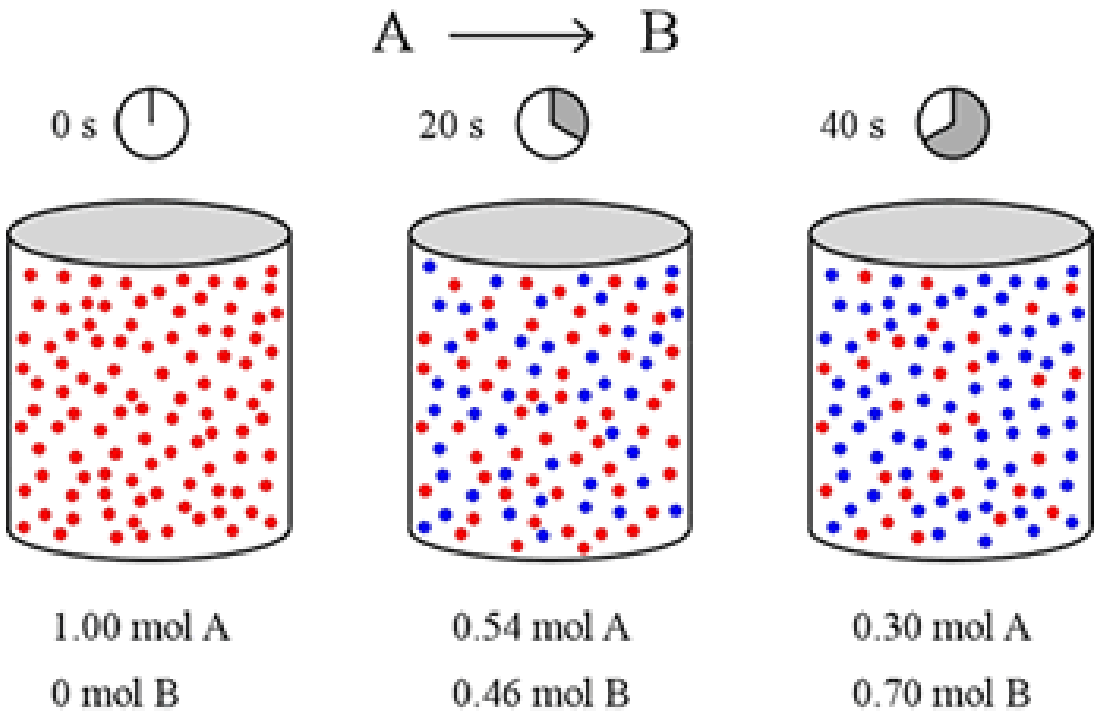
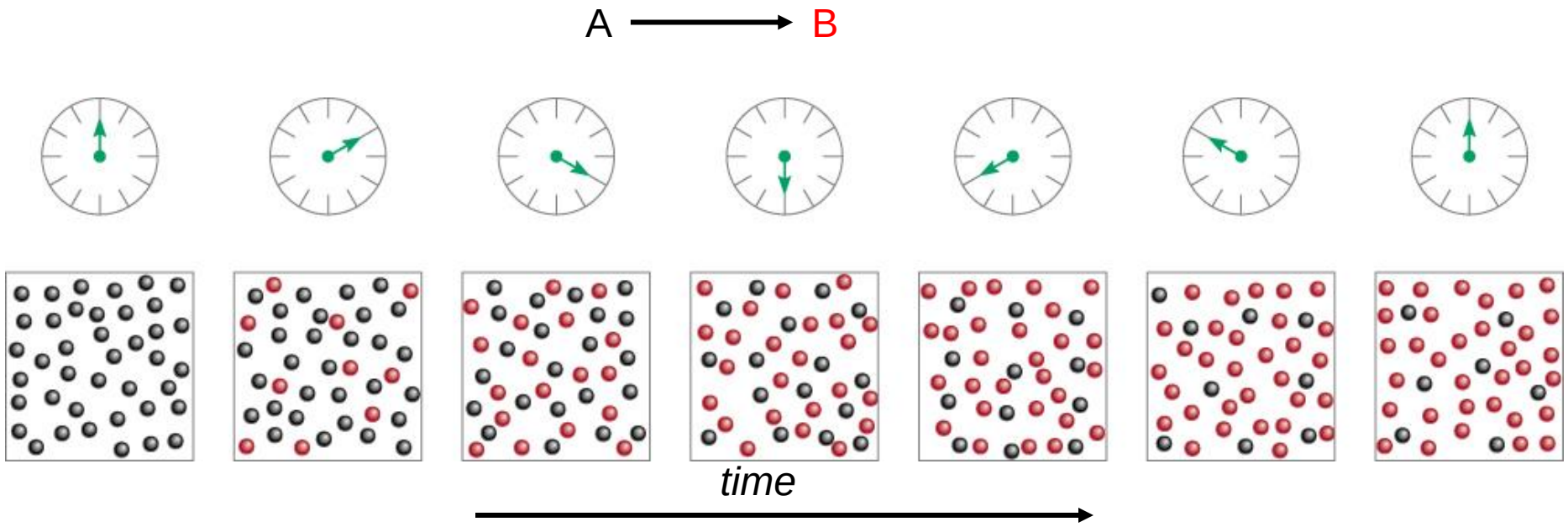
Ch 13 Chemical Kinetics

