GENERAL CHEMISTRY

Chemical Reactions

Reaction time

A chemical reaction takes time. Some reactions are complete in a fraction of a second; others take years. The reaction shown here is complete in less than a minute. The reaction is the formation of a product of formaldehyde with hydrogen sulfite ion. As the hydrogen sulfite ion is used up, the solution becomes less acidic and then changes to basic. Bromthymol-blue indicator marks the change from acidic to basic by changing from yellow to blue.

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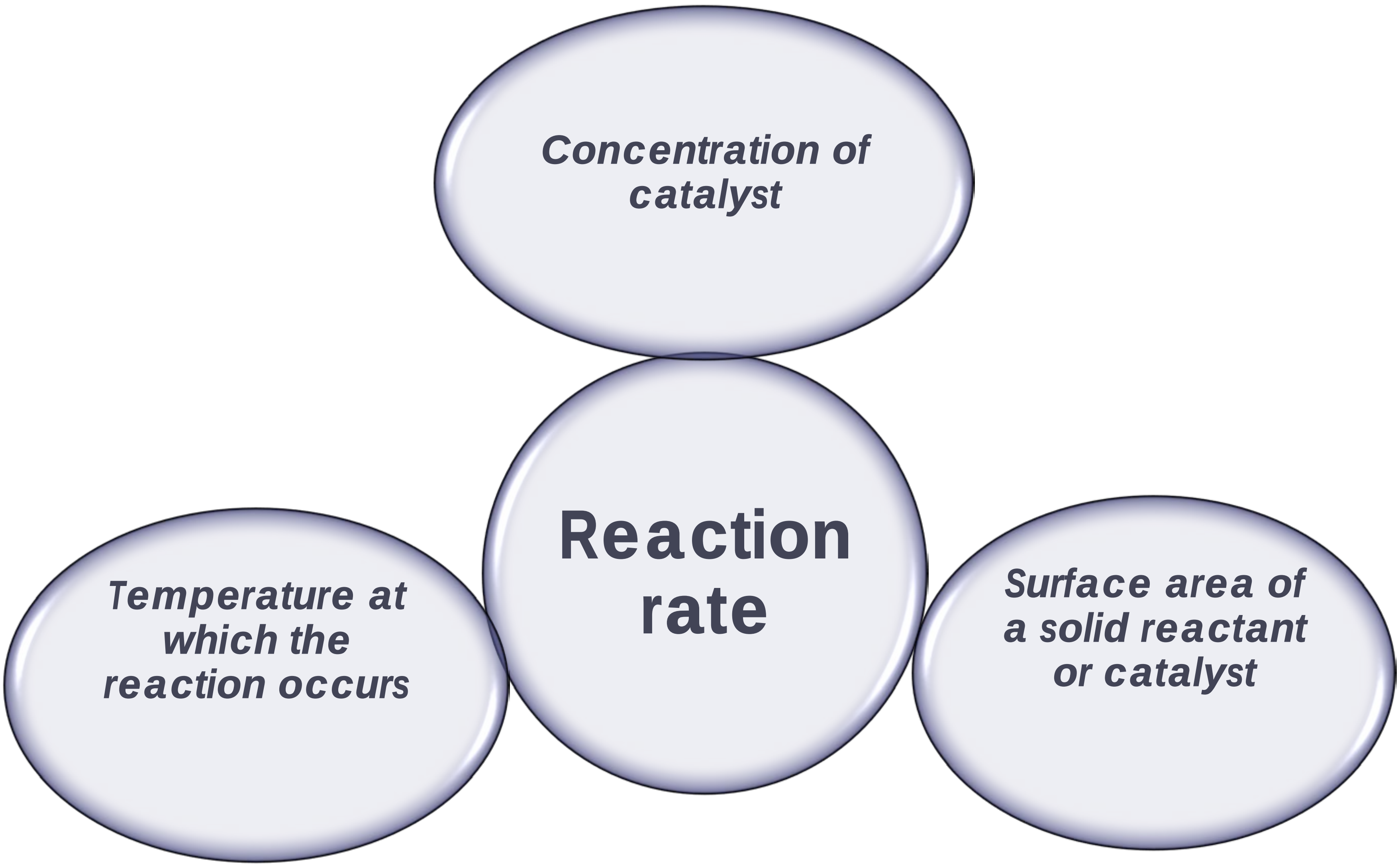
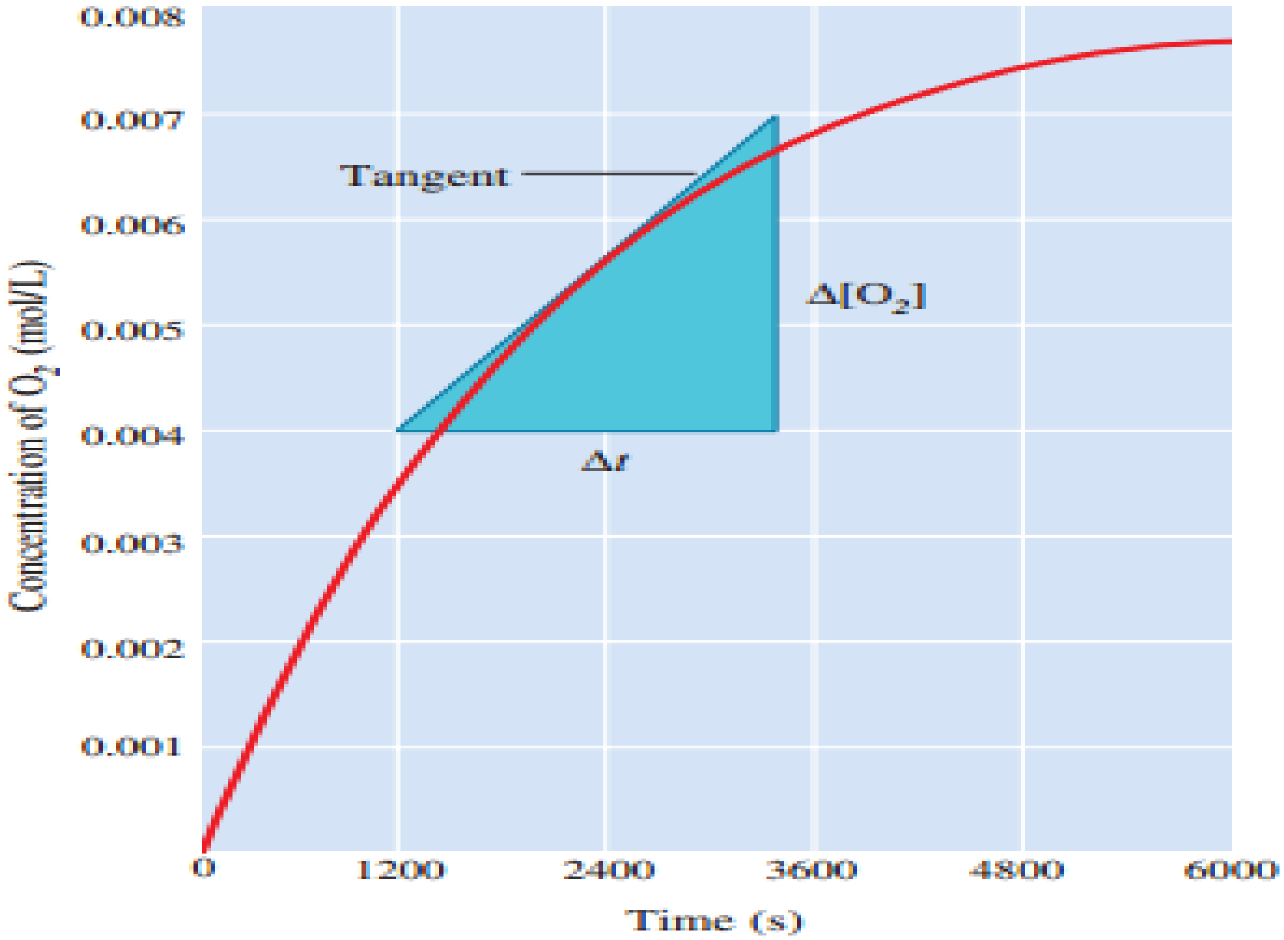

