Chapter 13

Chemical Kinetics:

Rates of Reactions

Disappearance of Color

(a) (b) (c)

Reaction Rates

average rate

- the rate over a specific time interval

instantaneous rate

- the rate for an infinitely small interval

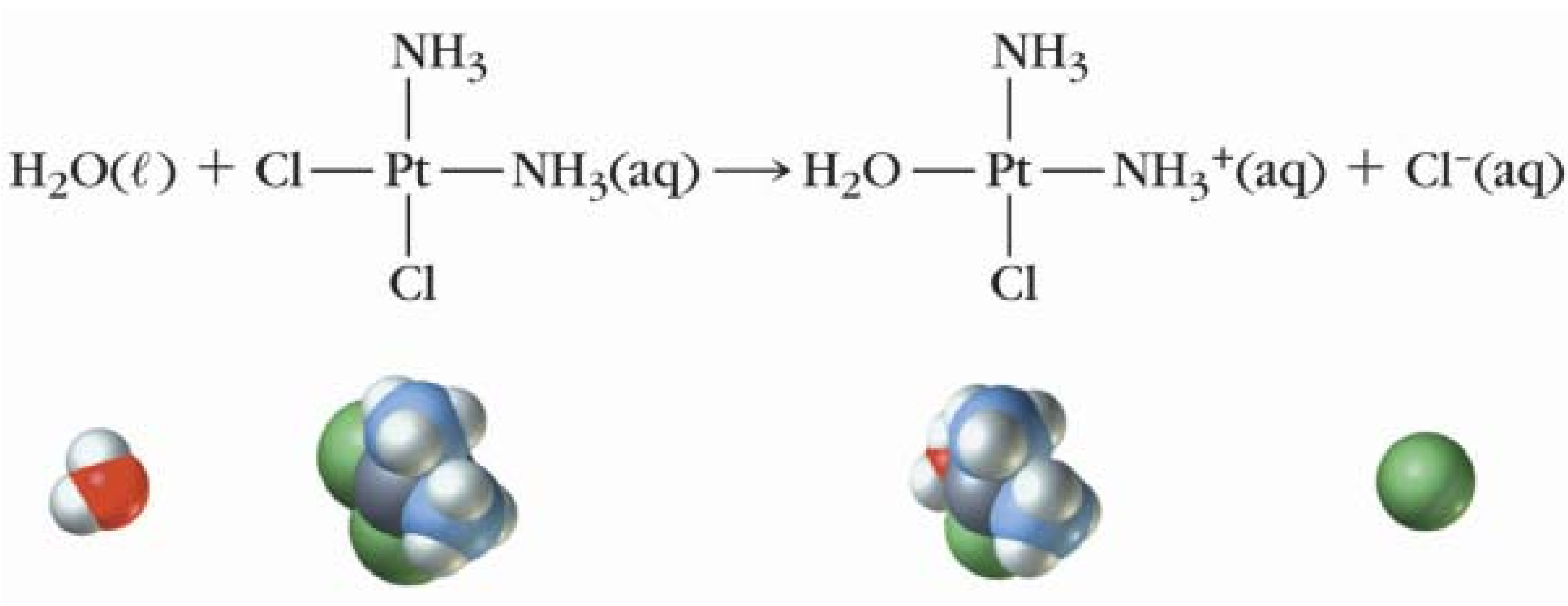
$$\text{rate of reaction} = -\Delta[\text{reactant}]/\Delta t$$