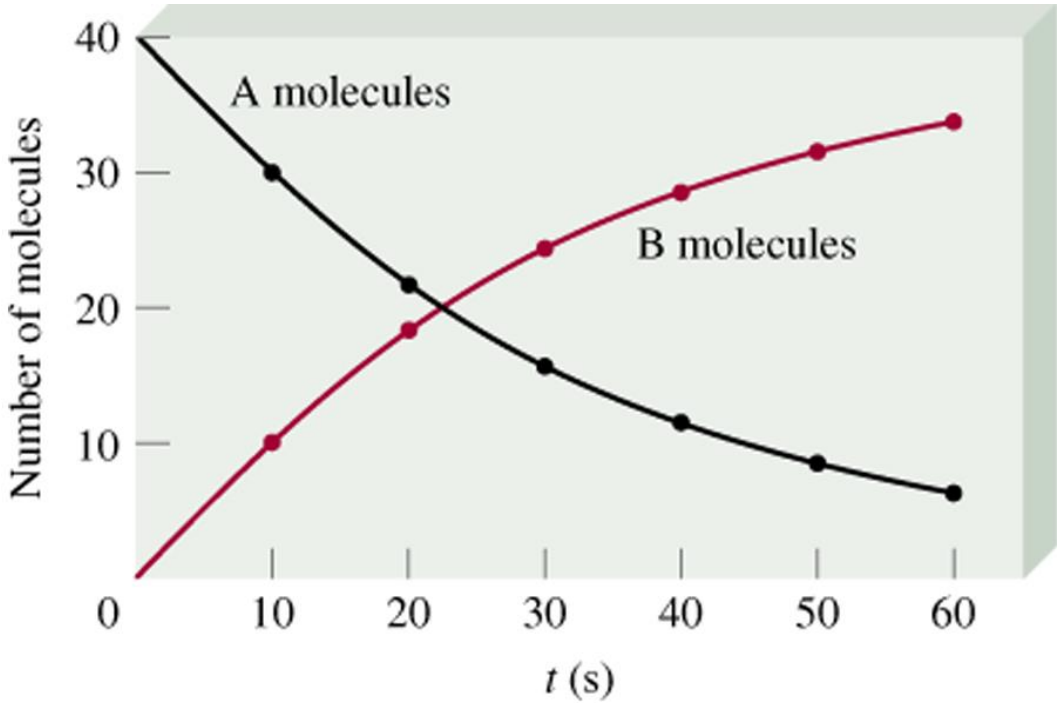


Modified by Dr. Cheng-Yu Lai

Outline

1. Meaning of reaction rate
2. Reaction rate and concentration
3. Writing a Rate Law
4. Reactant concentration and time
5. Reaction rate and temperature
6. Catalysis and Reaction mechanisms





