energy of the collisions

Rate \propto Collision Energy \propto Temperature

Chemical Kinetics

- A fundamental question addressed in chemical reactions is “how fast does the reaction occur?”
- Kinetics is the study of the rate of chemical reactions
 - rate is a time dependent process
- Rate units are concentration over time
- Consider the reaction $A \rightarrow B$
- Reactant concentrations $[A]$ decrease while product concentrations $[B]$ increase

$$\text{Rate of Reaction} = - \frac{\text{change in concentration of A}}{\text{change in time}} = - \frac{\text{conc } A_2 - \text{conc } A_1}{t_2 - t_1} = - \frac{\Delta(\text{conc } A)}{\Delta t}$$

- Note: Reaction rate is positive, but the concentration of A at t_2 (A_2) is always less than the concentration of A at t_1 (A_1), thus, the change in concentration (final – initial) of reactant A is always negative

Chemical Kinetics

- Consider the reaction:



- Concentrations of both reactants ([A] & [B]) decrease at the same rate

$$\text{Rate} = \frac{\text{change in concentration}}{\text{change in time}}$$

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

- **d** Indicates “Change in” (final - initial)
- **Brackets []** indicate concentration
- **Note minus sign in front of term reflecting the decrease in concentration with time**

Chemical Kinetics

- Reaction - Butyl Chloride (C_4H_9Cl) and Water (H_2O)



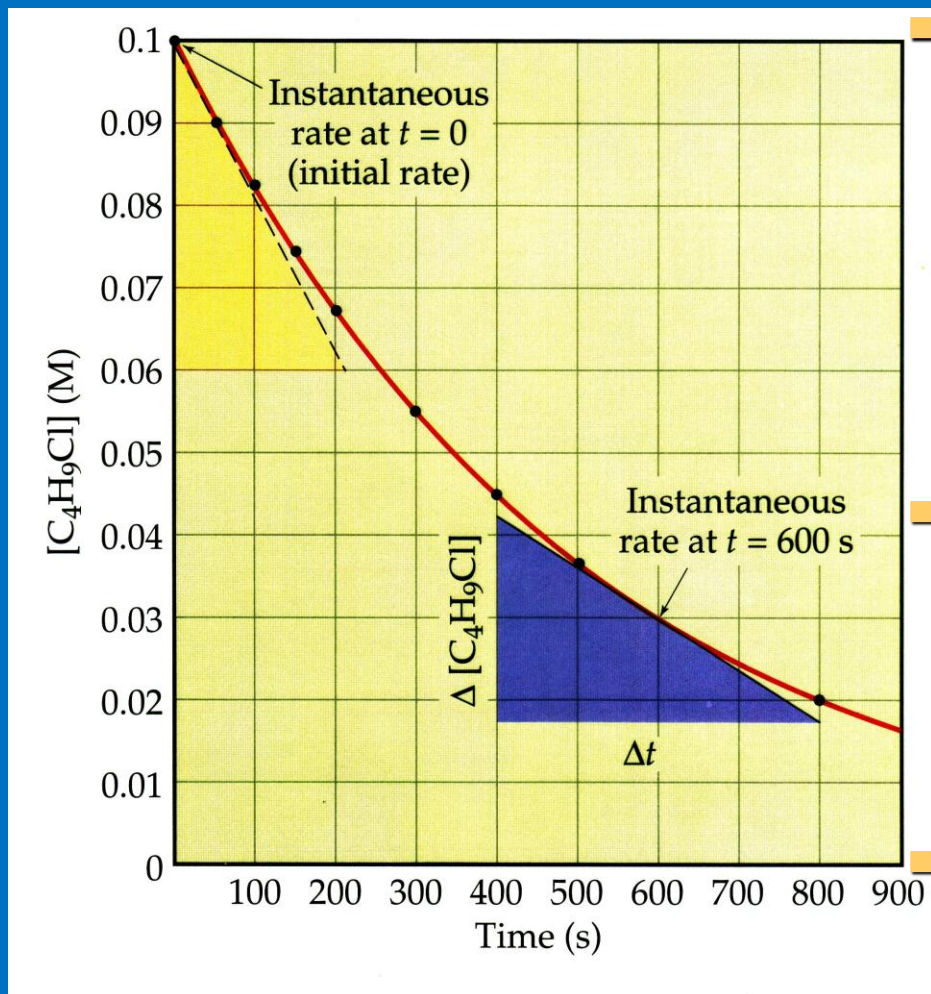
Rate Data for Reaction of C_4H_9Cl with Water

TABLE 14.2 Rate Data for Reaction of C_4H_9Cl with Water		
Time, t (s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

$$\text{Ex. rate} = -\frac{\Delta A}{\Delta t} = -\left(\frac{0.0905 \text{ mol/L} - 0.1000 \text{ mol/L}}{50.0 \text{ s} - 0.0 \text{ s}}\right) = 1.9 \times 10^{-4} \text{ mol/sec}$$

Chemical Kinetics

Butyl Chloride (C_4H_9Cl)



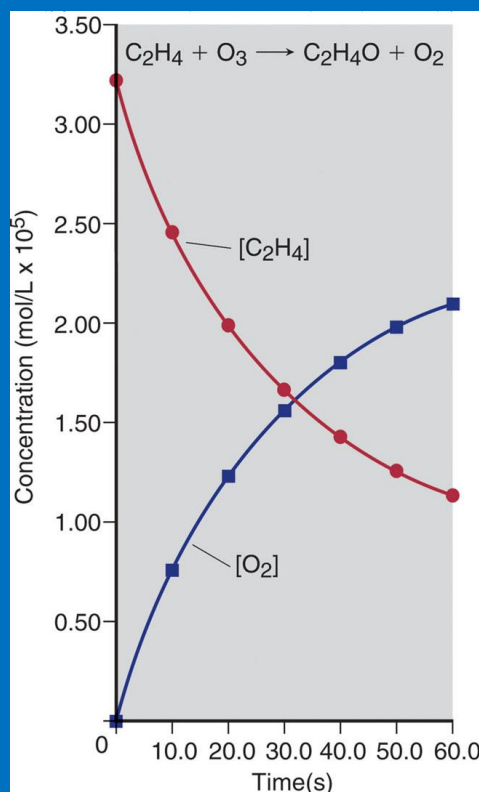
When plotting **Concentration versus Time** for a chemical reaction, the tangent at any point on the curve (drawn through the concentration points) defines the **instantaneous rate** of the reaction