Reaction Rates and Stoichiometry

$$aA + bB \rightarrow cC + dD$$

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

예시: Reaction of Cisplatin with Water

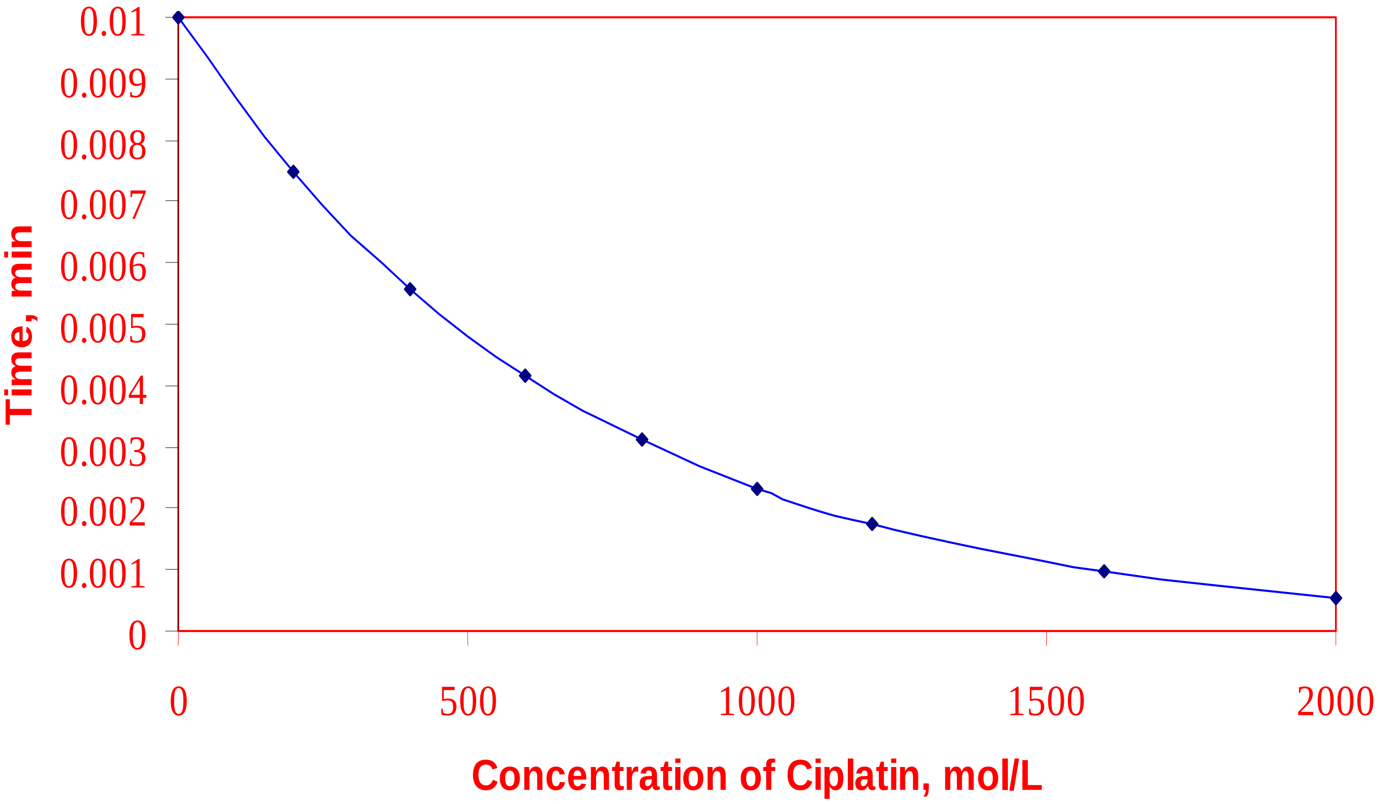


Reaction of Cisplatin with Water

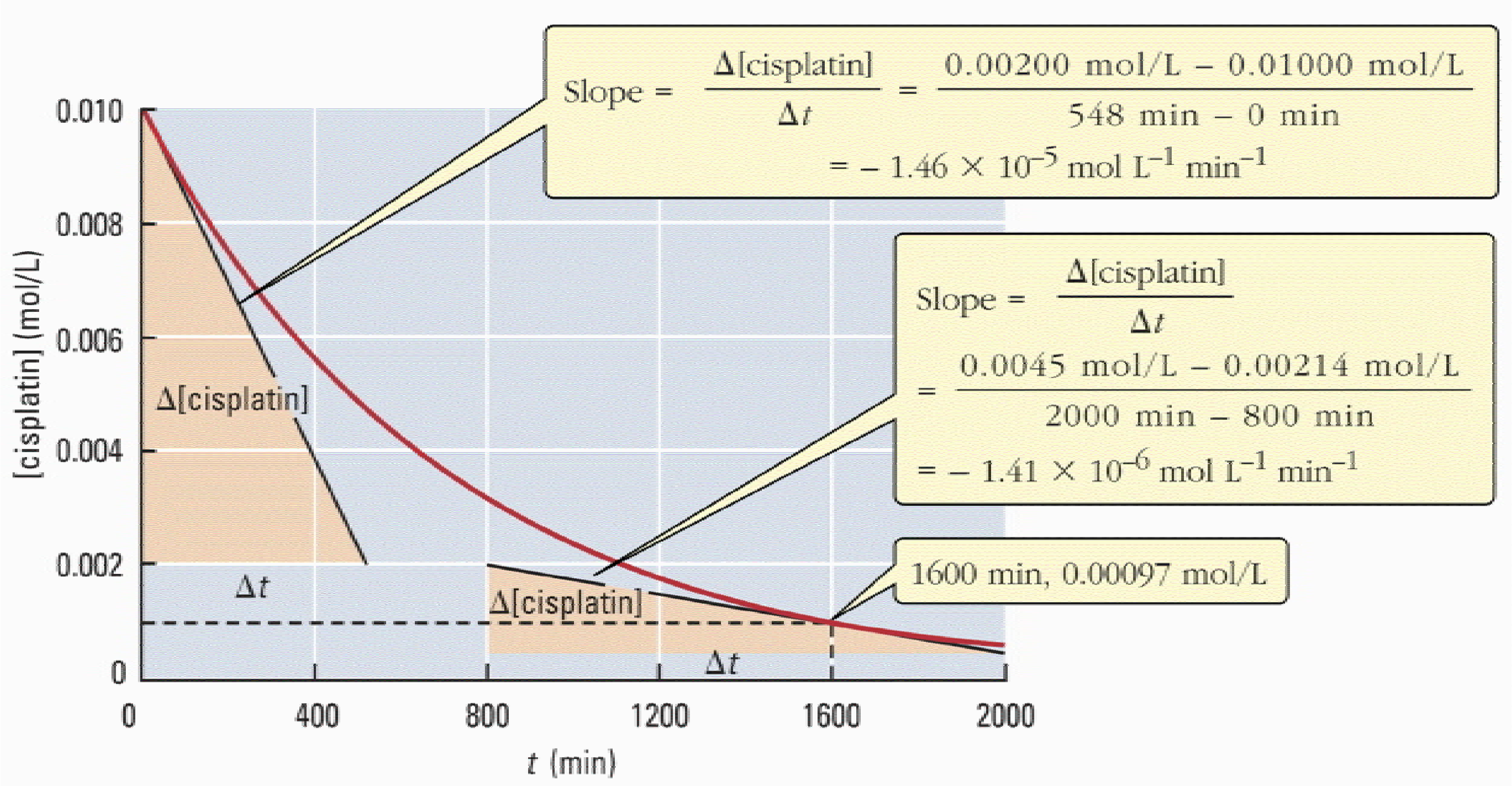
TABLE 13.1 Concentration-Time Data for Reaction of Cisplatin with Water at 25 °C

Time, t (min)	Concentration [cisplatin] (mol/L)	Average rate (mol L^{-1} min^{-1})
0.0	0.01000	
		12.7×10^{-6}
200.0	0.00747	
		9.46×10^{-6}
400.0	0.00558	
		7.06×10^{-6}
600.0	0.00416	
		5.27×10^{-6}
800.0	0.00311	
		3.94×10^{-6}
1000.0	0.00232	
		2.94×10^{-6}
1200.0	0.00173	
		1.92×10^{-6}
1600.0	0.00097	
		1.08×10^{-6}
2000.0	0.00054	

Reaction of Cisplatin with Water



Instantaneous Reaction Rate



Rate Law

- an expression which relates the rate to the concentrations and a specific rate constant
- reaction rate = $k\,[A]^m\,[B]^n$

where $m \rightarrow$ order with regard to A

$n \rightarrow$ order with regard to B

overall order = $m + n$

• order of reaction: exponent of the concentration for a reactant that implies the number of molecules of that species involved in the rate determining step

- first order, exponent equals one

- second order, exponent equals two

Integrated Rate Laws

Reaction: A $\rightarrow$ products

rate = $-(\Delta[A]/\Delta t) = k[A]^m$

average rate

rate = $-(d[A]/dt) = k[A]^m$

instantaneous rate

$\rightarrow$ Integration

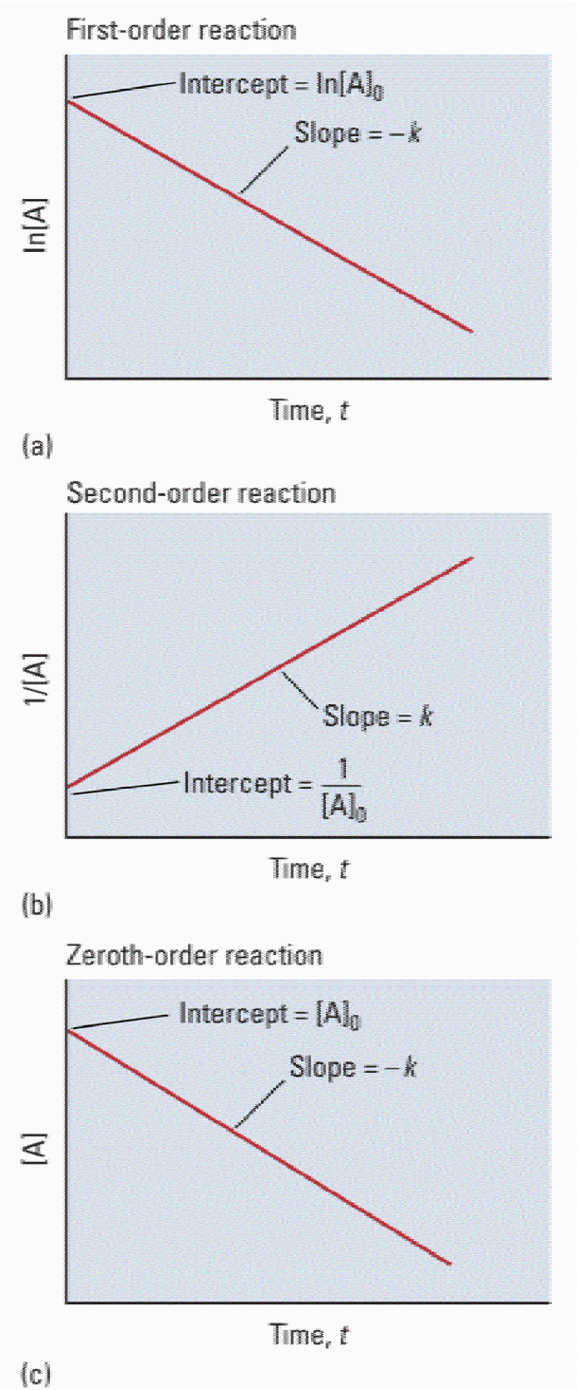
Integrated Rate Laws

TABLE 13.2 Integrated Rate Laws

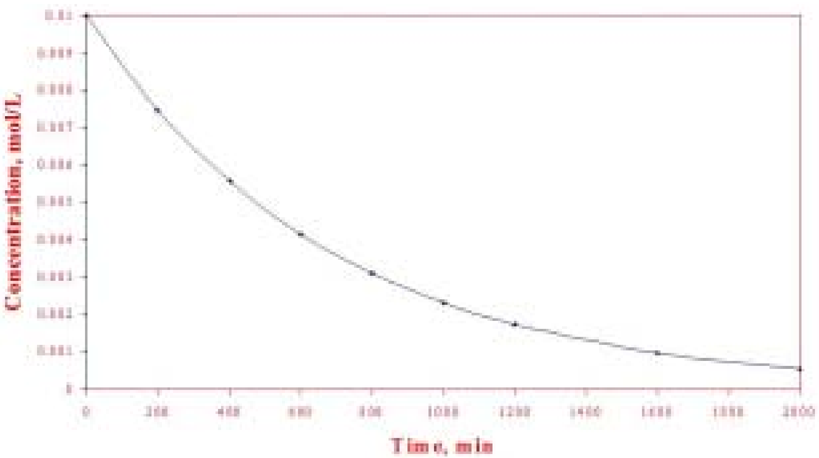
Order	Rate equals	Integrated rate law*	Straight-line plot	Slope of plot	Units of k
0	$k[A]^0 = k$	$[A]_t = -kt + [A]_0$	$[A]_t$ vs t	$-k$	conc time^{-1}
1	$k[A]$	$\ln[A]_t = -kt + \ln[A]_0$	$\ln[A]_t$ vs t	$-k$	time^{-1}
2	$k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]_t}$ vs t	k	conc^{-1} time^{-1}