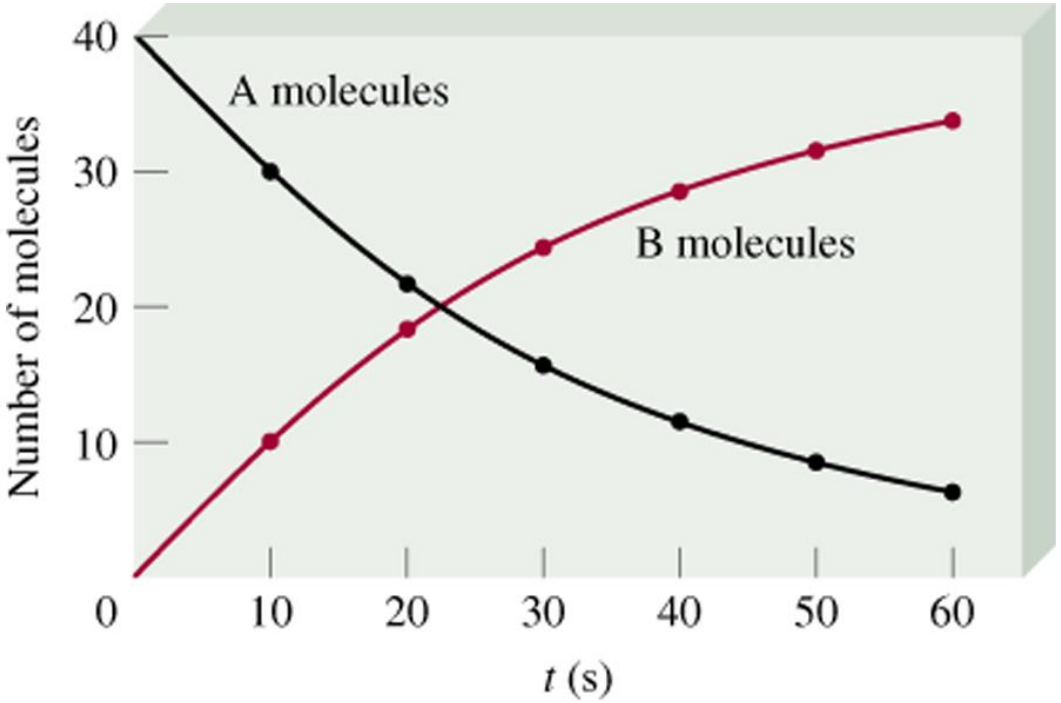
We want to know how fast is this reaction ?

Reaction Rate = ?

Reaction Rate

The change in concentration of a reactant or product per unit of time.

$$Rate = \frac{[A]\,at\,time\,t_2 - [A]\,at\,time\,t_1}{t_2 - t_1} \qquad Rate = \frac{\Delta[A]}{\Delta t}$$



Rate A = $-\frac{\Delta[A]}{\Delta t}$ = - (5-40)/60

Rate B = $\frac{\Delta[B]}{\Delta t}$ = (35-0)/60

Reaction Rate and Stoichiometry

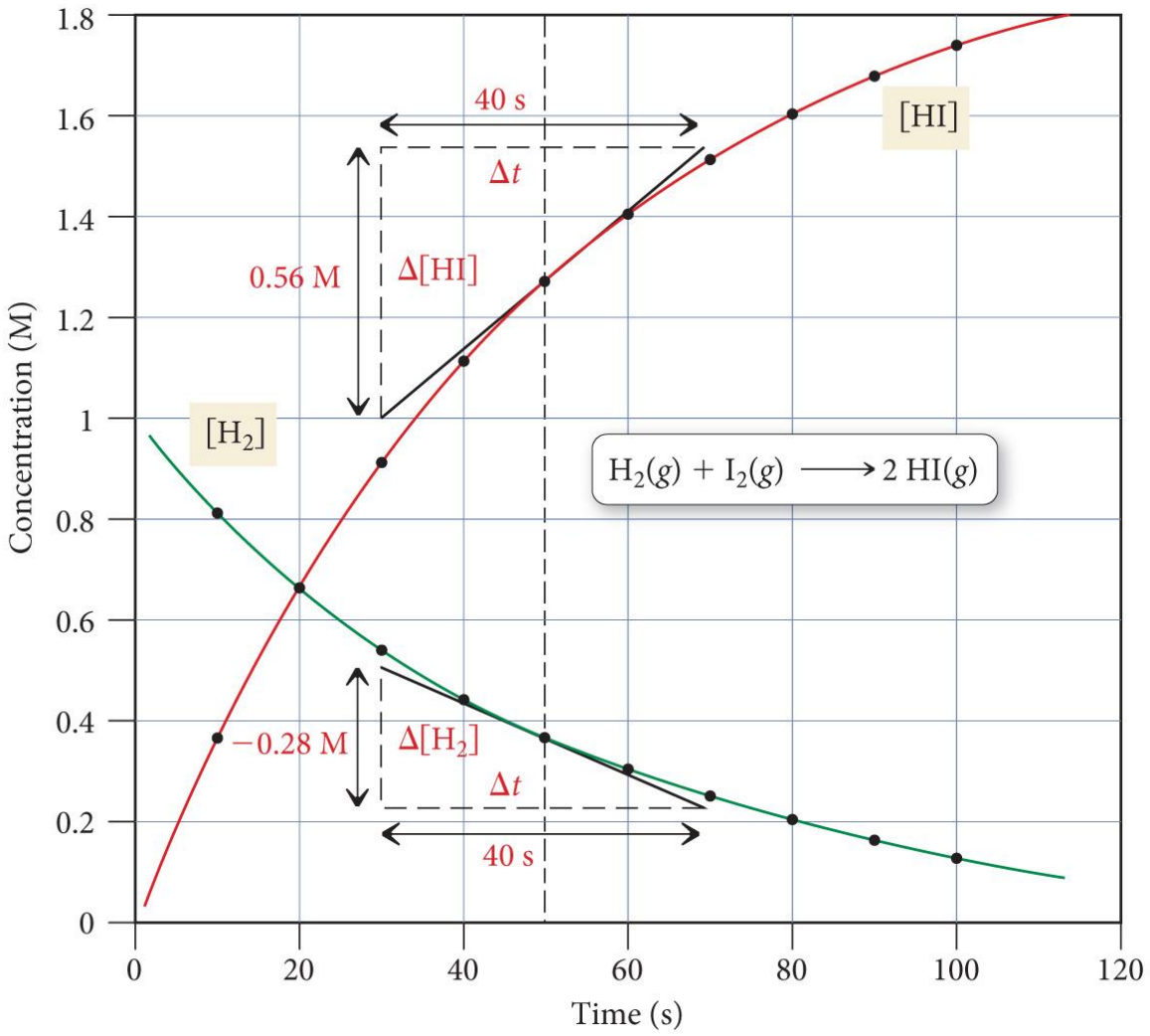
- In most reactions, the coefficients of the balanced equation are not all the same.