Concentration of catalyst
Reaction rate
Temperature at which the reaction occurs
Surface area of a solid reactant or catalyst

The instantaneous rate of reaction



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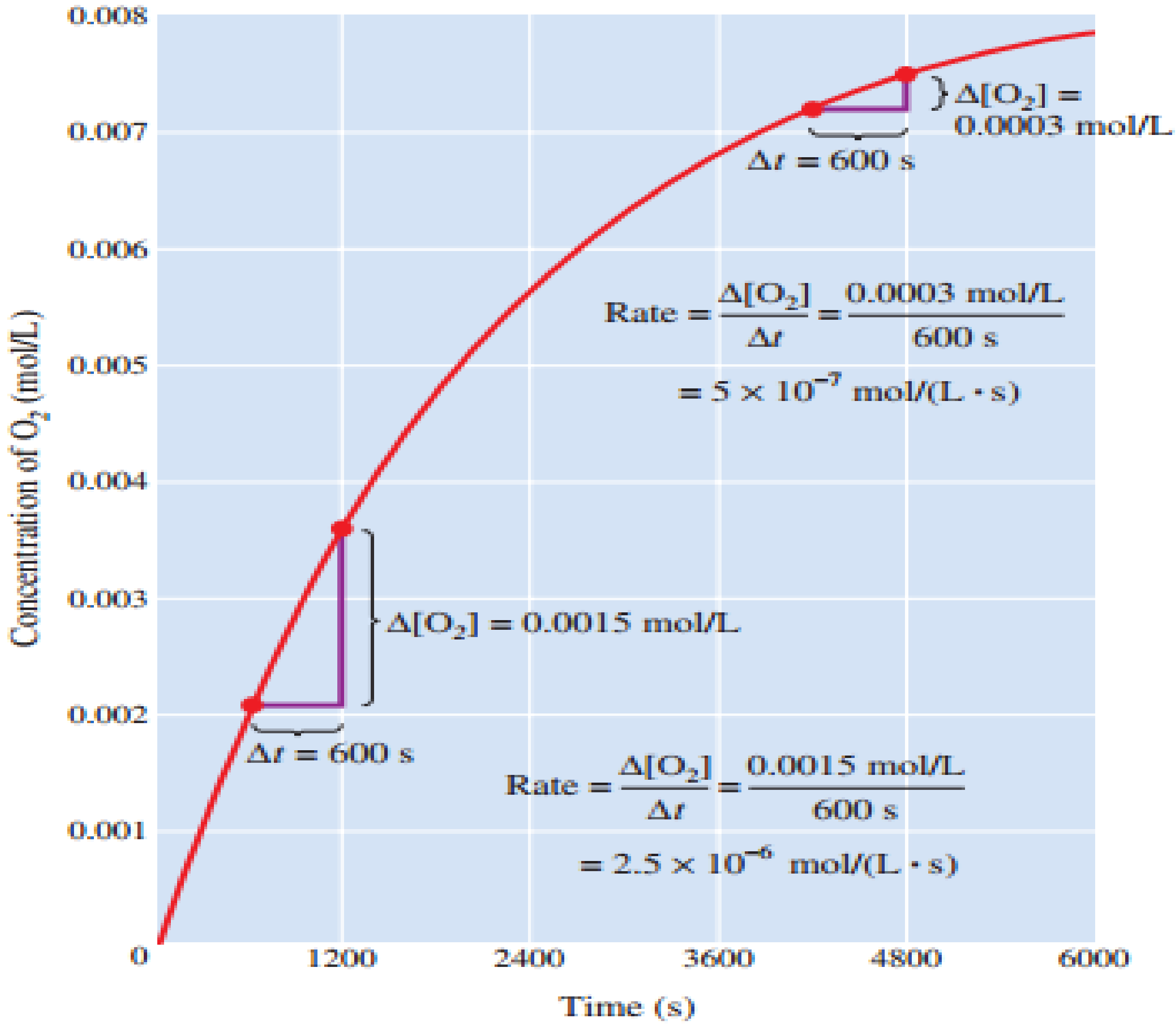
Calculation of the average rate



Time	$[O_2]$
0	0.0000
600	0.0021
1200	0.0036
1800	0.0048
2400	0.0057
3000	0.0063
3600	0.0068
4200	0.0072
4800	0.0075
5400	0.0077
6000	0.0078

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Example: Relating the Different Ways of Expressing Reaction Rates

Consider the reaction of nitrogen dioxide with fluorine to give nitryl fluoride, NO2F.