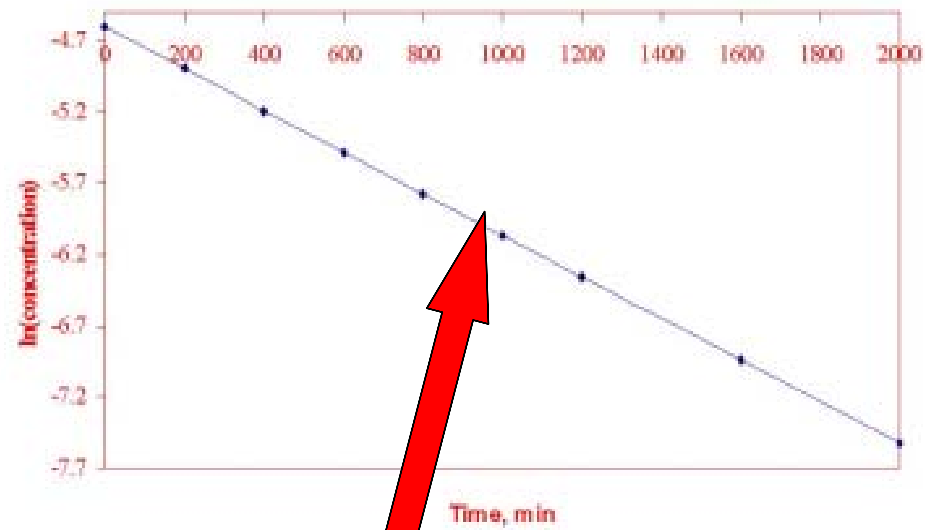
* In the table, $[A]_0$ indicates the initial concentration of substance A, that is, the concentration of A at $t = 0$, the time when the reaction was started.

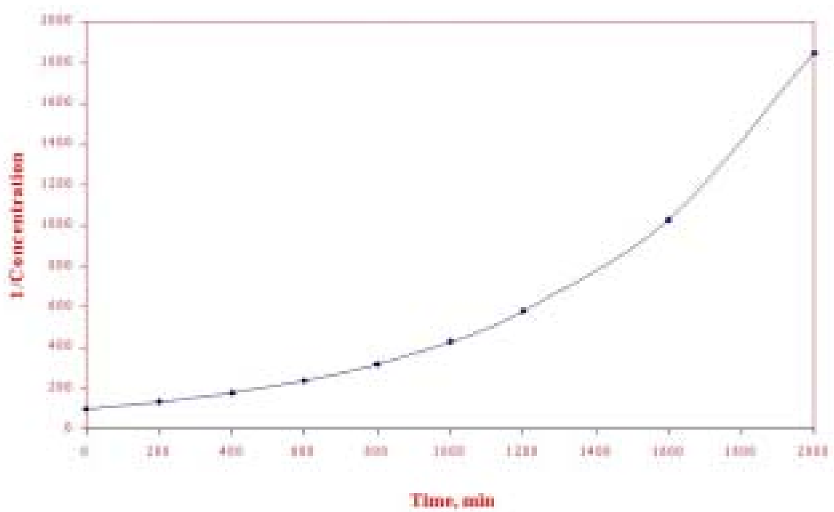
First-order, Second-order, and Zeroth-order Plots



Integrated Rate Laws Plots for Cisplatin Reaction with Water





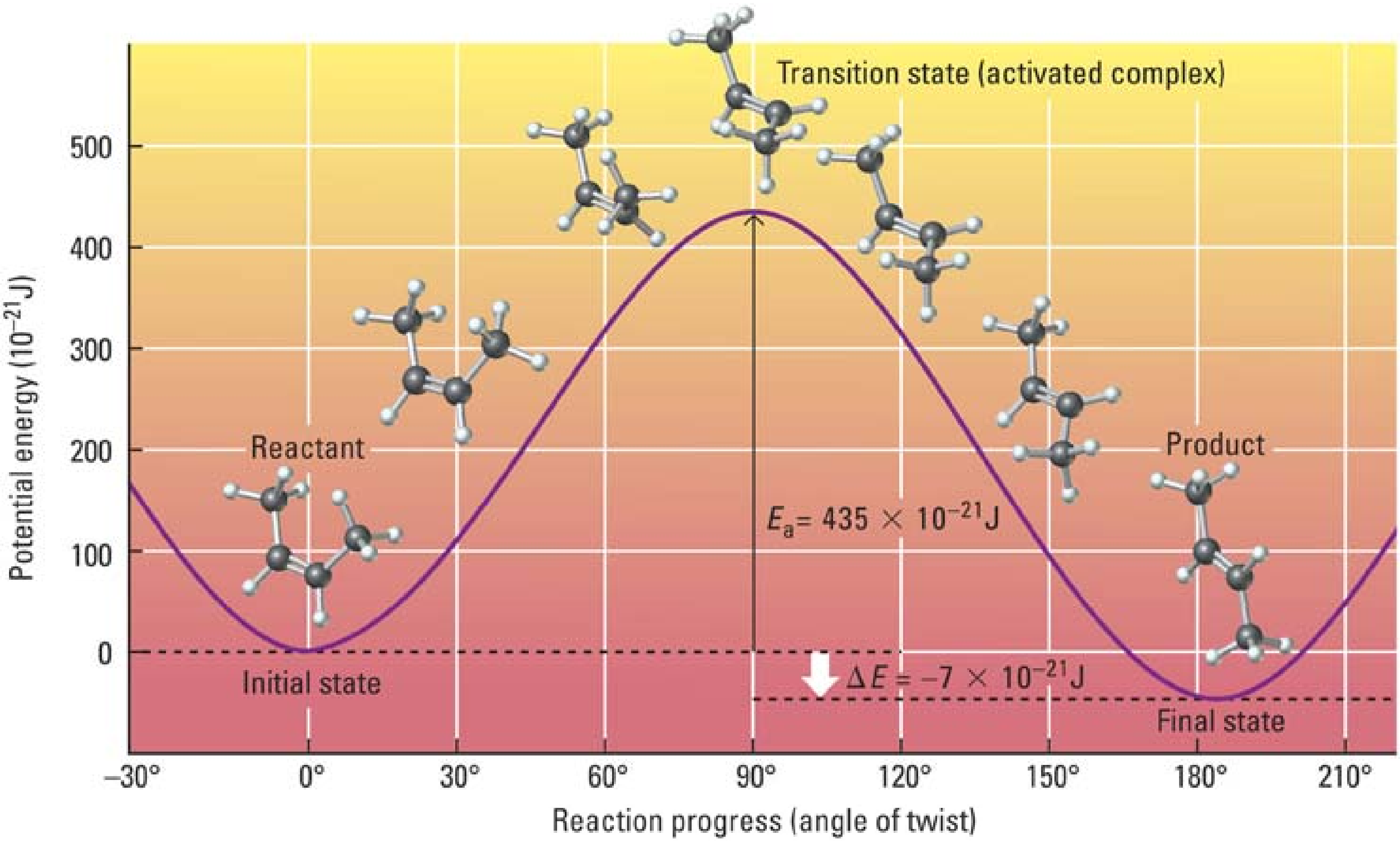


This plot of ln[Cisplatin] vs. time produces a straight line, suggesting that the reaction is first-order.