$$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2\,HI_{(g)}$$

- For these reactions, the change in the number of molecules of one substance is a multiple of the change in the number of molecules of another.
  - For the above reaction, for every 1 mole of H_2 used, 1 mole of I_2 will also be used and 2 moles of HI made.
  - Therefore, the rate of change will be different.
- To be consistent, the change in the concentration of each substance is multiplied by 1/coefficient.

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

$H_{2\,(g)} + I_{2\,(g)} \rightarrow 2\,HI_{\,(g)}$



Using $[H_2]$, the instantaneous rate at 50 s is as follows:

$$\text{Rate} = -\frac{-0.28\,\text{M}}{40\,\text{s}}$$

$$\text{Rate} = 0.0070\,\frac{\text{M}}{\text{s}}$$

Using [HI], the instantaneous rate at 50 s is as follows:

$$\text{Rate} = \left(\frac{1}{2}\right)\frac{0.56\,\text{M}}{40\,\text{s}}$$

$$\text{Rate} = 0.0070\,\frac{\text{M}}{\text{s}}$$

General Form of the Rate Relationship

- For a reaction where aA + bB → cC + dD

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

Example - Formation of Ammonia

- N_2 (g) + 3H_2 (g) → 2NH_3 (g)

$$\text{rate} = \frac{-\Delta[N_2]}{\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{2\Delta t}$$

- If the N_2 is disappearing at 0.10 mol/L-min, the H_2 is disappearing at the rate of 0.30 mol/L-min and ammonia is appearing at a rate of 0.20 mol/L-min

Reaction Rate Relationship between Reactants and Products Concentration

- N_2O_5 (g) → $2NO_2$ (g) + ½O_2 (g)
  - What happens to the concentrations with time?
    - [N_2O_5] decreases
    - [NO_2] and [O_2] increase
  - Mathematically, we can express the concentration change relationship between reactants and products as

$$-\Delta[N_2O_5] = \frac{\Delta[NO_2]}{2} = \frac{\Delta[O_2]}{\frac{1}{2}}$$

A short reminder

Reaction Rate : The change in concentration of a reactant or product per unit of time.

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

EXAMPLE 11.1

Consider the following balanced hypothetical equation.

$$A(g) + 3B(g) \longrightarrow C(g) + 2D(g)$$

a Express the average rate of the reaction with respect to each of the products and reactants.

b In the first 20 seconds of the reaction, the concentration of B dropped from 0.100 *M* to 0.0357 *M*. What is the average rate of the reaction in the given time interval?

c Predict the change in the concentration of D during this time interval.