The **average rate** of a reaction over some time interval is determined through triangulation of concentration plot (slope of hypotenuse of right triangle)

The rate of the reaction **decreases** over time as the reactants are consumed

Chemical Kinetics

- Rate of reaction of the Products
- The rate of reaction for the formation of the products is the same as for the reactants, but opposite, that is the concentrations are increasing



$$\text{Rate} = - \frac{\Delta[C_2H_4]}{\Delta t} = - \frac{\Delta[O_3]}{\Delta t} = + \frac{\Delta[C_2H_4O]}{\Delta t} = + \frac{\Delta[O_2]}{\Delta t}$$

The rate of change of Ethane (C₂H₄) and Ozone (O₃) is the same, but exactly opposite for Acetaldehyde (C₂H₄O) and Oxygen (O₂)

Product concentration increases at the same rate that the reactant concentrations decrease

The curves have the same shape, but are inverted

Chemical Kinetics

- The Rate expression must be consistent with stoichiometry
- When the stoichiometric molar ratios are not 1:1, the reactants still disappear and the products still appear, but at different rates



- For every molecule of H_2 that disappears, one molecule of I_2 disappears and 2 molecules of HI appear
- The rate of H_2 decrease is the same as the rate of I_2 decrease, but both are only half the rate of HI increase

$$\text{Rate} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$$

Chemical Kinetics

- Summary equation for any reaction



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

- The rate of a reaction is dependent on the concentration of reactants
- The average reaction rate is the change in reactant (or) product concentration over a change in time, Δt
- The instantaneous rate at a time, t , is obtained from the slope of the tangent to a concentration vs. time curve at a given time, t

Chemical Kinetics

- As reactant concentrations decrease, the reaction rates decrease with time
- Product concentrations increase at the same rate as the reactants relative to the stoichiometric ratios
- The rate of a reaction depends on the following variables:
 - ***reactant concentration***
 - ***temperature***
 - ***presence and concentration of a catalyst***
 - ***surface area of solids, liquids or catalysts***

Sample Problem

Write an expression defining equivalent rates for the loss of NO_2 and the formation of NO in the following reaction with respect to the rate of formation of O_2



$$\text{Rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t}$$

Chemical Kinetics –The Rate Law

- The dependence of reaction rate on concentrations is expressed mathematically by the **rate law**
- The **rate law** expresses the rate as a function of *reactant concentrations, product concentrations, and temperature*
- In the following development:

Only the Reactants Appear in the Rate Law

- For a general reaction at a fixed temperature:



the rate law has the form:

$$\text{Rate} = k[A]^m[B]^n \dots$$

Note: The Stoichiometric Coefficients – a, b, c – are not used in the rate law equation; they are not related to the reaction order terms – m, n, p, etc

Rate Law

■ Components of the rate law

➤ $aA + bB + \dots \rightarrow$ products

$$\text{Rate} = -\Delta[A]/\Delta t = k[A]^m[B]^n[C]^p$$

➤ $[A]$ & $[B]$ = concentrations of reactants (M)

➤ $[C]$ = concentration of catalyst (M, if used)

➤ k = rate constant

➤ m , n , & p = Reaction Orders

Note: Reaction Orders are not related to the Stoichiometric coefficients in the chemical equation

Chemical Kinetics

■ The Rate Law

- The rate constant " **k** " is a proportionality constant
- " **k** " changes with temperature; thus it determines how temperature affects the rate of the reaction
- The exponents (m , n , p , etc.) are called **reaction orders, which must be determined experimentally**
- Reaction orders define how the rate is affected by the reactant concentration
 - ◆ If the rate **doubles** when $[A]$ doubles, the rate depends on $[A]$ **raised to the first power, i.e.,**
 $m = 1$ (a 1st order reaction)
 - ◆ If the rate **Quadruples** when $[B]$ doubles, the rate depends on $[B]$ raised to the second power, i.e.,
 $n = 2$ (a 2nd order reaction)

Rate Constant - Units

- Units of the Rate Constant k change depending on the overall Reaction Order

Overall Reaction Order	Units of k (t in seconds)
0	$\text{mol/L}\cdot\text{s}$ (or $\text{mol L}^{-1} \text{s}^{-1}$)
1	$1/\text{s}$ (or s^{-1})
2	$\text{L/mol}\cdot\text{s}$ (or $\text{L mol}^{-1} \text{s}^{-1}$)
3	$\text{L}^2 / \text{mol}^2 \cdot \text{s}$ (or $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$)

The Rate Law

■ The Rate Law

- If the rate **does not change** even though $[A]$ doubles, the rate **does not** depend on the concentration of A and $m = 0$
- The Stoichiometric coefficients, a, b, c, etc. in the general balanced equation are not necessarily related in any way to the reaction orders m, n, etc.
- The components of the Rate Law – rate, reaction orders, rate constant – must be determined experimentally; they cannot be deduced or inferred from the balanced stoichiometric equation

Rate Law

■ The Rate Law - Examples



$$\text{Rate} = k[\text{NO}]^1[\text{O}_3]^1$$

Reaction is 1st order with respect to NO, $m=1$

Rate depends on [NO] raised to 1st power

Reaction is 1st order with respect to O₃, $n=1$

The overall reaction is 2nd order:

$$m + n = 1 + 1 = 2$$

Rate Law

The Rate Law - Examples



$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]^1$$

Reaction is 2nd order in NO and 1st order in H₂

Overall reaction is 2 + 1 = 3rd order

Note: [NO] coefficient (2) is not related to the [NO] reaction order (2)

Rate Law

- The rate law – Examples



$$\text{Rate} = k [(\text{CH}_3)_3\text{CBr}]^1 [\text{H}_2\text{O}]^0$$

or

$$\text{Rate} = k [(\text{CH}_3)_3\text{CBr}]^1$$

Reaction is first order in 2-bromo-2-methyl propane

Reaction is zero order ($n=0$) in water $[\text{H}_2\text{O}]^0$

Note: zero order reaction order terms, ex. $[\text{H}_2\text{O}]^0$ can be eliminated from the overall rate equation, i.e. any term raised to the "0" power is equal to 1

$$[\text{H}_2\text{O}]^0 = 1$$

Rate Law

■ The Rate Law - Examples



$$\text{Rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$$

The reaction order means that the rate depends on the square root of the Chlorine (Cl_2) concentration