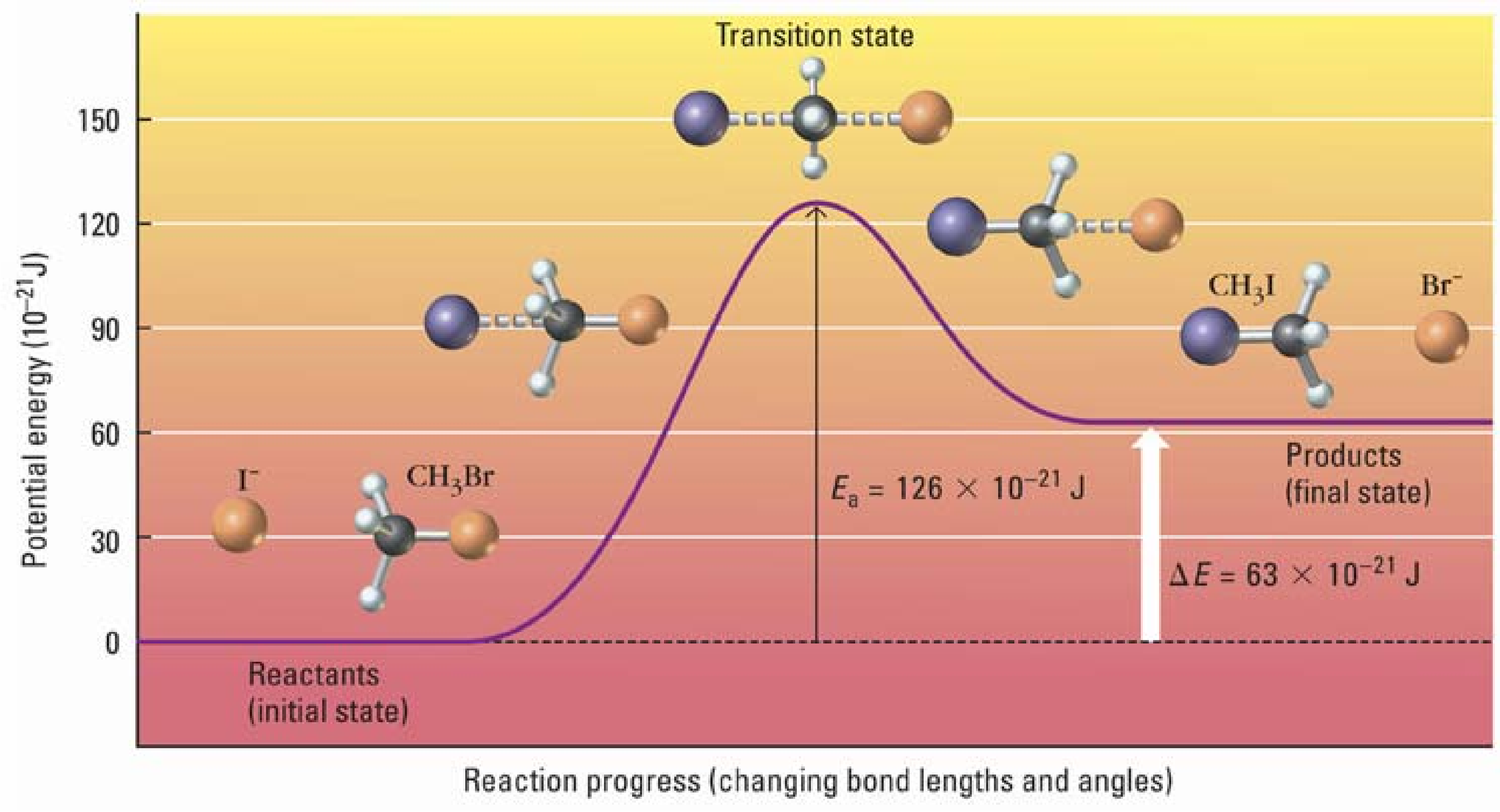
A Nanoscale View: Elementary Reactions

- unimolecular - rearrangement of a molecule
- bimolecular - reaction involving the collision of two particles
- termolecular - reaction involving the collision of three particles

Unimolecular Reaction



Bimolecular Reaction

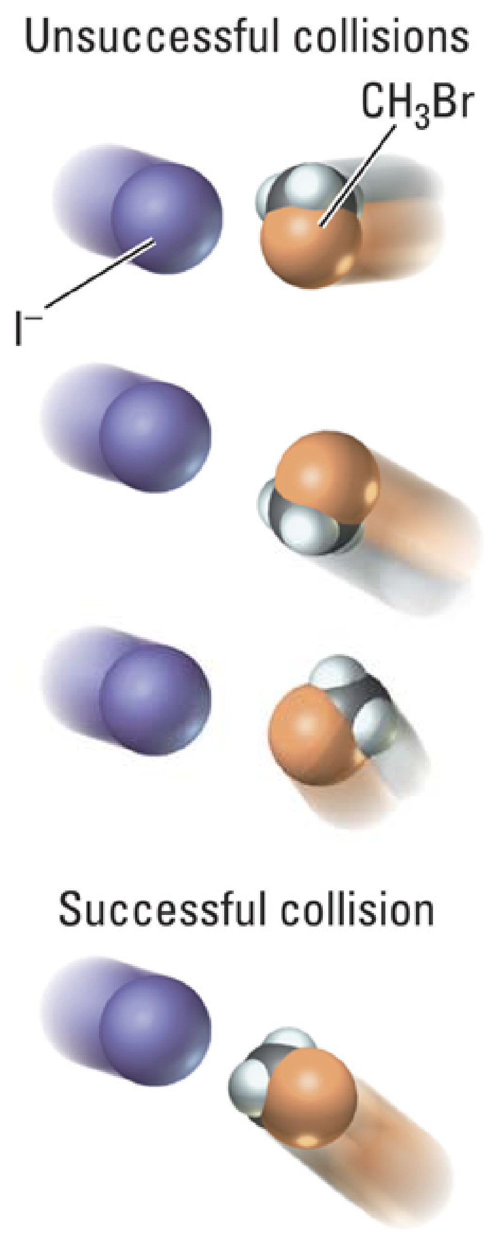


Collision Rate Model

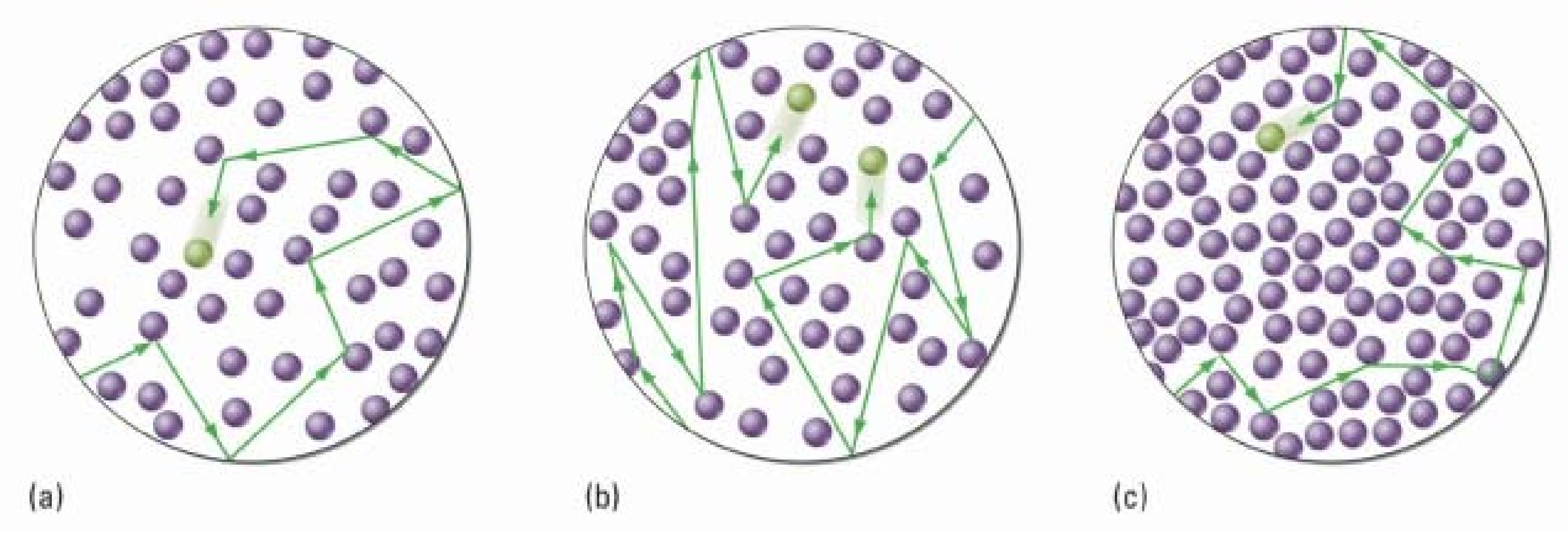
Three conditions must be met at the nanoscale level if a reaction is to occur:

- the molecules must *collide*;
- they must be positioned so that the reacting groups are together in a *transition state* between reactants and products;
- and the collision must have enough *energy* to form the transition state and convert it into products.