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

solution

$$\text{Rate of formation of } NO_2F = \frac{\Delta[NO_2F]}{\Delta t}$$

$$\text{Rate of reaction of } F_2 = -\frac{\Delta[F_2]}{\Delta t}$$

$$\frac{1}{2}\frac{\Delta[NO_2F]}{\Delta t} = -\frac{\Delta[F_2]}{\Delta t}$$

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Example: Calculating the Average Reaction Rate

Calculate the average rate of decomposition of N_2O_5, $-\Delta[N_2O_5]/\Delta t$, by the reaction

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

during the time interval from $t = 600$ s to $t = 1200$ s (regard all time figures as significant). Use the following data:

Time	*[N_2O_5]*
600 s	1.24×10^{-2} *M*
1200 s	0.93×10^{-2} *M*

Solution:

$$\text{Average rate of decomposition of } N_2O_5 = -\frac{\Delta[N_2O_5]}{\Delta t} =$$

$$-\frac{(0.93 - 1.24) \times 10^{-2}\,M}{(1200 - 600)\,\text{s}} = -\frac{-0.31 \times 10^{-2}\,M}{600\,\text{s}} = \mathbf{5.2 \times 10^{-6}\,M/s}$$

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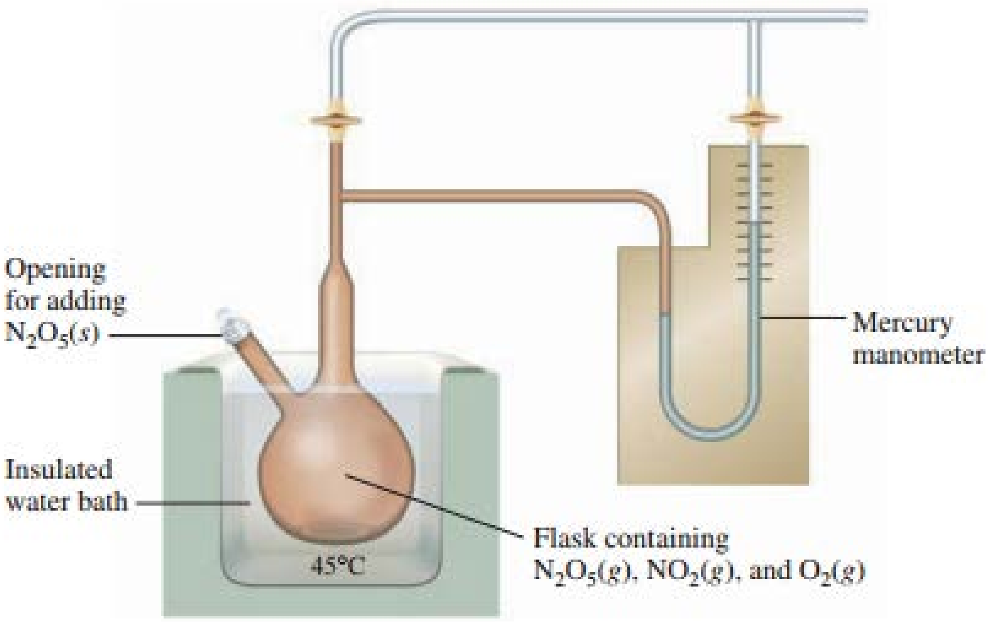
Experimental determination of rate



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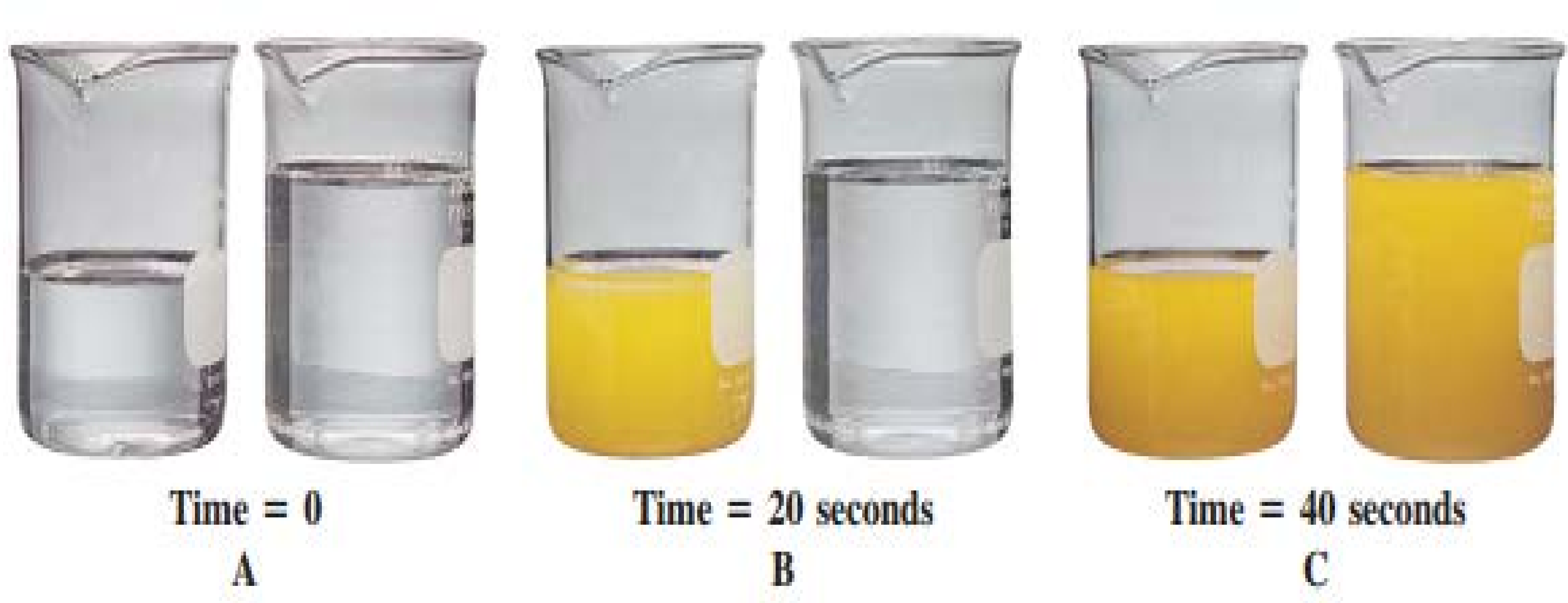
Dependence of rate on concentration



Effect of reactant concentrations on rate of reaction

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Example : Determining the Order of Reaction from the Rate Law

Bromide ion is oxidized by bromate ion in acidic solution

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

The experimentally determined rate law is

$$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$$

What is the order of reaction with respect to each reactant species? What is the overall order of the reaction?