If the initial Cl_2 concentration is increased by a factor of 4, while the initial concentration of CHCl_3 is kept the same, the rate increases by a factor of 2, the square root of the change in Cl_2

Rate Law

■ The Rate Law - Examples



$$\text{Rate} = k[\text{O}_3]^2[\text{O}_2]^{-1} = k \frac{[\text{O}_3]^2}{[\text{O}_2]^1}$$

Negative reaction orders are used when the law includes the product(s)

If the O_2 concentration doubles, the reaction proceeds at one half (1/2) the rate

Rate Law – Reaction Order

- Overall reaction order

Sum of Exponents in Rate Equation

<u>Order of Rxn</u>	<u>Possible Expression of Rate Law</u>
1	$k[A]$
2	$k[A]^2$
2	$k[A][B]$
3	$k[A]^2[B]$
3	$k[A][B][C]$

Practice Problem

- What is the reaction order of Acetaldehyde and the overall order in the following reaction



$$\text{Rate} = k [\text{CH}_3\text{CHO}]^{3/2}$$

Ans:

3/2 order in CH_3CHO

Overall order: 3/2

Practice Problem

Experiments are performed for the reaction



and the rate law has the been determined to be of the form

$$\text{Rate} = k [A]^x$$

Determine the value of the exponent "x" for each of the following:

a. [A] is tripled and you observe no rate change

$$\text{Ans: } x = 0 \quad k[3A]^0$$

b. [A] is doubled and the rate doubles

$$\text{Ans: } x = 1 \quad k[2A]^1$$

c. [A] is tripled and the rate increases by a factor of 27

$$\text{Ans: } x = 3 \quad k[3A]^3$$

Experimental Rate Law

- Concentration Exponents (reaction orders) must be determined ***experimentally*** because the stoichiometric balanced equation with its reaction coefficients, does not indicate the mechanism of the reaction
- Experimentally, the reaction is run with varying concentrations of the reactants, while observing the change in rate over time
- The initial rate of reaction is observed, where the rate is linear with time (instantaneous rate = average rate); usually just when the reaction begins

Experimental Rate Law

- Initial rates of reaction from experiments on the reaction:



$$\text{Rate} = k[\text{O}_2]^m[\text{NO}]^n$$

Determine "m" & "n" from experimental data

Initial Reactant Concentration (mol/L)			
Experiment	O ₂	NO	Initial Rate Mol/L•s
1	1.10x10 ⁻²	1.30x10 ⁻²	3.21x10 ⁻³
2	2.20x10 ⁻²	1.30x10 ⁻²	6.40x10 ⁻³
3	1.10x10 ⁻²	2.60x10 ⁻²	12.8x10 ⁻³
4	3.30x10 ⁻²	1.30x10 ⁻²	9.60x10 ⁻³
5	1.10x10 ⁻²	3.90x10 ⁻²	28.8x10 ⁻³

Rate equations from two applicable experiments are combined, depending on the reactant order to be determined

cont'd

Experimental Rate Law

Select the 1st two experiments where the effect of doubling the concentration of O₂ is observed at constant temperature

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{O}_2]_2^m [\text{NO}]_2^n}{k[\text{O}_2]_1^m [\text{NO}]_1^n}$$

K is constant and [NO] does not change

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{O}_2]_2^m}{[\text{O}_2]_1^m} = \left(\frac{[\text{O}_2]_2}{[\text{O}_2]_1} \right)^m$$

Substitute rate values and concentration values

$$\frac{6.40 \times 10^{-3} \text{ mol/l}\cdot\text{s}}{3.21 \times 10^{-3} \text{ mol/l}\cdot\text{s}} = \left(\frac{2.20 \times 10^{-2} \text{ mol/L}}{1.10 \times 10^{-2} \text{ mol/L}} \right)^m$$

$$1.99 = 2.00^m$$

$$\log(1.99) = m \times \log(2.00)$$

$$m = 1(\text{rounded})$$

Reaction is 1st order in O₂:
When [O₂] doubles, the rate doubles

cont'd

Experimental Rate Law

- Determining the Rate Constant (k)
- The rate data from any one of the experiments in the previous table can be used to compute the rate constant
- Using the first experiment:

$$[\text{O}_2] = 1.10 \times 10^{-2} \text{ mol/L}$$

$$[\text{NO}] = 1.30 \times 10^{-2} \text{ mol/L}$$

$$\text{Rate 1} = 3.21 \times 10^{-3} \text{ mol/L}\cdot\text{s}$$

$$\text{Rate 1} = k[\text{O}_2]^m[\text{NO}]^n$$

$$k = \frac{\text{Rate 1}}{[\text{O}_2]^m[\text{NO}]^n}$$

$m=1$; $n=2$ (From a 2nd calc using reactions 1 & 3) (Overall reaction order = $1 + 2 = 3$)

$$k = \frac{3.21 \times 10^{-3} \text{ mol/L}\cdot\text{s}}{\left(1.10 \times 10^{-2} \text{ mol/L}\right)^1 \left(1.30 \times 10^{-2} \text{ mol/L}\right)^2}$$

$$k = 1.73 \times 10^3 \text{ L}^2 / \text{mol}^2 \cdot \text{s} \quad (\text{Note units for overall reaction order} = 3)$$

Integrated Rate Laws

- Concentration changes over time
- Previous notes assume that time is not a variable and the rate or concentration for a reaction is at a given instant in time
- By using time as a factor in the reaction, the rate law can be integrated

“How long will it take for x moles per liter of reactant ‘A’ to be used up?”

“What are the concentrations of ‘A’ after ‘ y ’ minutes of the reaction?”