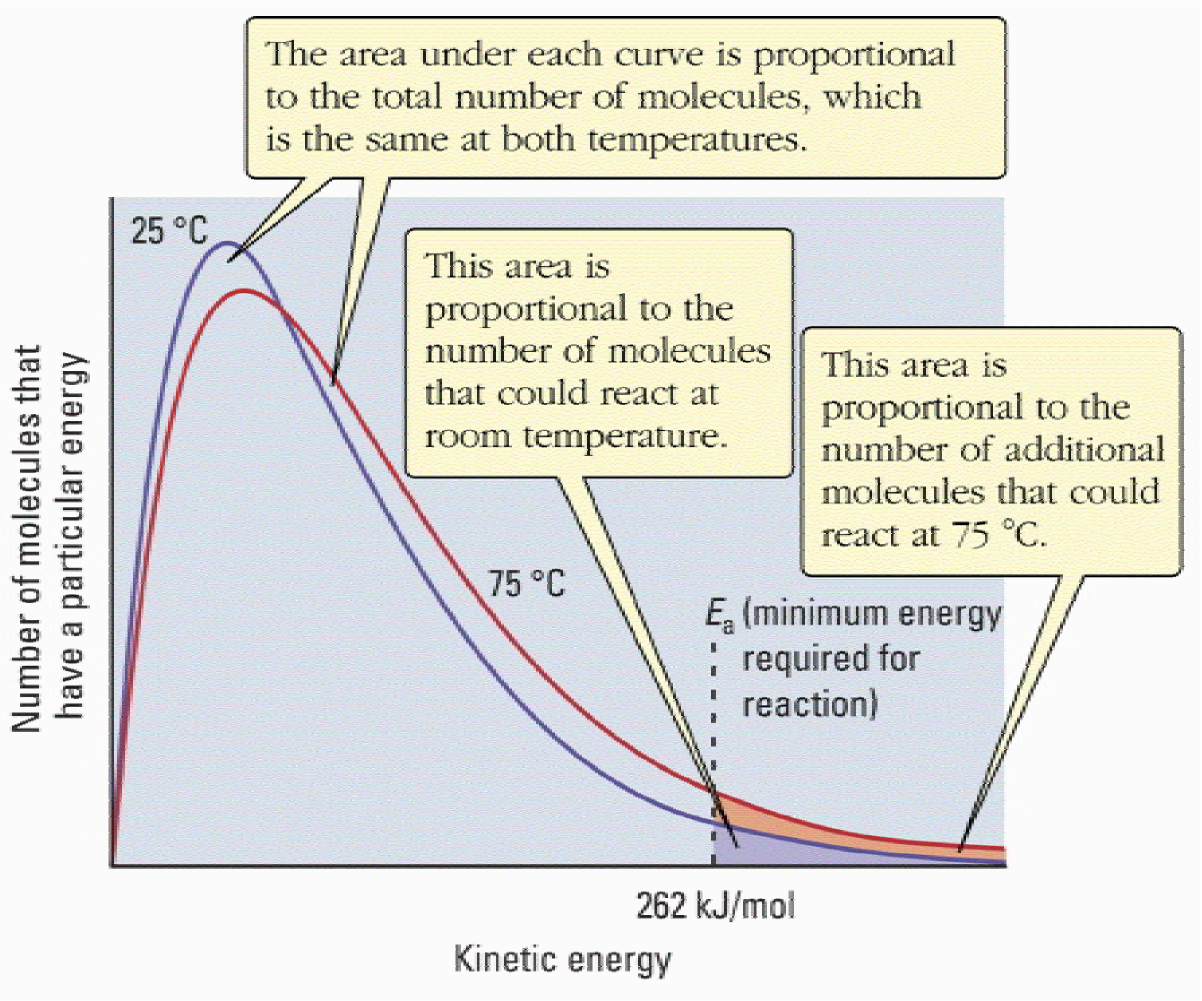
Unsuccessful Collisions



Effect of Concentration on Frequency of Bimolecular Collisions



Energy Distribution Curves



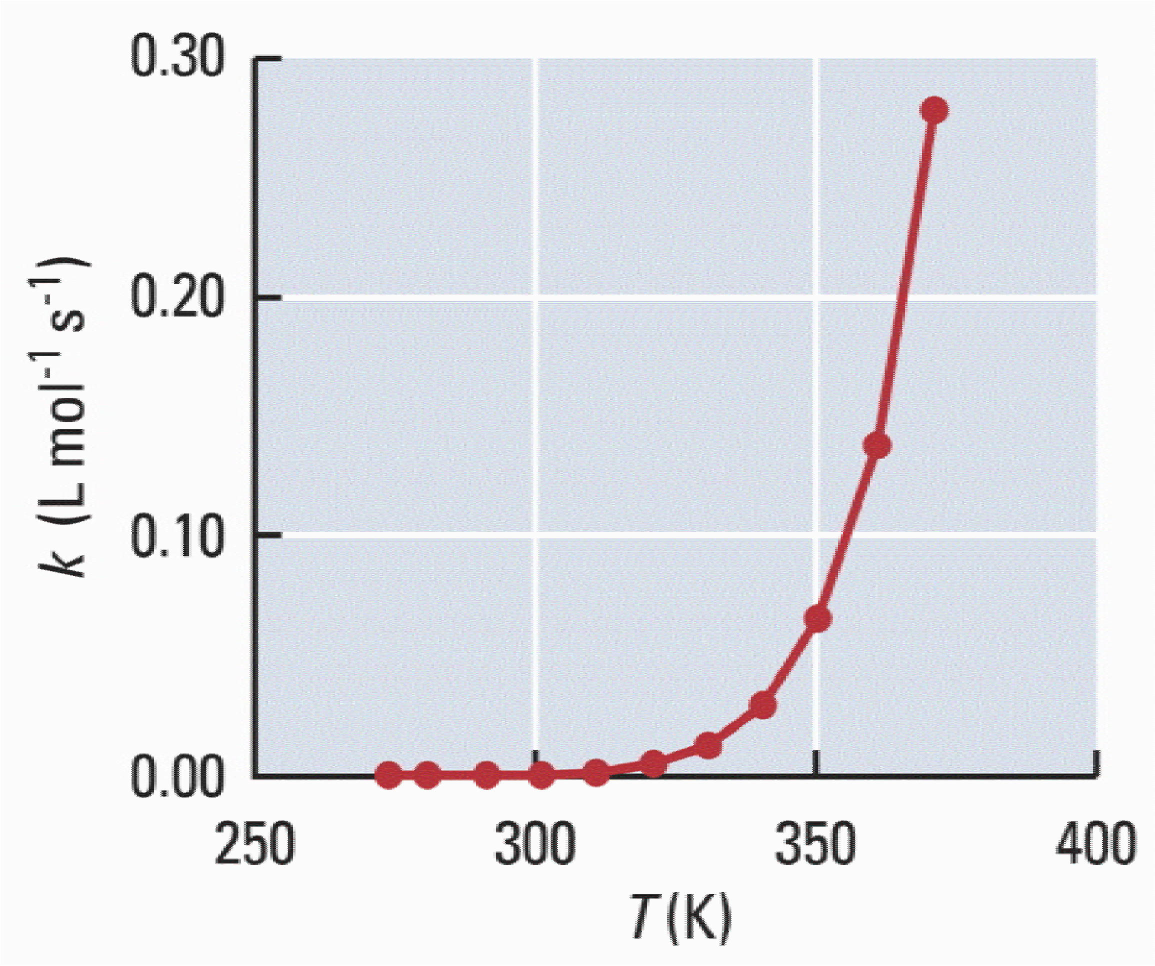
Transition State:Activated Complex

an unstable arrangement of atoms that has the highest energy reached during the rearrangement of the reactant atoms to give products of a reaction