(a)

SOLUTION

$$\text{rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-\Delta[B]}{3\Delta t} = \frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{2\Delta t}$$

continued

(b)

ANALYSIS

Information given:	time, t (20 s) $[B]_o$ (0.100 M); [B] after 20 seconds (0.0357M) from part (a): the reaction rate for B $\left(\frac{-\Delta[B]}{3\Delta t}\right)$
Asked for:	average rate of the reaction

STRATEGY

Substitute into the rate equation obtained in part (a).

SOLUTION

average rate	$\text{rate} = \left(\frac{-\Delta[B]}{3\Delta t}\right) = -\frac{(0.0357\ M - 0.100\ M)}{3(20\ \text{s})} = 1.07 \times 10^{-3}\ M/\text{s}$

(c)

ANALYSIS

Information given:	from part (a): the rate equation for D $\left(\frac{-\Delta[D]}{2\Delta t}\right)$; rate of reaction ($1.07 \times 10^{-3}\ M$/s)
Asked for:	change in the concentration of D after 20 s, (Δ[D])

STRATEGY

Substitute into the rate equation obtained in part (a).

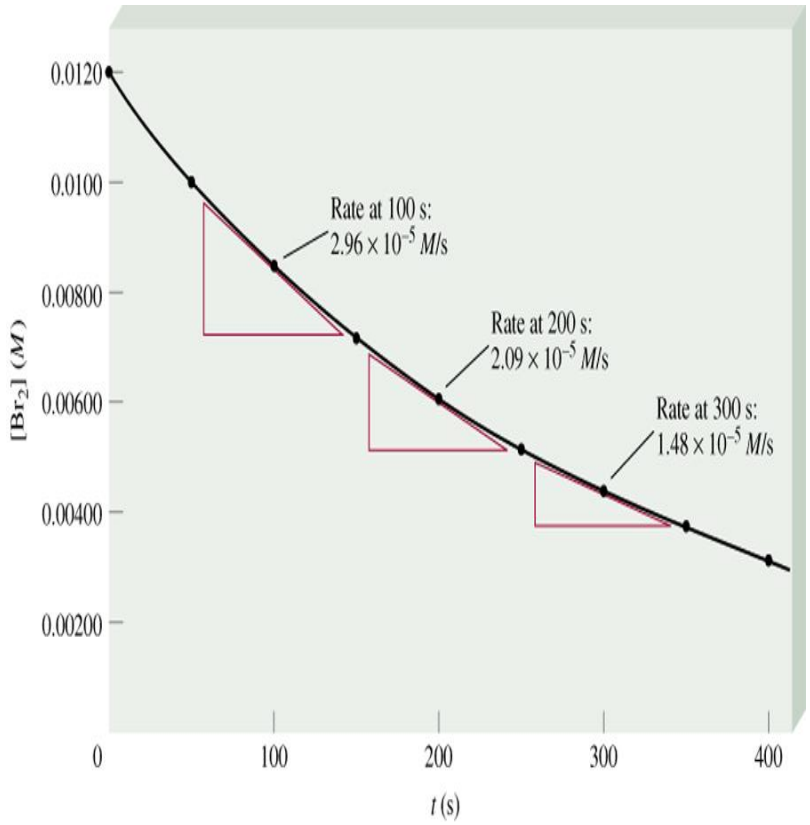
SOLUTION

Δ[D]	$\text{rate} = \frac{\Delta[D]}{2\Delta t}$; $\Delta[D] = (1.07 \times 10^{-3}\ M/\text{s})(2)(20\ \text{s}) = 0.0428\ M$

END POINT

The answer obtained in part (c) is not the concentration of D after 20 s but rather the change in the concentration of D. If you were given an initial concentration of D ($[D]_o$), then you would be able to obtain [D] after 20 s.

Curved Rather than Straight Line Tell Us That.....