Integration of Rate Equation

First Order Reaction

$$-\frac{\Delta[A]}{\Delta t} = k[A]^1$$

Rearrange Equation

$$-\frac{\Delta[A]}{[A]} = k\Delta t \quad \left[\text{from calculus notation} \quad \left(\frac{1}{x} dx \right) = kdt \quad \int \frac{1}{x} dx = \ln x \right]$$

$$-\ln[A] = kt + C \quad (\text{at } t = 0, C = -\ln[A_0] \quad A_0 = \text{concentration at time} = 0)$$

$$-\ln([A]_t - [A]_0) = kt$$

$$\ln([A]_0 - [A]_t) = kt$$

$$\ln \frac{[A]_0}{[A]_t} = kt \quad \text{or} \quad \log \frac{[A]_0}{[A]_t} = \frac{kt}{2.303}$$

Integration of Rate Equation

■ Second Order Reaction

$$-\frac{\Delta[\mathbf{A}]}{\Delta t} = k[\mathbf{A}]^2$$

$$-\frac{\Delta[\mathbf{A}]}{[\mathbf{A}]^2} = k\Delta t \quad \left(\frac{1}{x^2} dx\right) = kdt \quad \int \frac{1}{x^n} dx = \frac{x^{n+1}}{n+1} = \frac{x^{-2+1}}{-2+1} = -\frac{1}{x}$$

$$-\left(-\frac{1}{[\mathbf{A}]}\right) = kt + C \quad \left(\text{at } t=0, C = \frac{1}{[\mathbf{A}]_0}\right)$$

$$-\left(-\frac{1}{[\mathbf{A}]_t}\right) = kt + \left(\frac{1}{[\mathbf{A}]_0}\right)$$

$$\left(\frac{1}{[\mathbf{A}]_t}\right) - \left(\frac{1}{[\mathbf{A}]_0}\right) = kt$$

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

Integration of Rate Equation

■ Zero Order Reaction

$$-\frac{\Delta[A]}{\Delta t} = k[A]^0 = k \times 1$$

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

$$-\Delta[A] = k\Delta t$$

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

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

Any number raised to the “zero” power is equal to 1

Integrated Rate Law

■ Integrated Rate Law – Straight Line Plot

For a zero - order reaction :

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

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

$$y = mx + b$$

For a 1st order reaction

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

Rearrange into equation for a straight line

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

$$y = mx + b \quad (m = \text{slope} = -k; \quad x = t; \quad b = y\text{-axis intercept})$$

For a simple 2nd order reaction :

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

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

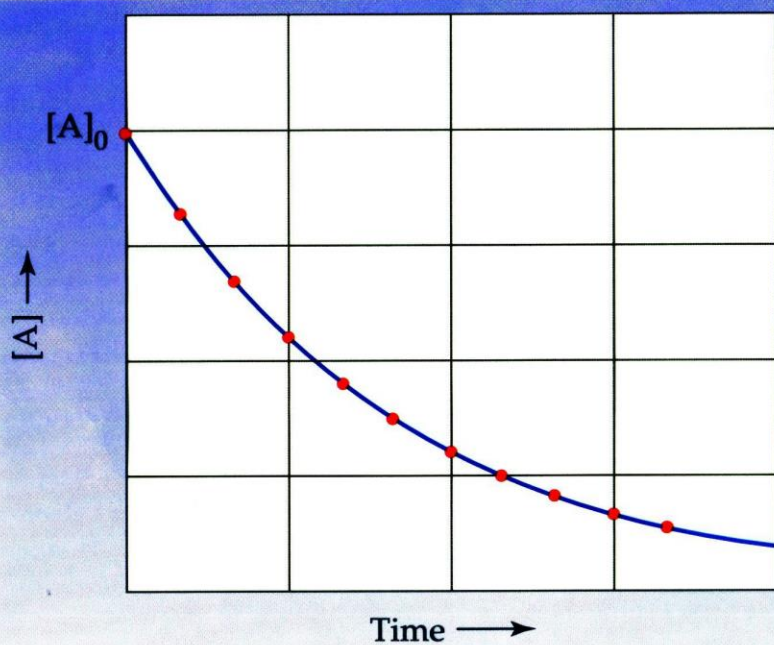
$$y = mx + b \quad (m = \text{slope} = k; \quad x = t; \quad b = y\text{-axis intercept})$$

Integrated Rate Law

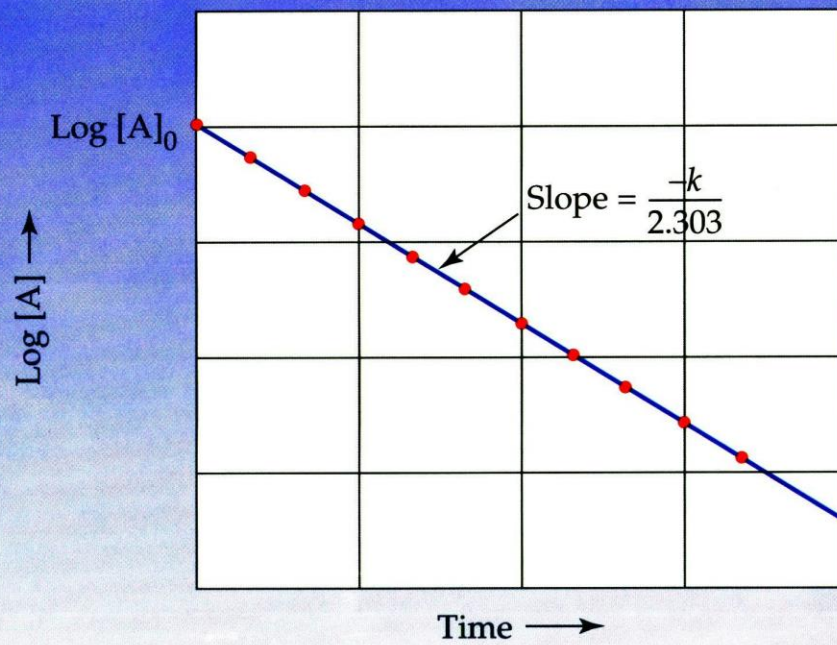
Relationships for Zero-Order, First-Order, and Second-Order Reactions

Order	Rate Law	Integrated Rate Law	Half-Life	Straight-Line Plot
0	Rate = k	$[A] = -kt + [A]_0$	$\frac{[A]_0}{2k}$	$[A]$ vs t
1	Rate = $k[A]$	$\ln \frac{[A]_t}{[A]_0} = -kt$	$0.693/k$	$\ln[A]$ vs t
2	Rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$1/(k[A]_0)$	$\frac{1}{[A]}$ vs t

First-Order Concentration vs. Time Graphs



(a)



(b)

Integrated Rate Law – Half-Life

- Zero Order Reaction Half-Life

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

After one half - life, $t = t_{1/2}$, and $[A]_t = \frac{1}{2}[A]_0$

$$t_{1/2} = \frac{[A]_t - [A]_0}{-k} = \frac{1/2[A]_0 - [A]_0}{-k} = \frac{-0.5[A]_0}{-k}$$