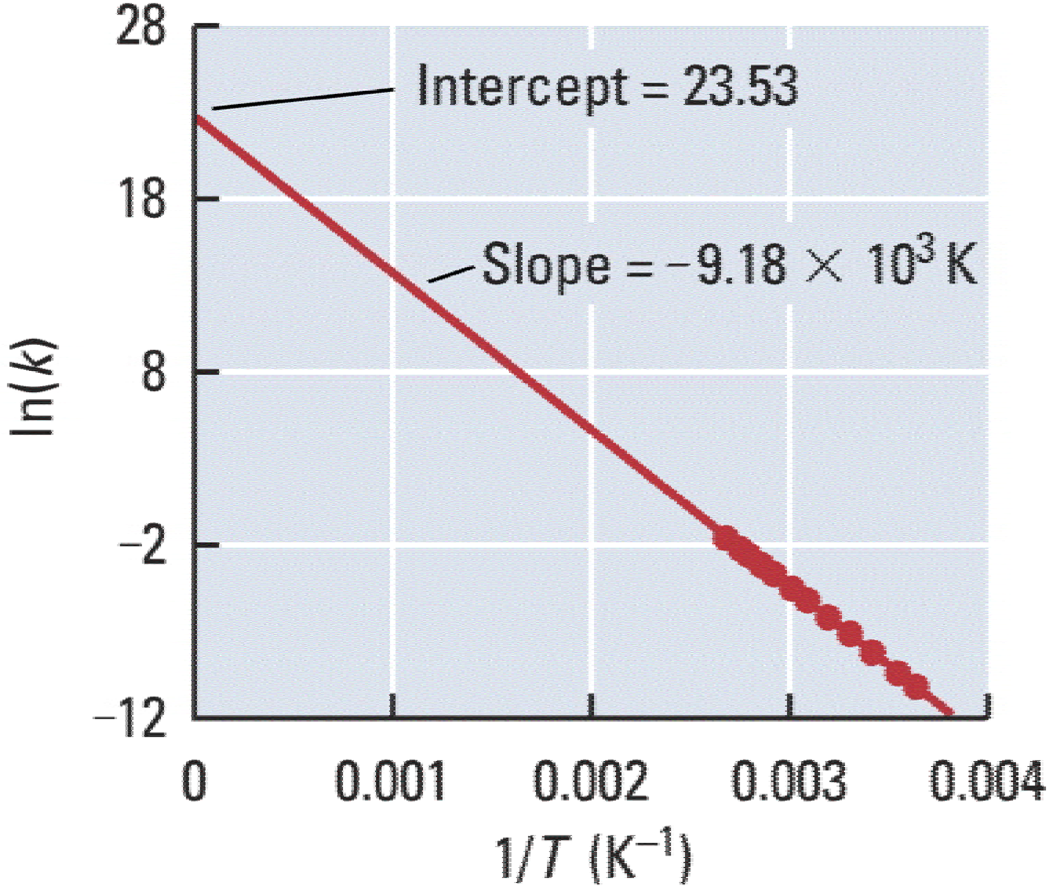
Activation Energy

the minimum energy required to start a reaction

Effect of Temperature on Rate Constant



Determining Graphically the Activation Energy



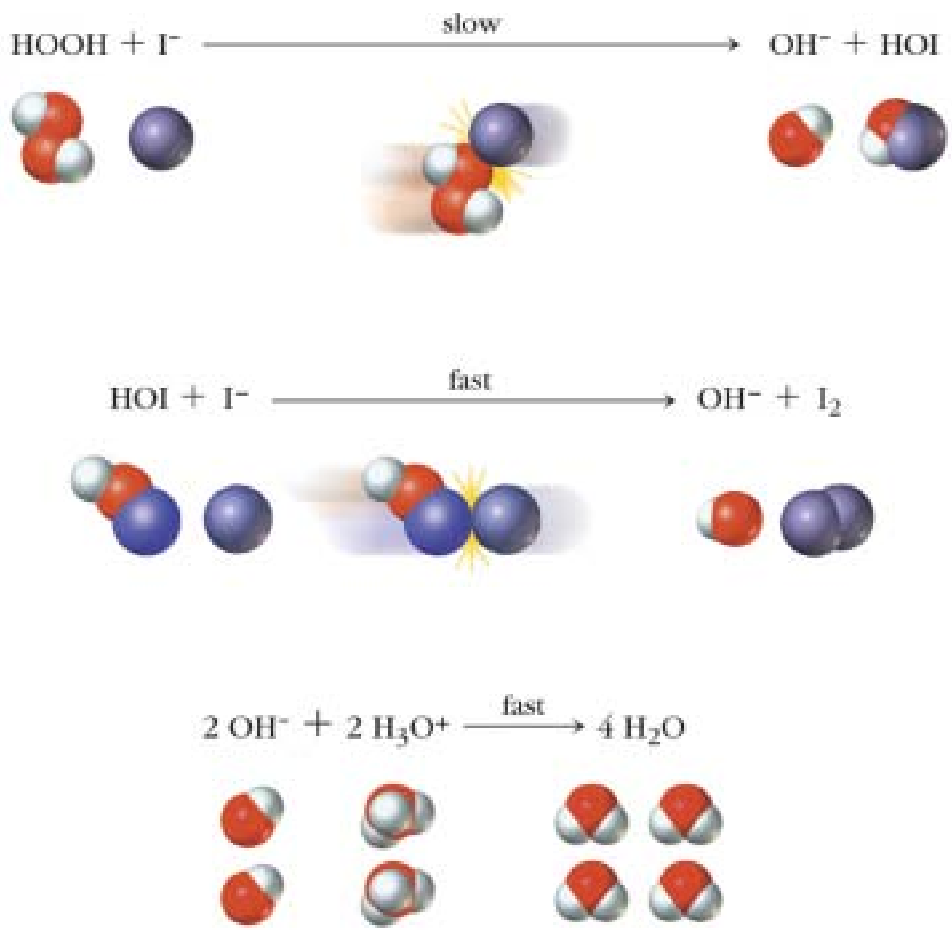
Reaction Mechanism

- A set of elementary reactions which represent the overall reaction

Rate Determining Step

- slowest step in a multistep mechanism
- the step which determines the overall rate of the reaction

Mechanism Oxidation of Iodide Ion by Hydrogen Peroxide



Rate Law of Oxidation of Iodide Ion by Hydrogen Peroxide

Step 1.

$$HOOH + I^{-} \rightarrow HOI + OH^{-}$$

slow step - rate determining step, suggests that the reaction is first order with regard to hydrogen peroxide and iodide ion

$$\text{rate} = k[HOOH][I^{-}]$$

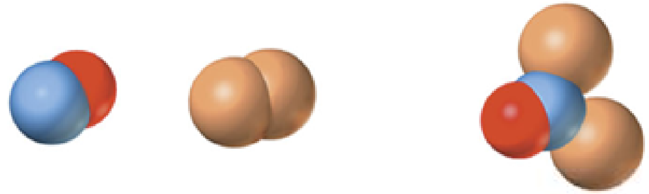
Mechanisms with a Fast Initial Step

$$2\ NO_{(g)} + Br_{2(g)} \rightarrow 2NOBr_{(g)}$$

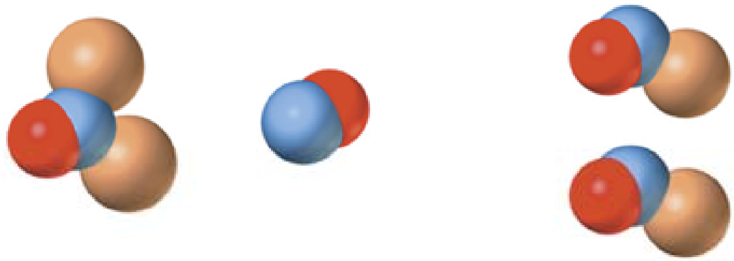
$$rate_{experimental} = k[NO]^2[Br_2]$$

Mechanism of NO + Br_2

$$NO(g) + Br_2(g) \underset{\text{Step-1}}{\overset{\text{Step+1}}{\rightleftharpoons}} NOBr_2(g) \qquad \text{fast}$$



$$NOBr_2(g) + NO(g) \xrightarrow{\text{Step+2}} 2\ NOBr(g) \qquad \text{slow}$$



Rate = $k[NOBr_2][NO]$

Rate Constants for NO + Br_2

Step +1(forward), rate constant k_1

Step -1(backward), rate constant k_{-1}

Step 2, rate constant k_2

$$rate_{Step+1} = rate_{Step-1} + rate_{Step2}$$

$$k_1[NO][Br_2] = k_{-1}[NOBr_2] + k_2[NOBr_2][NO]$$

Relationships of Rate Constants

$k_1[NO][Br_2] \sim k_{-1}[NOBr_2]$

(steady state approximation)