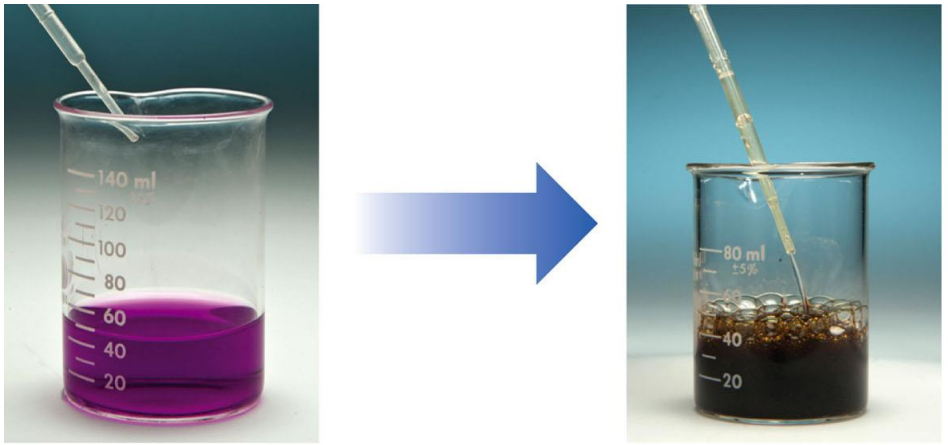


I. Rate is not Constant Throughout Reaction- just like 5K racing

II. Reaction Rate is Higher with Higher Concentration

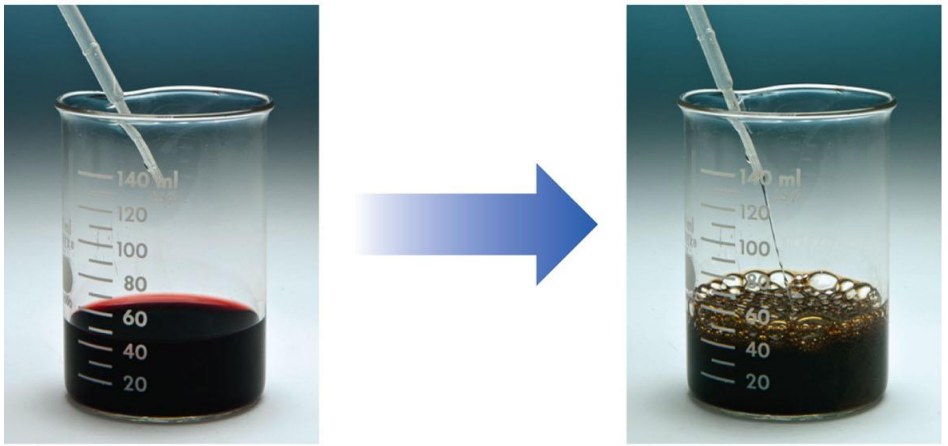
(-) slope means concentration is decreasing, less steep

Rate and Each Reactant Concentration



0.1 *M* $KMnO_4$ | 0.1 *M* $KMnO_4$ + 10 mL H_2O_2

a



5 *M* $KMnO_4$ | 5 *M* $KMnO_4$ + 10 mL H_2O_2

b

MORE CHANCE FOR MOLECULES TO COLLIDE

Rate and Rate Law

Differentiated Rate Law : expressed the relationship between the concentration of reactants and the rate of reaction. The differentiated Rate Law is usually just called rate law.

$$aA + bB \rightarrow cD + dD$$

The rate law for the above equation is

$$\text{rate} \propto [A]^x[B]^y$$

The symbol α is the proportionality sign.

$$\text{rate} = k\,[A]^x[B]^y \qquad (1)$$

Rate unt is always in mol/L-time

where k is known as **rate constant** is the proportionality constant between the reaction rate and reactant concentrations. The above equation is known as *rate law or rate*

There are three orders:

The order with respect to A - x

The order with respect to B - y

The overall order (x+y)

- **X,Y Determined by experimental data- Stoichiometry of equation is irrelevant**
- **Only reactants in rate law**

Writing a Rate Law

Example

Consider the following reaction

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

From the following data collected at 25^0 C, determine (a) the rate law (rate equation), (b) rate constant, and (c) rate of the reaction when [NO] = 5×10^{-3} M and [O_2] = 7×10^{-3} M.