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

Integrated Rate Law

- 1st Order Reaction Half-Life
 - The half-life of a reaction is the time required for the reactant concentration to reach 1/2 its initial value
 - At fixed conditions, the half-life of a 1st order reaction is a constant, independent of reactant concentration

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

After one half - life, $t = t_{1/2}$, and $[A]_t = \frac{1}{2}[A]_0$

Substituting

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

$$\ln 2 = kt_{1/2}$$

[Recall Radioactivity half-life (Chap 24)]

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

Integrated Rate Law – Half-Life

■ 2nd Order Reaction Half-Life

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

After one half - life, $t = t_{1/2}$, and $[A]_t = \frac{1}{2}[A]_0$

$$t_{1/2} = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{k} = \frac{\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0}}{k} = \frac{\frac{2}{[A]_0} - \frac{1}{[A]_0}}{k} = \frac{1}{k[A]_0}$$

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

Practice Problem

A reaction is first order with respect to A. The first-order rate constant is 2.61 /min. How long will it take the concentration of A to decrease from 0.100 M to 0.00812 M? What is the half-life of the reaction? How long will it take for the concentration of A to decrease by 85%?

$$k = 2.61 / \text{min}$$

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

$$t = \frac{\ln[A]_0 - \ln[A]_t}{k} = \frac{\ln\left(\frac{[A]_0}{[A]_t}\right)}{k} = \frac{\ln\left(\frac{0.100}{0.00812}\right)}{2.61 / \text{min}} = \frac{\ln(12.3152709)}{2.61} = \frac{2.51084}{2.61}$$

$$t = 0.962 \text{ min}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{2.61 / \text{min}} = \frac{0.693}{2.61} = 0.266 \text{ min}$$

$$t = \frac{\ln[A]_0 - \ln[A]_t}{k} = \frac{\ln\left(\frac{[A]_0}{[A]_t}\right)}{k} = \frac{\ln\left(\frac{0.1}{0.1 \times 0.15}\right)}{2.61} = \frac{\ln(6.66667)}{2.61} = \frac{1.89712}{2.61} = 0.727 \text{ min}$$

Practice Problem

A reaction is second order with respect to B.
The second-order rate constant is 1.5 L/mol•min

How long will it take the concentration of B to decrease from 0.100 M to 0.025 M?

$$k = 1.5 \text{ L / mol} \cdot \text{min}$$

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

$$t = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{k}$$

$$t = \frac{\frac{1}{0.025 \text{ mol / L}} - \frac{1}{0.100 \text{ mol / L}}}{1.5 \text{ L / mol} \cdot \text{min}}$$

$$t = \frac{40 - 10}{1.5} = 20 \text{ min}$$

Temperature Dependence of Reaction Rate

- An **increase** in Temperature (T) generally **increases** the reaction rate
- A 10°C increase in Temperature usually doubles the rate
- Temperature affects the **rate constant (K)** of the rate equation
- Temperature effect process is described by **Collision Theory**
- Can calculate the effect of T on rate of a reaction using the **Arrhenius Equation**

Effects of Concentration & Temperature

- Two major models explain the observed effects of Concentration & Temperature on reaction rate
 - Collision Theory
 - ◆ Views the reaction rate as a result of particles colliding with a certain frequency and minimum energy
 - Transition State Theory
 - ◆ Close-up view of how the energy of a collision converts reactant to product

Collision Theory

- Why concentrations are “Multiplied” in the Rate Law

- Consider 2 particles of “A” & 2 particles of “B”

- Total A-B collisions = 4 (2 x 2)

A1B1 A1B2 A2B1 A2B2

- Add additional Particle of “A”

- Total A-B collisions = 6 (3 x 2)

A1B1 A1B2 A2B1 A2B2 A3B1 A3B2

- It is the product of the number of different particles, not the sum (6 vs 5), that determines the number of collisions (reactions) possible

- The number of particles of reactant A (concentration) must be multiplied by the number of particles of Reactant B to account for the total number of collisions (reactions) that occur.

Collision Theory

- Increasing the temperature of a reaction increases the average speed of particles; thus, the frequency of collision
- Most collisions do not result in a “reaction”
- Collision Theory assumes that, for a reaction to occur, reactant molecules must collide with an energy greater than some minimum value and with proper orientation

Activation Energy (E_a)

- The rate constant, k , for a reaction is a function of 3 collision related factors:
 - Z collision frequency
 - f fraction of collisions \Rightarrow activation energy
 - p fraction of collisions in proper orientation

$$k = Zpf$$

Collision Theory

- At a given temperature, the fraction of molecular collisions, f , with energy greater than or equal to the **activation energy**, E_a , is related to activation energy by the expression:

$$f = e^{-E_a/RT}$$

- An equation (Arrhenius) expressing the dependence of the rate constant, k , on temperature can be obtained by combining the relationship between the rate constant and fraction of collisions, f , that are \geq to the "activation energy", E_a

$$k = Zpf$$

Let $A = Zp =$ frequency factor

$$k = Af$$

Since $f = e^{-E_a/RT}$

Then $k = Ae^{-E_a/RT}$

Arrhenius Equation

- Temperature dependence of reaction rate

$$k = Ae^{-E_a/RT} \quad \text{Arrhenius Equation}$$

k = rate constant

A = frequency factor (pZ)

E_a = activation energy (J)

R = gas constant (8.314 J/mol•K)

T = temperature (K)

- The Relationship between temperature (T) in the $e^{-E_a/RT}$ term and the rate constant (k) means that as the temperature increases, the negative exponent ($-E_a/RT$) becomes smaller, and the $e^{-E_a/RT}$ term becomes larger, so the value of k becomes larger, which means that the rate of the reaction increases

Higher $T \Rightarrow$ Larger $k \Rightarrow$ Increased Reaction Rate

Arrhenius Equation

- The activation energy (E_a) can be calculated from the Arrhenius equation by taking the natural logarithm (\ln_e) of both sides and rearranging the equation into a "straight line ($y = b + mx$)" form

$$k = Ae^{-E_a/RT}$$

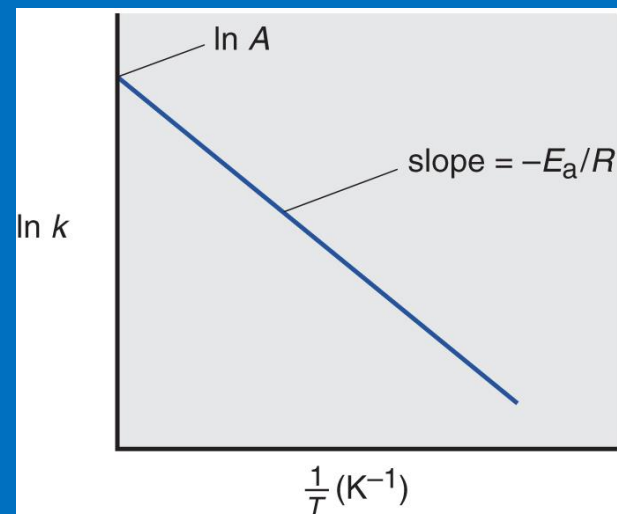
$$\ln k = \ln A + \ln\left(e^{-E_a/RT}\right)$$