thus

$[NOBr_2] = (k_1/k_{-1})[NO][Br_2]$

substituting into

rate = $k_2[NOBr_2][NO]$

rate = $k_2((k_1/k_{-1})[NO][Br_2])[NO]$

rate = $(k_2k_1/k_{-1})[NO]^2[Br_2]$

Catalyst

susbstance which speeds up the rate of a reaction while not being consumed

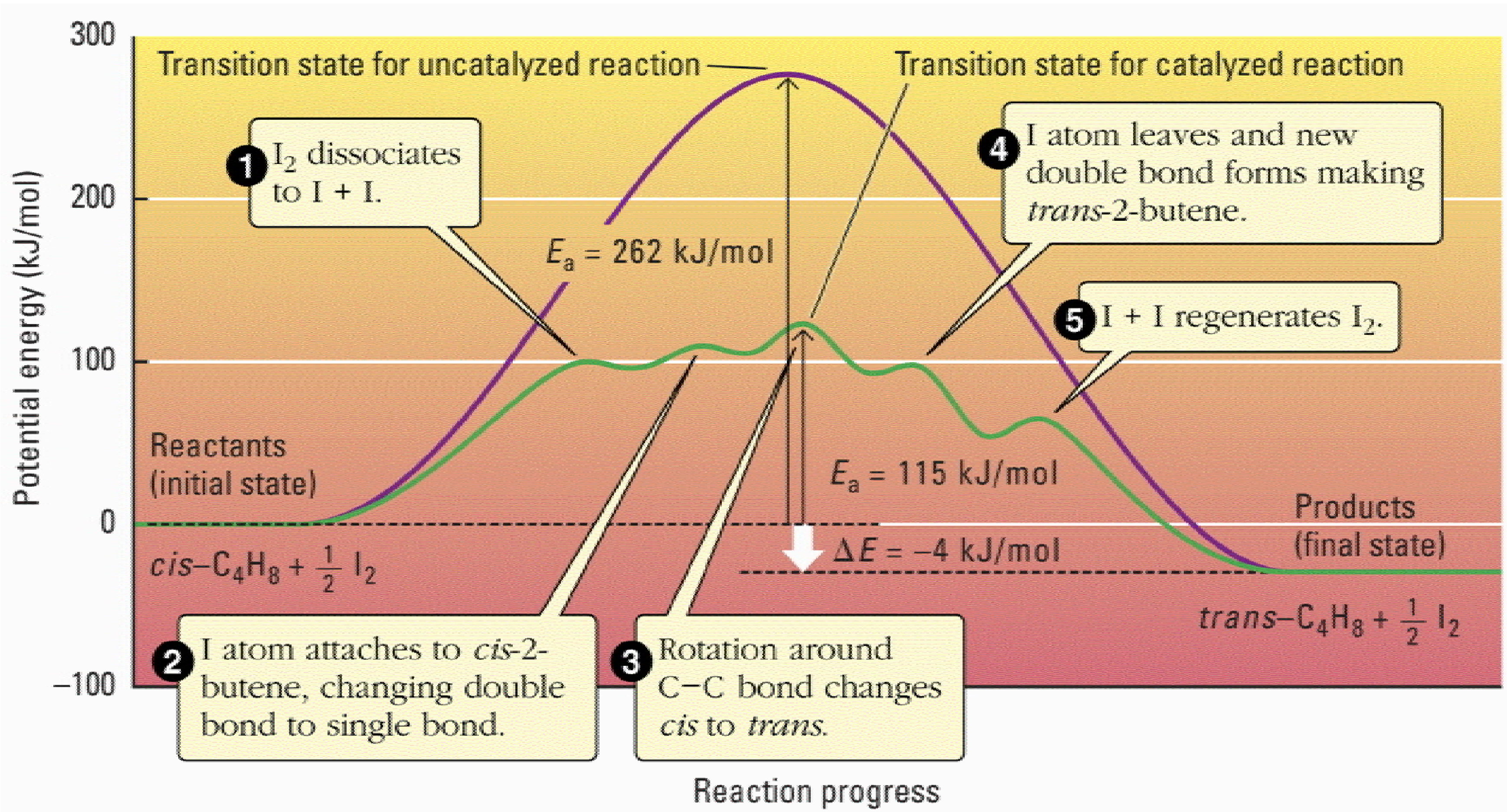
Homogeneous Catalysis - a catalyst which is in the same phase as the reactants

Heterogeneous Catalysis - a catalyst which is in the different phase as the reactants

catalytic converter

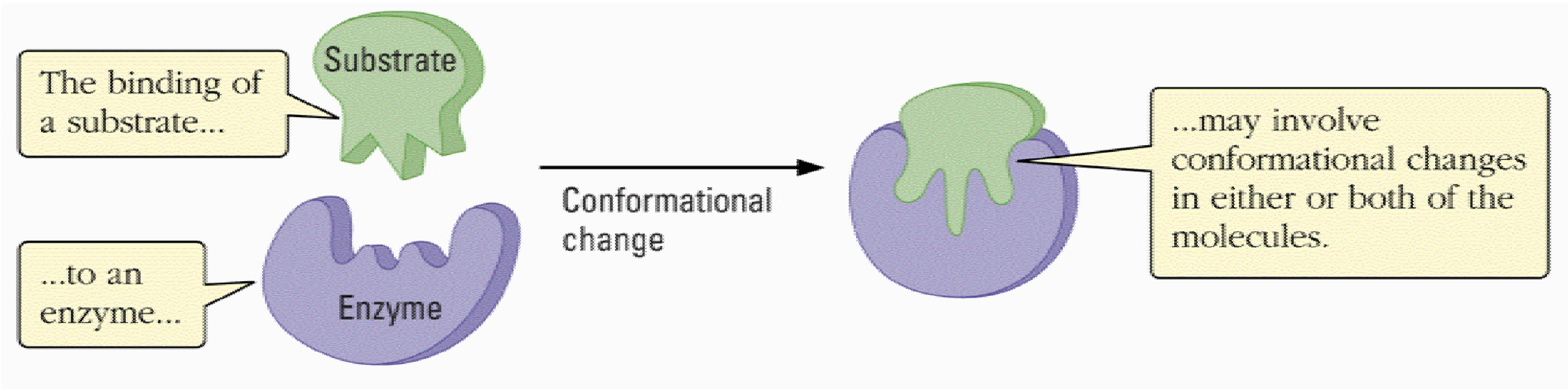
ex. solid catalyst working on gaseous materials