Solution:

The reaction is **first order with respect to Br** and **first order with respect to BrO3;** it is **second order with respect to H. The reaction is fourth order overall (=1+1+2)**

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Example : Determining the Rate Law from Initial Rates

Iodide ion is oxidized in acidic solution to triiodide ion, I3, by hydrogen peroxide.

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \longrightarrow I_3^-(aq) + 2H_2O(l)$$

A series of four experiments was run at different concentrations, and the initial rates of I_3^- formation were determined (see table). a. From these data, obtain the reaction orders with respect to H_2O_2, I^-, and H^+. b. Then find the rate constant.

	Initial Concentrations (mol/L)			*Initial Rate*
	H_2O_2	I^-	H^+	*[mol/(L·s)]*
Exp. 1	0.010	0.010	0.00050	1.15×10^{-6}
Exp. 2	0.020	0.010	0.00050	2.30×10^{-6}
Exp. 3	0.010	0.020	0.00050	2.30×10^{-6}
Exp. 4	0.010	0.010	0.00100	1.15×10^{-6}

Solution:

To solve a problem such as this in a general way, you approach it algebraically. It should be write the rate law for two experiments. (The subscripts denote the experiments.)

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$$(\text{Rate})_1 = k[H_2O_2]_1^m[I^-]_1^n[H^+]_1^p$$

$$(\text{Rate})_2 = k[H_2O_2]_2^m[I^-]_2^n[H^+]_2^p$$

Now you divide the second equation by the first.

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k[H_2O_2]_2^m[I^-]_2^n[H^+]_2^p}{k[H_2O_2]_1^m[I^-]_1^n[H^+]_1^p}$$

The rate constant cancels. Grouping the terms, you obtain

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \left(\frac{[H_2O_2]_2}{[H_2O_2]_1}\right)^m \left(\frac{[I^-]_2}{[I^-]_1}\right)^n \left(\frac{[H^+]_2}{[H^+]_1}\right)^p$$

Now you substitute values from Experiment 1 and Experiment 2. (In a ratio the units cancel and can be omitted.)

$$\frac{2.30 \times \cancel{10^{-6}}}{1.15 \times \cancel{10^{-6}}} = \left[\frac{0.020}{0.010}\right]^m \cancel{\left[\frac{0.010}{0.010}\right]^n} \cancel{\left[\frac{0.00050}{0.00050}\right]^p}$$

Calculate the rate constant by substituting values from any of the experiments into the rate law. Using Experiment 1, it should be obtained

$$1.15 \times 10^{-6} \frac{\cancel{\text{mol}}}{\cancel{\text{L}}\cdot\text{s}} = k \times 0.010 \frac{\cancel{\text{mol}}}{\cancel{\text{L}}} \times 0.010 \frac{\text{mol}}{\text{L}}$$

$$k = \frac{1.15 \times 10^{-6}/\text{s}}{0.010 \times 0.010 \times \text{mol/L}} = \mathbf{1.2 \times 10^{-2}\ L/(mol \cdot s)}$$

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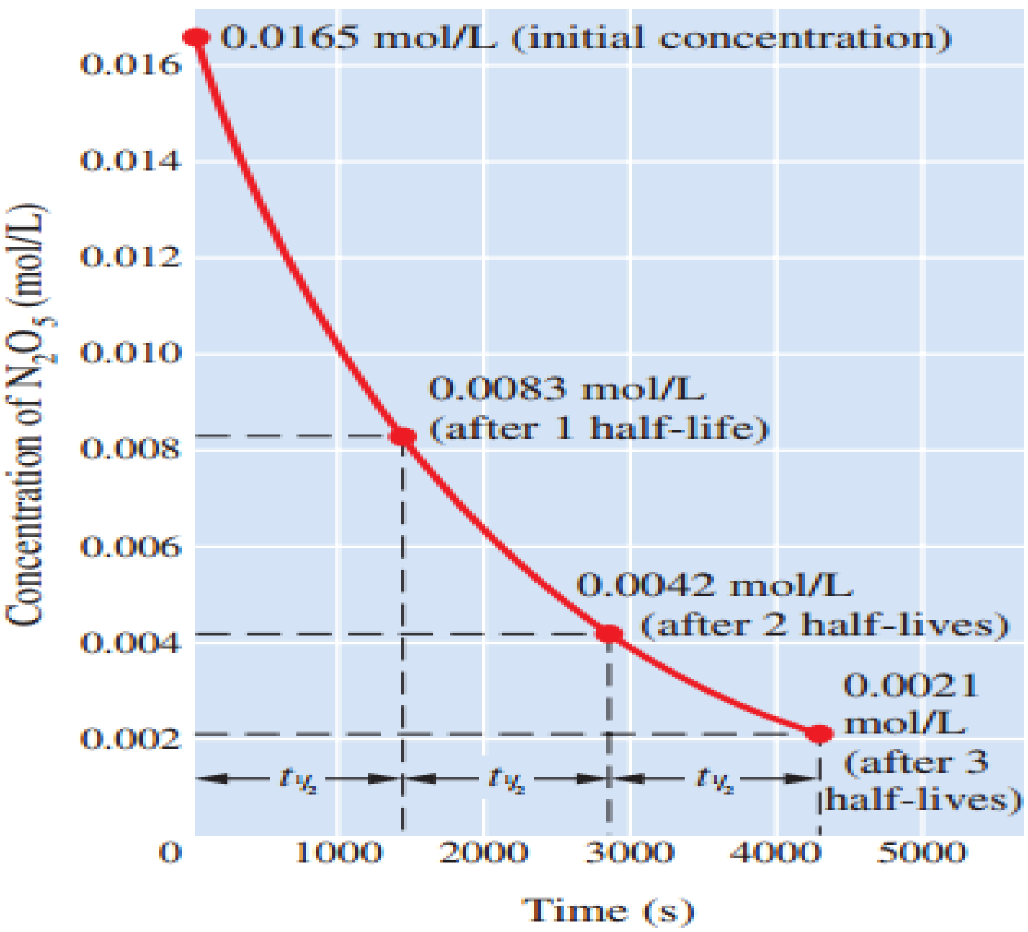
Half-Life of a Reaction