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

Note: The natural logarithm (\ln_e) is usually presented as: "ln" omitting the subscript "e"

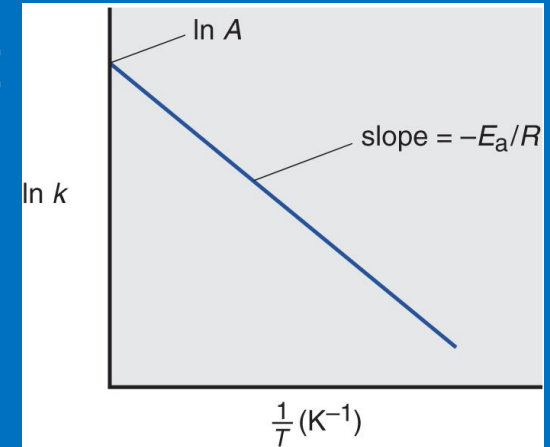
A plot of $\ln k$ (y) vs. $1/T$ (x) gives a straight line whose slope (m) is $-E_a/R$ and whose y intercept is $\ln A$ (b)

$$y = b + mx$$



Arrhenius Equation

- E_a can be determined graphically from a series of k values at different temperatures
 - Determine the slope from the plot
 - Use slope formula = $-E_a/R$
- Alternate Approach - Compute E_a mathematically if the rate constants at two temperatures are known



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

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

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

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

“ln A” term
drops out

Practice Problem

- Find the Activation Energy (E_a) for the decomposition of Hydrogen Iodide (HI)



The rate constants are:

$$9.51 \times 10^{-9} \text{ L/mol}\cdot\text{s at } 500^\circ\text{K}$$

$$1.10 \times 10^{-5} \text{ L/mol}\cdot\text{s at } 600^\circ\text{K}$$

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

$$E_a = -(8.314 \text{ J/mol}\cdot\text{K}) \times \ln\left(\frac{1.10 \times 10^{-5} \text{ L/mol}\cdot\text{s}}{9.51 \times 10^{-9} \text{ L/mol}\cdot\text{s}}\right) \times \left(\frac{500^\circ\text{K} \times 600^\circ\text{K}}{500^\circ\text{K} - 600^\circ\text{K}}\right)$$

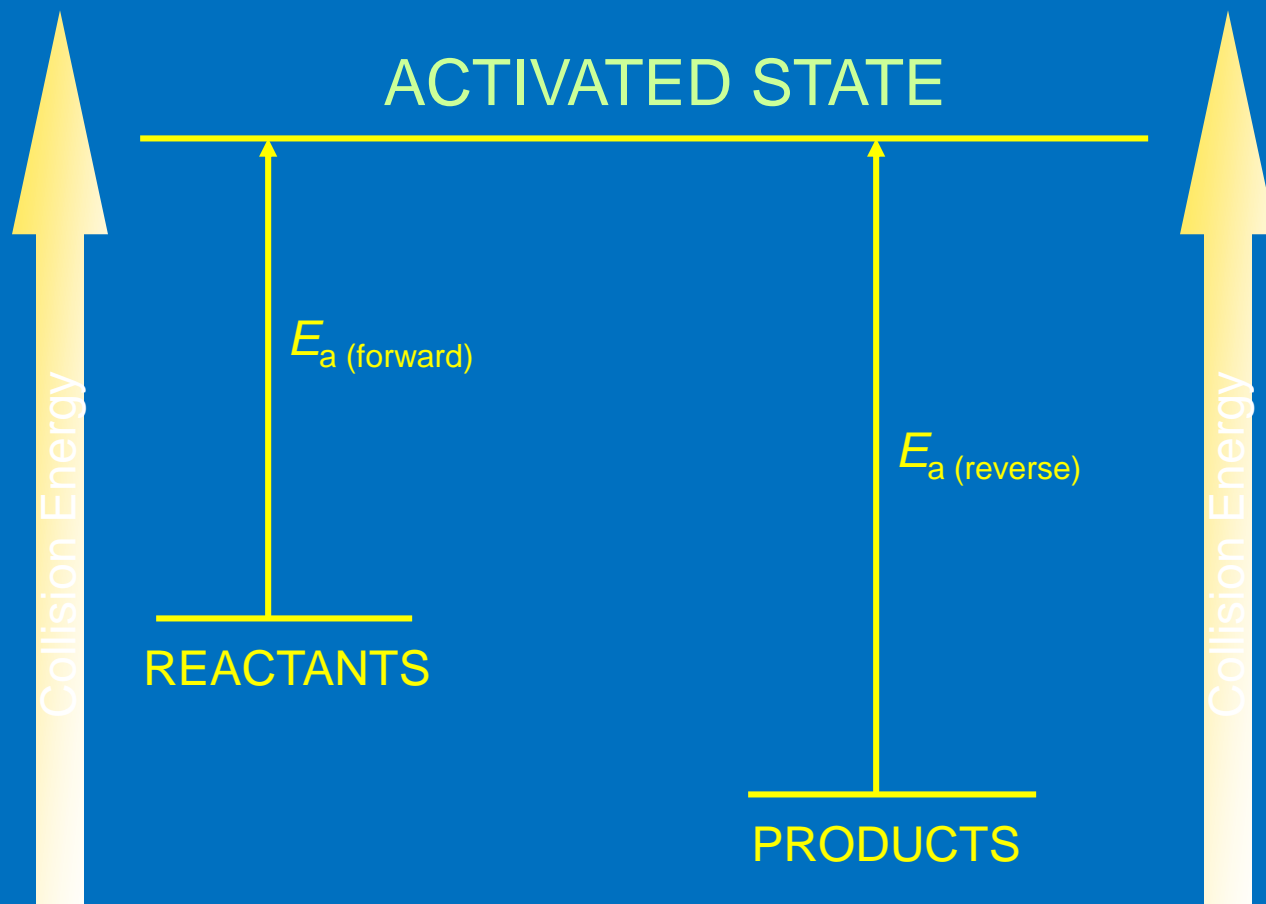
$$E_a = -(8.314 \text{ J/mol}\cdot\text{K}) \times \ln(1.156677 \times 10^3) \times (-3.00 \times 10^3)$$

$$E_a = -(8.314 \text{ J/mol}\cdot\text{K}) \times (7.053307) \times (-3.00 \times 10^3)$$

$$E_a = 1.76 \times 10^5 \text{ J/mol} \times \frac{1 \text{ kJ}}{1 \times 10^3 \text{ J}}$$