Catalyzed & Uncatalyzed Reactions

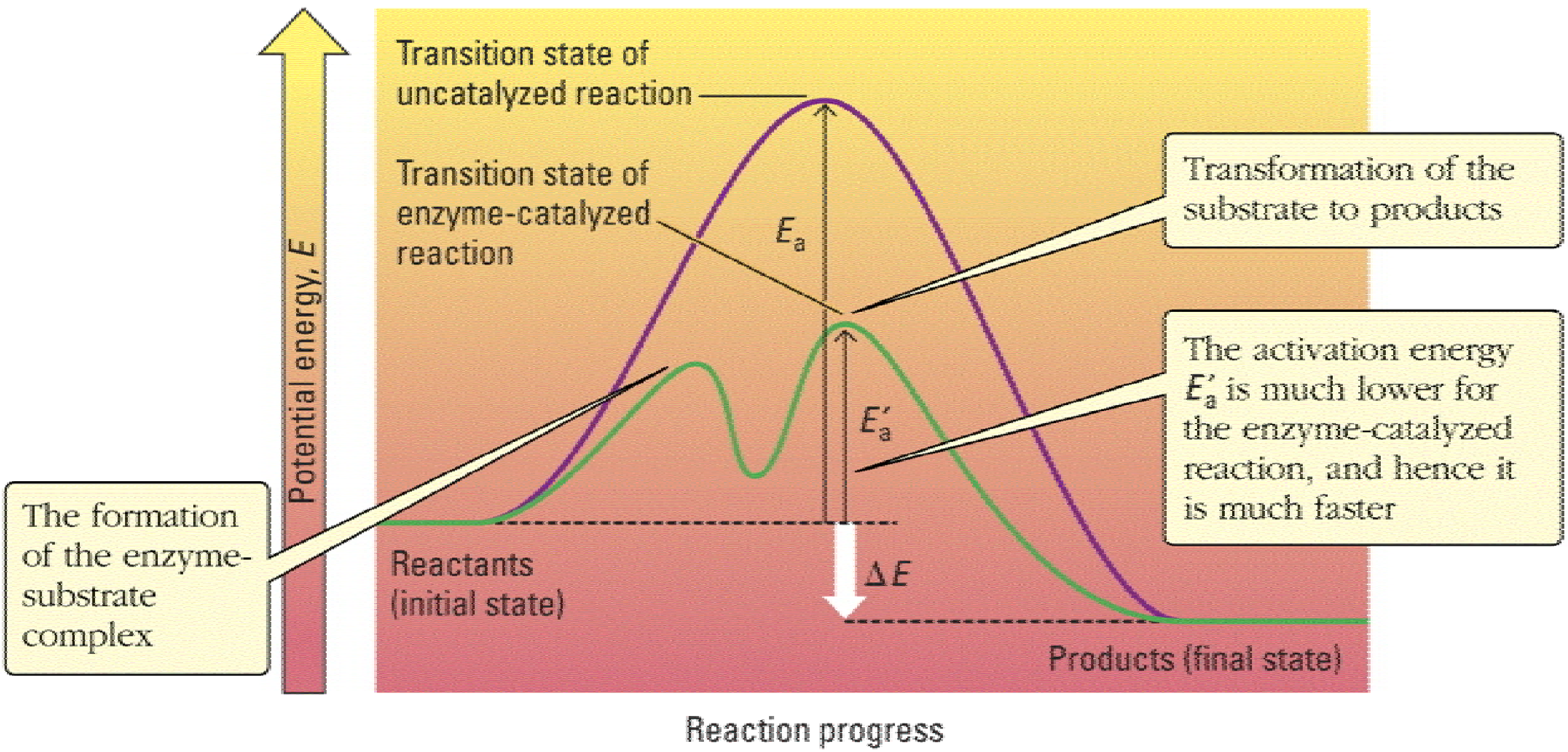


Enzymes

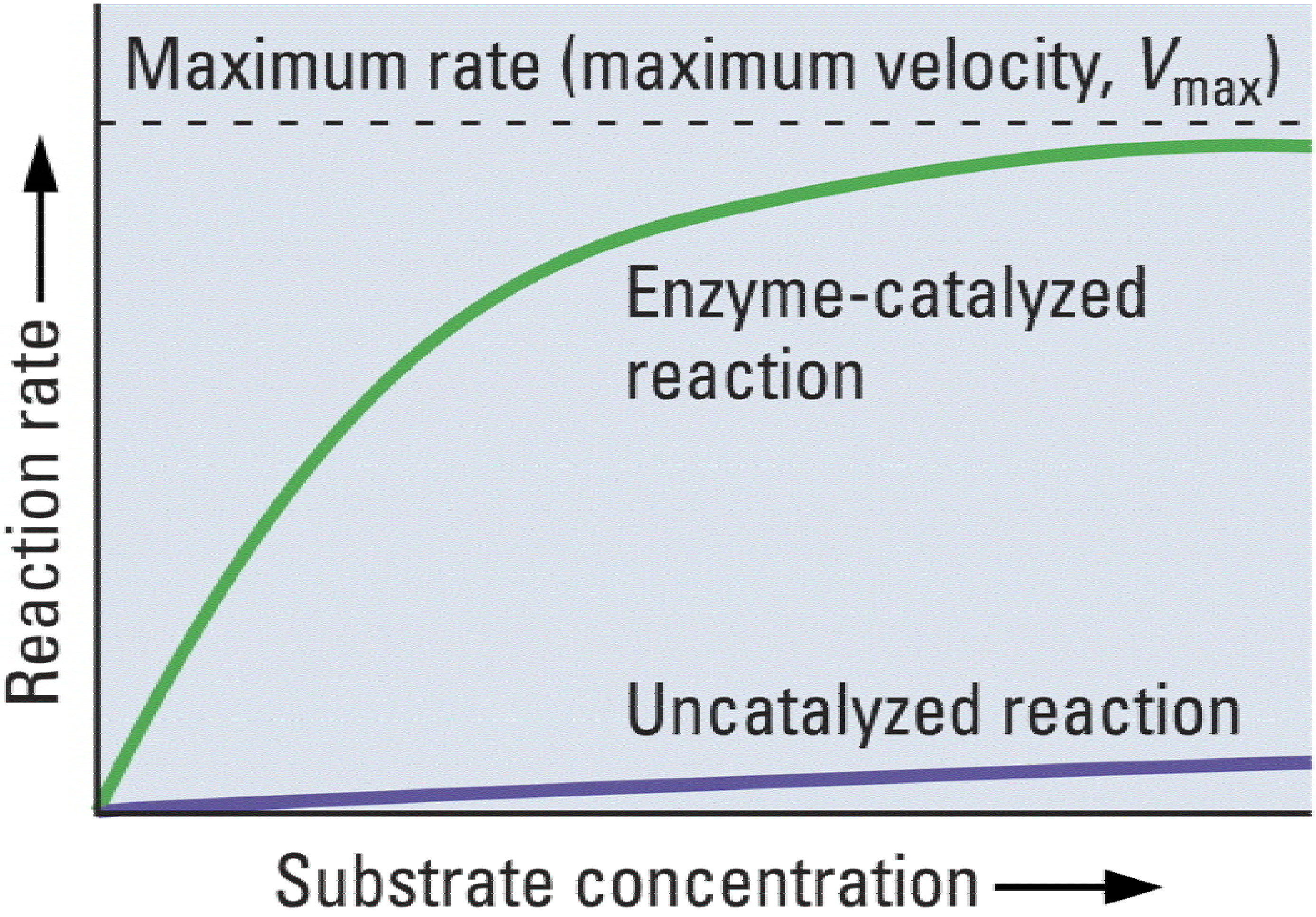
any one of many specialized organic substances, composed of polymers of amino acids, that act as catalysts to regulate the speed of the many chemical reactions involved in the metabolism of living organisms.



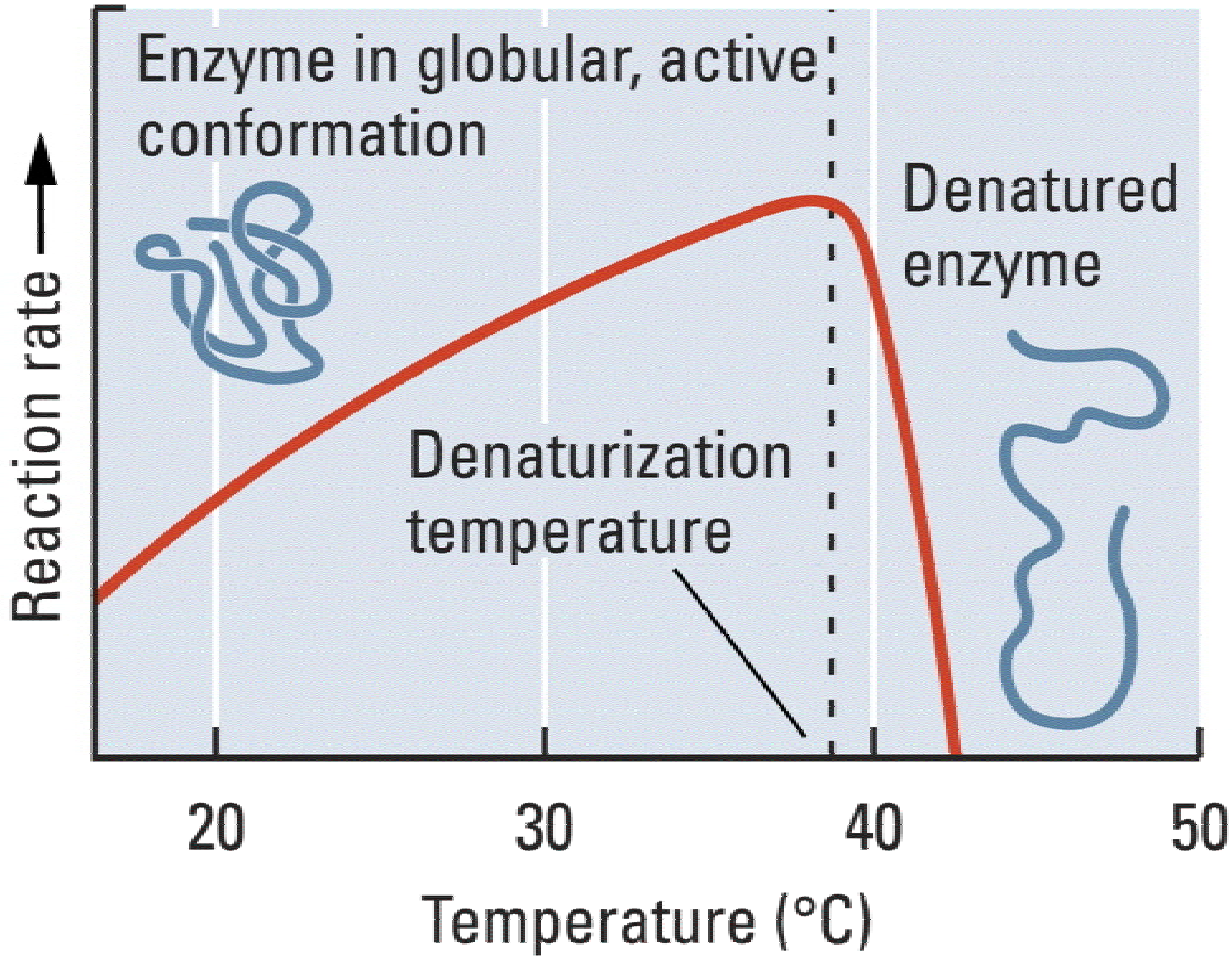
Enzyme Catalyzed Reaction



Maximum Velocity for an Enzyme Catalyzed Reaction



Enzyme Activity Destroyed by Heat



Conversion of NO to N_2 + O_2