A graph illustrating that the half-life of a first-order reaction is independent of initial concentration

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

Order	Rate Law	Integrated Rate Law	Half-Life	Straight-Line Plot
0	Rate = k	$[A]_t = -kt + [A]_0$	$\frac{[A]_0}{2k}$	[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

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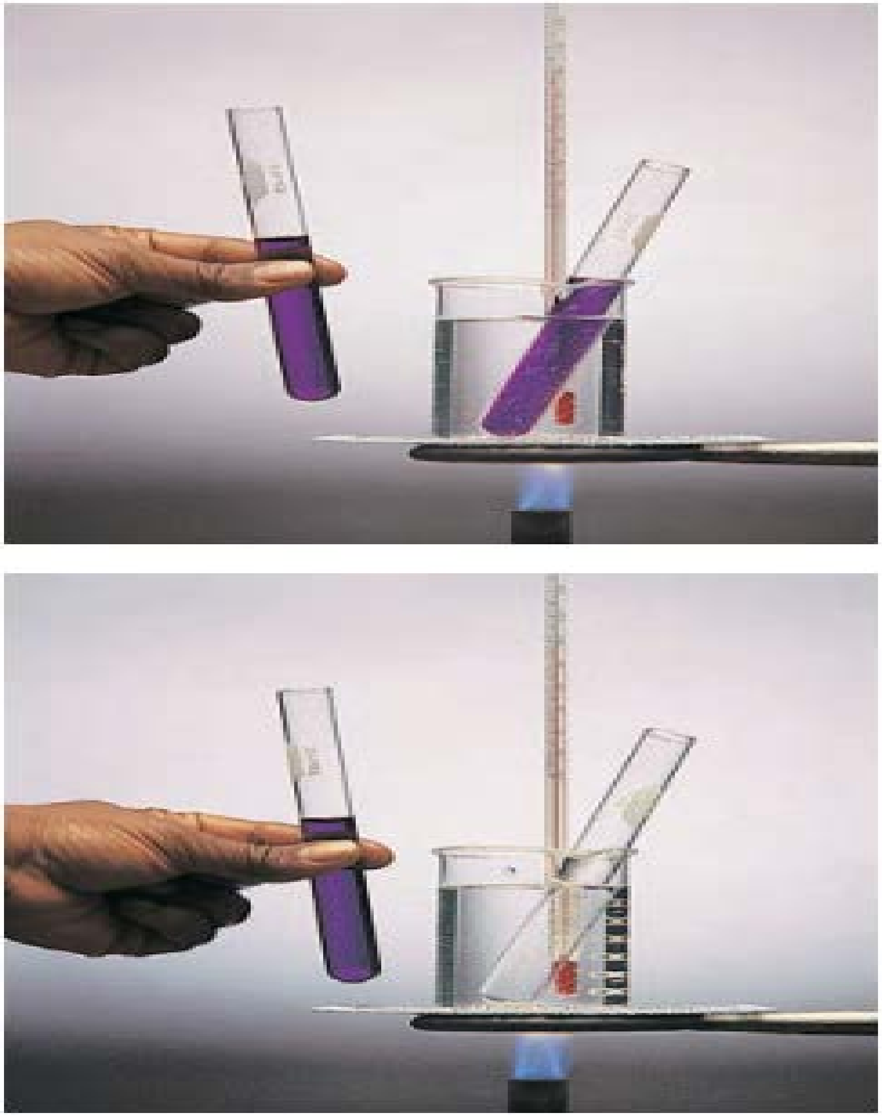
Temperature and rate; Collision and transition – state theories

Effect of temperature
reaction rate



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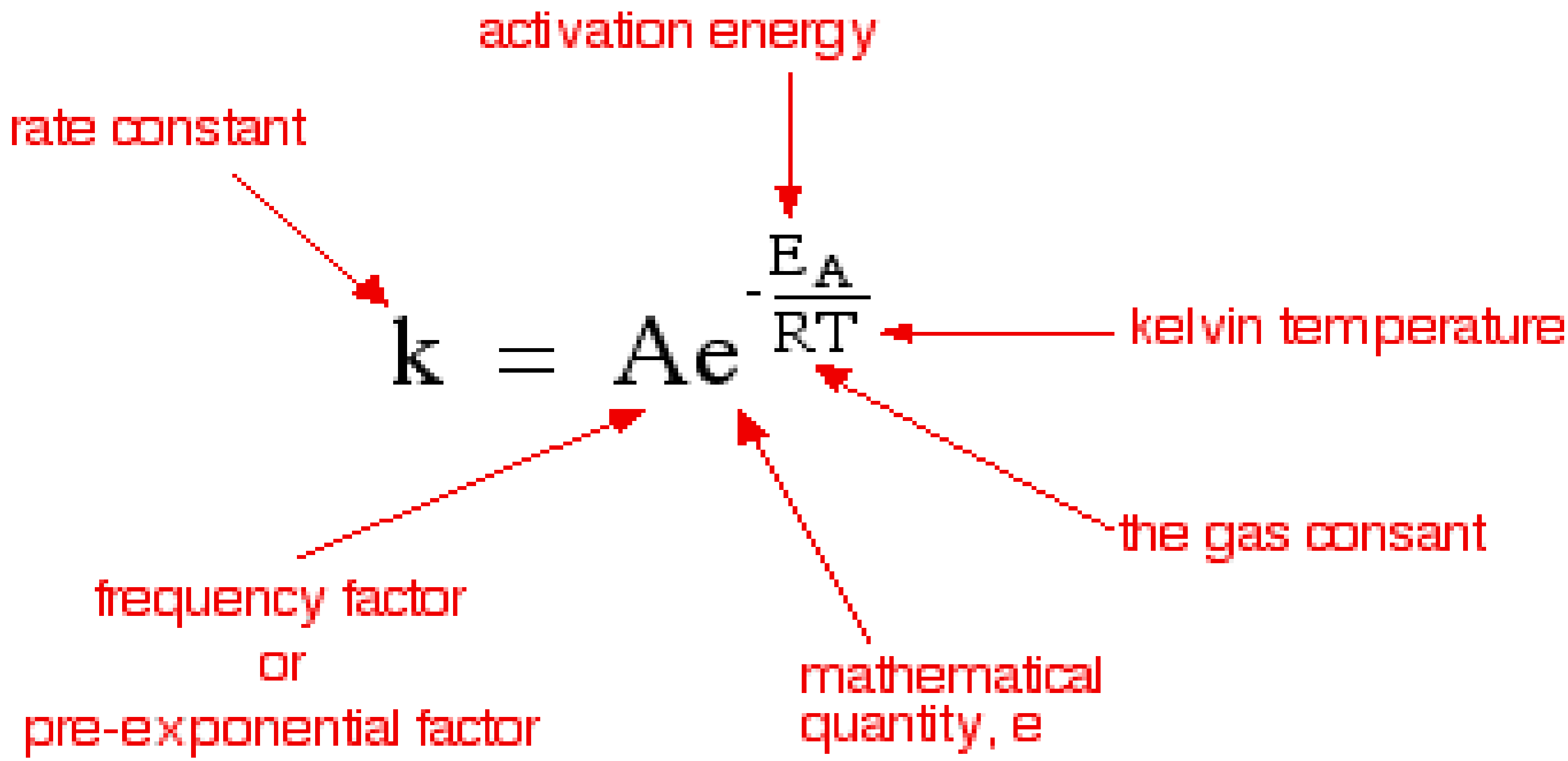
Arrhenius equation