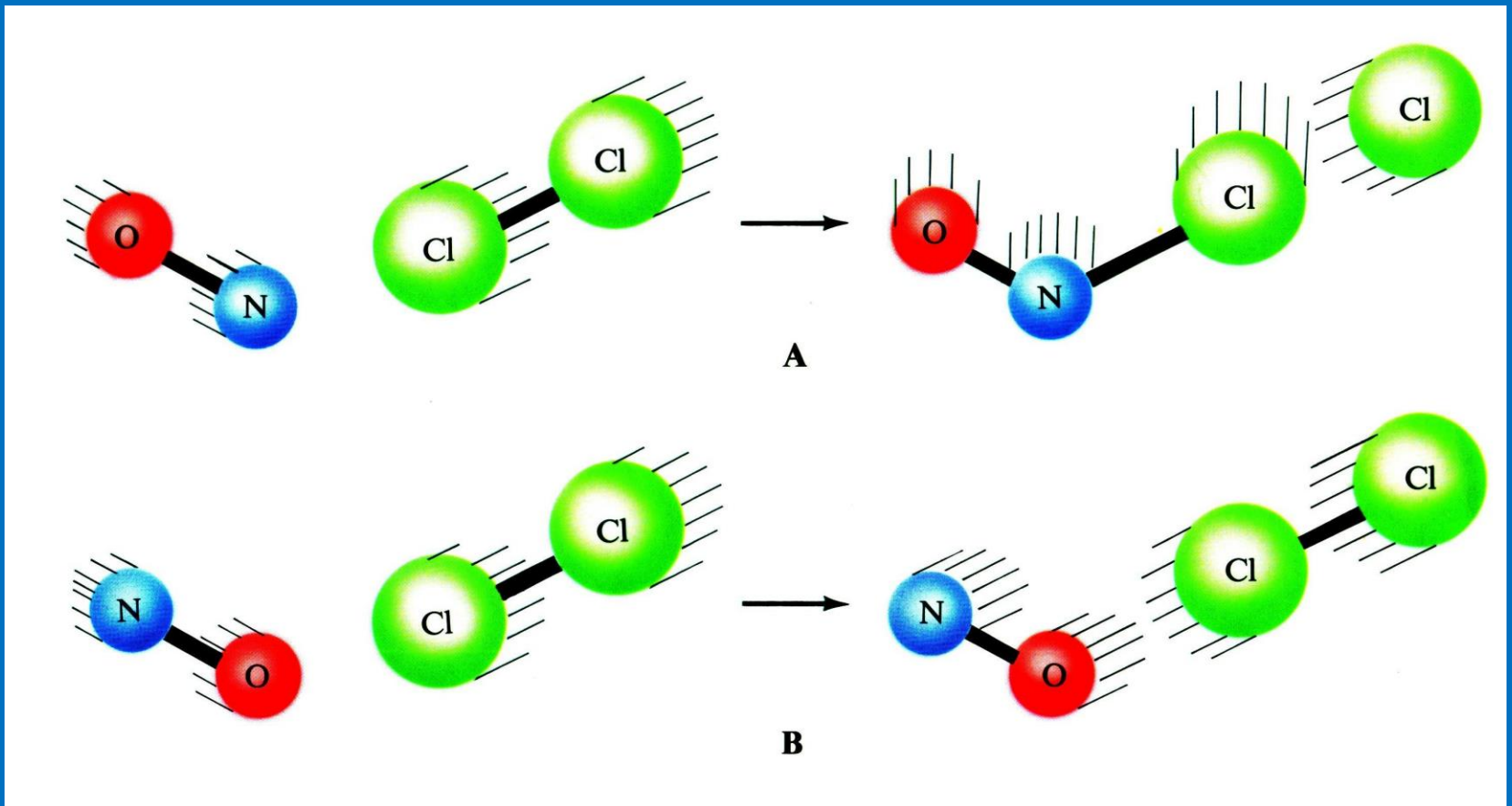
$$E_a = 1.76 \times 10^2 \text{ kJ/mol}$$

Rate – Affects of Temperature



- Molecules must collide with sufficient energy to reach “activation” status
- Minimum collision energy is “energy of activation, E_a ”
- The forward reaction is Exothermic because the reactants have more energy than the products.

Collision Theory: Proper Orientation (p)



Transition-State Theory

- **Transition-state theory** explains the reaction in terms of the collision of two high energy species – activated complexes
 - An **activated complex** (transition state) is an unstable grouping of atoms that can break up to form products
 - A simple analogy would be the collision of three billiard balls on a billiard table
 - Suppose two balls are coated with a slightly sticky adhesive
 - We'll take a third ball covered with an extremely sticky adhesive and collide it with our joined pair