$$k = Ae^{-\frac{E_A}{RT}}$$

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Example: Using the Arrhenius Equation

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

is 2.7×10^{-4} L/(mol·s) at 600 K and 3.5×10^{-3} L/(mol·s) at 650 K. a. Find the activation energy E_a. b. Then calculate the rate constant at 700 K.

a. Substitute the data given in the problem statement into the equation noted just before this example, then solve for *Ea*. b. Use the same equation, but substitute for *k*1, *T*1, *T*2, and *Ea* obtained in a, and solve for *k*2.

Solution:

a. $$\ln \frac{3.5 \times 10^{-3}}{2.7 \times 10^{-4}} = \frac{E_a}{8.31\ \text{J/(mol·K)}} \left(\frac{1}{600\ \text{K}} - \frac{1}{650\ \text{K}} \right)$$

$$\ln 1.30 \times 10^{1} = 2.56 = \frac{E_a}{8.31\ \text{J/mol}} \times (1.28 \times 10^{-4})$$

Hence,

$$E_a = \frac{2.56 \times 8.31\ \text{J/mol}}{1.28 \times 10^{-4}} = \mathbf{1.66 \times 10^5\ J/mol}$$

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b. Substitute $E_a = 1.66 \times 10^5$ J/mol and

$$k_1 = 2.7 \times 10^{-4}\ \text{L/(mol·s)} \qquad (T_1 = 600\ \text{K})$$
$$k_2 = \text{unknown as yet} \qquad (T_2 = 700\ \text{K})$$

You get

$$\ln \frac{k_2}{2.7 \times 10^{-4}\ \text{L/(mol·s)}} = \frac{1.66 \times 10^5\ \text{J/mol}}{8.31\ \text{J/(mol·K)}} \times \left(\frac{1}{600\ \text{K}} - \frac{1}{700\ \text{K}}\right) = 4.77$$

Taking antilogarithms,

$$\frac{k_2}{2.7 \times 10^{-4}\ \text{L/(mol·s)}} = e^{4.77} = 1.2 \times 10^2$$

Hence,

$$k_2 = (1.2 \times 10^2) \times (2.7 \times 10^{-4})\ \text{L/(mol·s)} = \mathbf{3.2 \times 10^{-2}\ L/(mol·s)}$$

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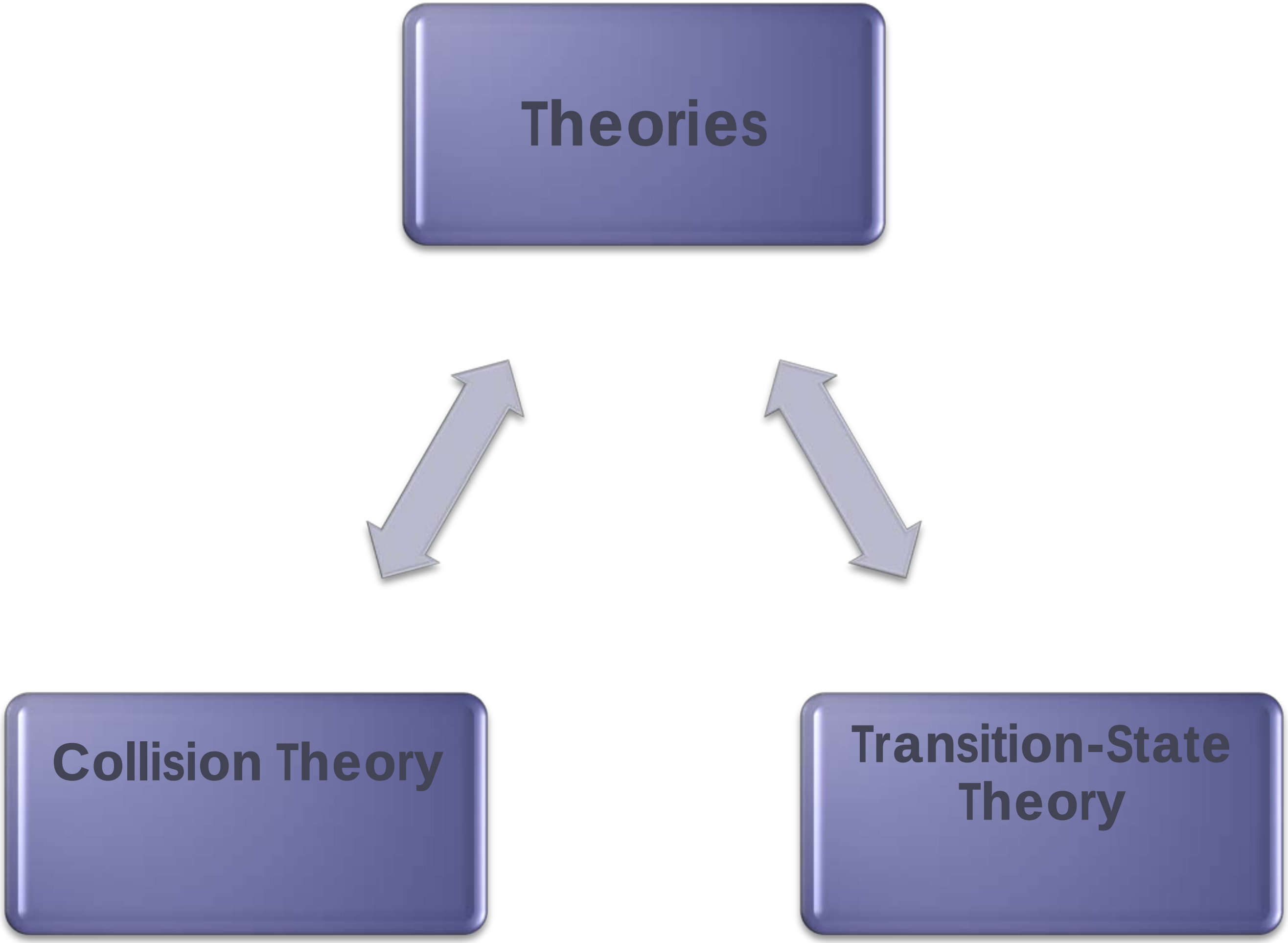
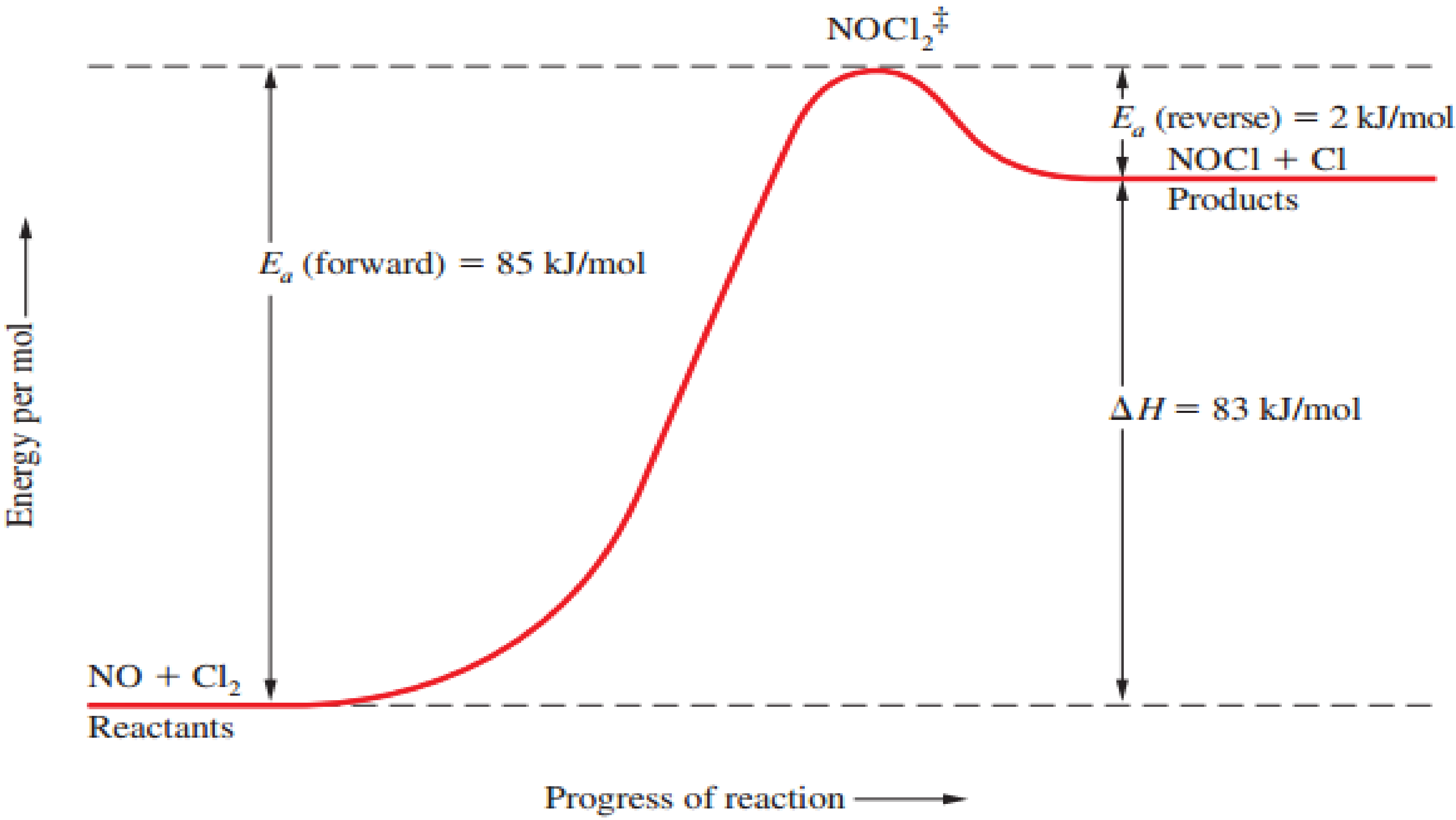

Theories
Collision Theory
Transition-State Theory

Potential-Energy Diagrams for Reactions



Potential-energy curve (not to scale) for the endothermic reaction $NO + Cl_2 \longrightarrow NOCl + Cl$