Transition-State Theory

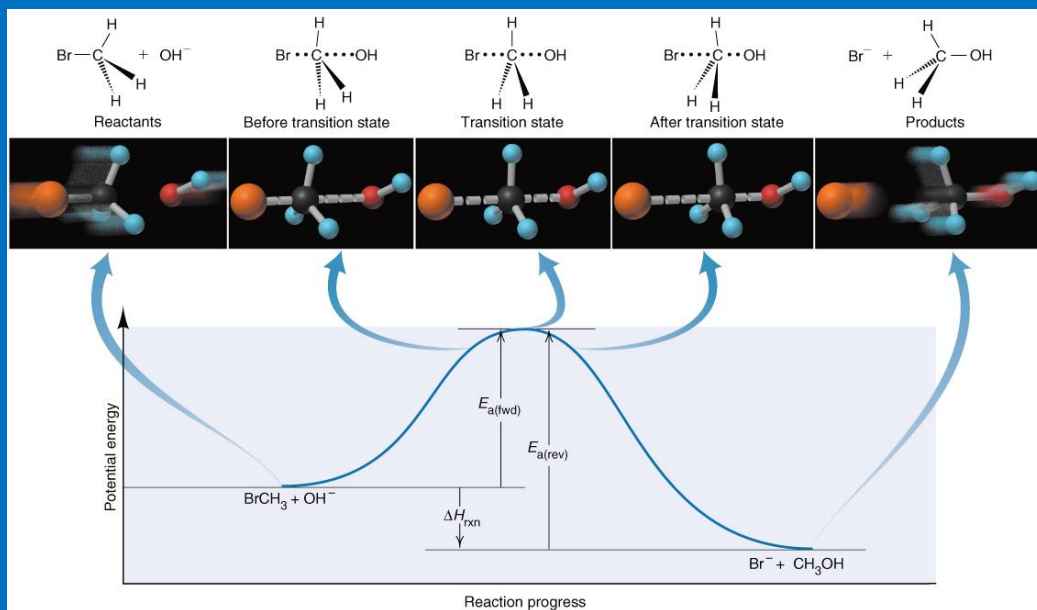
■ Transition-state theory (cont')

- At the instant of impact, when all three spheres are joined, we have an unstable **transition-state complex**
- The “incoming” billiard ball would likely stick to one of the joined spheres and provide sufficient energy to dislodge the other, resulting in a **new “pairing”**
- If we repeated this scenario several times, some collisions would be successful and others (because of either insufficient energy or improper orientation) would not be successful.
- We could compare the energy we provided to the billiard balls to the **activation energy, E_a**

Transition State Theory

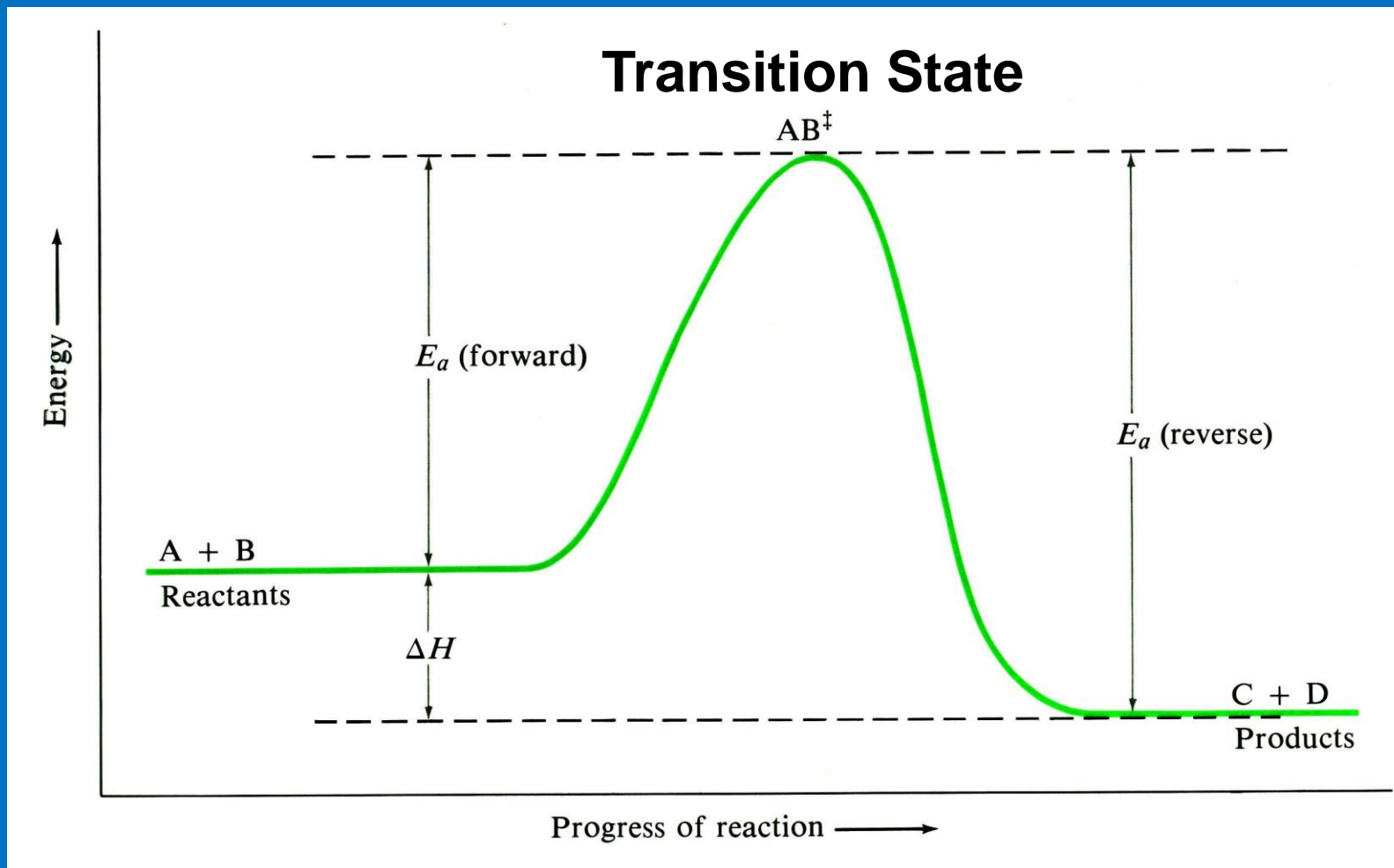
- Reaction of Methyl Bromide & OH⁻
- Reaction is Exothermic – reactants are higher in energy than products
- Forward activation energy $E_{a(\text{fwd})}$ is less than reverse $E_{a(\text{rev})}$
- Difference in activation energies is “Heat of Reaction”

$$\Delta H_{\text{rxn}} = E_{a(\text{fwd})} - E_{a(\text{rev})}$$



Note the partial elongated C-O and C-Br bonds and the trigonal bipyramidal shape of the transition state

Exothermic Reaction Pathway



$$\Delta H_{\text{rxn}} = E_{a(\text{fwd})} - E_{a(\text{rev})}$$

$$E_{a(\text{fwd})} < E_{a(\text{rev})}$$

$\therefore \Delta H_{\text{rxn}} < 0$ Reaction is Exothermic