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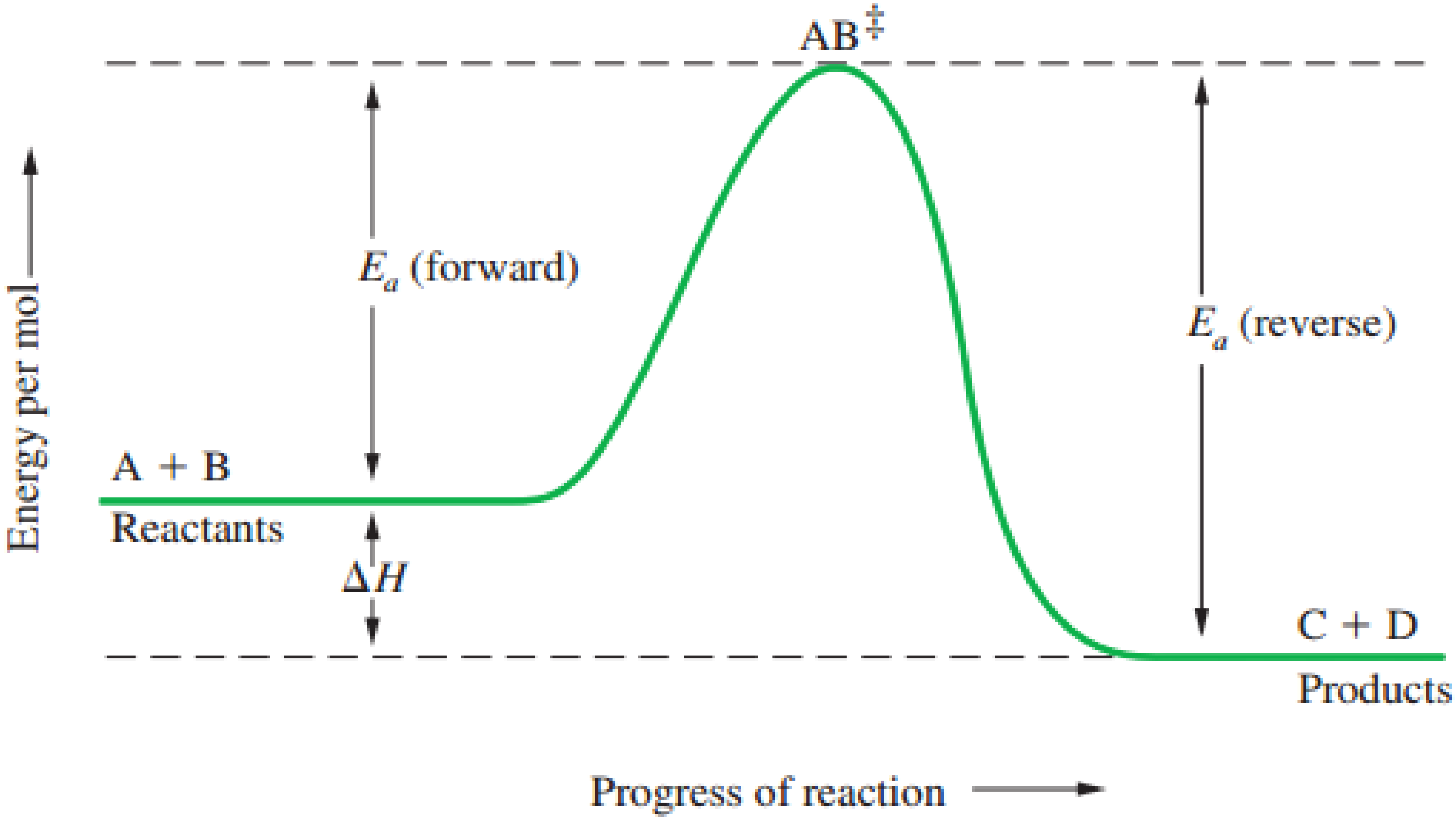
Potential-energy curve for an exothermic reaction



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$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \qquad \text{(net chemical equation)}$$

$$NO_2 + NO_2 \longrightarrow NO_3 + NO \qquad \text{(elementary reaction)}$$
$$NO_3 + CO \longrightarrow NO_2 + CO_2 \qquad \text{(elementary reaction)}$$

$$NO_2 + NO_2 \longrightarrow NO_3 + NO \qquad \text{(elementary reaction)}$$
$$NO_3 + CO \longrightarrow NO_2 + CO_2 \qquad \text{(elementary reaction)}$$

$$NO_2 + \cancel{NO_2} + \cancel{NO_3} + CO \longrightarrow \cancel{NO_3} + NO + \cancel{NO_2} + CO_2 \qquad \text{(overall equation)}$$

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Example for overall equation

Obtain the net, or overall, chemical equation from this mechanism.

$$
\begin{array}{rcll}
Cl_2 & \rightleftharpoons & 2Cl & \text{(elementary reaction)} \\
Cl + CHCl_3 & \longrightarrow & HCl + CCl_3 & \text{(elementary reaction)} \\
Cl + CCl_3 & \longrightarrow & CCl_4 & \text{(elementary reaction)}
\end{array}
$$

Solution:

$$
\begin{array}{rcll}
Cl_2 & \rightleftharpoons & 2\cancel{Cl} & \\
\cancel{Cl} + CHCl_3 & \longrightarrow & HCl + \cancel{CCl_3} & \\
\cancel{Cl} + \cancel{CCl_3} & \longrightarrow & CCl_4 & \\
\hline
\mathbf{Cl_2 + CHCl_3} & \longrightarrow & \mathbf{HCl + CCl_4} & \textbf{(overall equation)}
\end{array}
$$

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Molecularity

Chemical Reaction	Molecularity
$PCl_5 \rightarrow PCl_3 + Cl_2$	Unimolecular
$2HI \rightarrow H_2 + I_2$	Bimolecular
$2SO_2 + O_2 \rightarrow 2SO_3$	Trimolecular
$NO + O_3 \rightarrow NO_2 + O_2$	Bimolecular
$2CO + O_2 \rightarrow 2CO_2$	Trimolecular
$2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$	Trimolecular

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Types of chemical reactions

Oxidation-Reduction or Redox Reaction

$$2\,S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2\,I^-(aq)$$

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Direct Combination or Synthesis Reaction

Synthesis reaction

$$A + B \rightarrow AB$$

Combination of iron and sulfur

$$8\,Fe + S_8 \rightarrow 8\,FeS$$

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Chemical Decomposition or Analysis Reaction

In a decomposition reaction

$$AB \rightarrow A + B$$

The electrolysis of water into oxygen and hydrogen gas is an example of a decomposition reaction:

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

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Single displacement or substitution reaction

Single displacement

$$A + BC \rightarrow AC + B$$

Substitution reaction

$$Zn + 2\ HCl \rightarrow ZnCl_2 + H_2$$

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Metathesis or Double Displacement Reaction

In a double displacement or metathesis reaction two compounds exchange bonds or ions in order to form different compounds.

$$AB + CD \rightarrow AD + CB$$

An example of double displacement reaction occurs between sodium chloride and silver nitrate to form sodium nitrate and silver chloride.

$$NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl(s)$$

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Acid-Base Reaction

An acid-base reaction is a type of double displacement reaction that occurs between an acid and a base. The H^+ ion in the acid reacts with the OH^- ion in the base to form water and an ionic salt:

$$HA + BOH \rightarrow H_2O + BA$$

The reaction between hydrobromic acid (HBr) and sodium hydroxide is an example of an acid-base reaction:

$$HBr + NaOH \rightarrow NaBr + H_2O$$

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