Experiment	[NO] (M)	[O_2] (M)	Initial Rate (M/s)
1	2×10^{-3}	1×10^{-3}	1.25×10^{-4}
2	4×10^{-3}	1×10^{-3}	5.0×10^{-4}
3	4×10^{-3}	2×10^{-3}	10.0×10^{-4}

(a) The rate law

The rate equation for the above reaction is

$$\text{rate} = k\,[NO]^x\,[O_2]^y$$

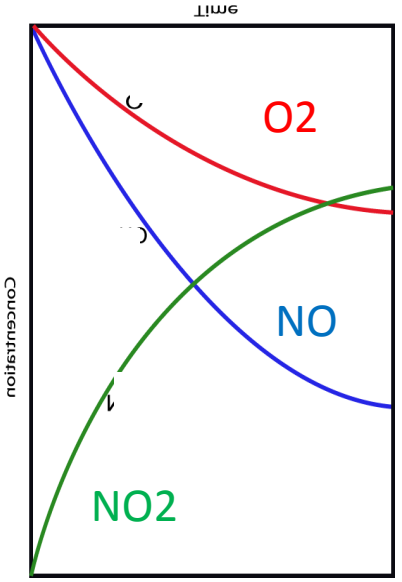
- step 1. determine x
- step 2. determine y

For the general reaction: $aA + bB \rightarrow cC + dD$

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

x and y are the reactant orders determined from experiment.

x and y are **NOT** the stoichiometric coefficients.



Writing a Rate Law

Experiment	[NO] (M)	[O_2] (M)	Initial Rate (M/s)
1	2×10^{-3}	1×10^{-3}	1.25×10^{-4}
2	4×10^{-3}	1×10^{-3}	5.0×10^{-4}
3	4×10^{-3}	2×10^{-3}	10.0×10^{-4}

Step 1. Determination of x

$\text{rate1} = k [2 \times 10^{-3}]^x [1 \times 10^{-3}]^y$ (experiment 1)

$\text{rate2} = k [4 \times 10^{-3}]^x [1 \times 10^{-3}]^y$ (experiment 2)

$$\frac{rate2}{rate1} = \frac{k\,[4x10^{-3}M]^x\,[1x10^{-3}M]^y}{k\,[2x10^{-3}M]^x\,[1x10^{-3}M]^y} = \frac{[5x10^{-4}M/s]}{[1.25x10^{-4}M/s]}$$

Therefore,

$$\frac{[4x10^{-3}M]^x}{[2x10^{-3}M]^x} = 4 \text{ or } 2^x = 4$$

Hence x = 2

Determination of y

$\text{rate2} = k [4 \times 10^{-3}]^x [1 \times 10^{-3}]^y$ (experiment 2)

$\text{rate3} = k [4 \times 10^{-3}]^x [2 \times 10^{-3}]^y$ (experiment 3)

$$\frac{rate3}{rate2} = \frac{k\,[4x10^{-3}M]^x\,[2x10^{-3}M]^y}{k\,[4x10^{-3}M]^x\,[1x10^{-3}M]^y} = \frac{[10x10^{-4}M/s]}{[5x10^{-4}M/s]}$$

ore,

$$\frac{[2x10^{-3}M]^y}{[1x10^{-3}M]^y} = 2 \text{ or } 2^y = 2$$

Hence y =1

The rate equation for this chemical equation is written as

$$\text{rate} = k [NO]^2 [O_2]^1 = k [NO]^2 [O_2]$$

Writing a Rate Law

Experiment	[NO] (M)	[O_2] (M)	Initial Rate (M/s)
1	2×10^{-3}	1×10^{-3}	1.25×10^{-4}
2	4×10^{-3}	1×10^{-3}	5.0×10^{-4}
3	4×10^{-3}	2×10^{-3}	10.0×10^{-4}

(b) Rate constant

The rate constant k can be evaluated by rearranging the above rate equation as

$$k = \frac{rate}{[NO]^2[O_2]}$$

To calculate the k you can take the concentrations of [NO] and [O_2] from **any one of the experiment.** It does not make any difference which data you take, all should yield the same result. Suppose, we take the data from the experiment 2, we get

$$k = \frac{5x10^{-4}}{[4 \times 10^{-3}]^2[1 \times 10^{-3}]} = 3.1 \times 10^4 \, / \, M^2 \, .s$$

Therefore, the rate law (equation) becomes

$$\text{rate} = 3.1 \times 10^4 \, [NO]^2 \, [O_2] \, / \, M^2.s$$

Overall order =3

Writing a Rate Law

Experiment	[NO] (M)	[O_2] (M)	Initial Rate (M/s)
1	2×10^{-3}	1×10^{-3}	1.25×10^{-4}
2	4×10^{-3}	1×10^{-3}	5.0×10^{-4}
3	4×10^{-3}	2×10^{-3}	10.0×10^{-4}

(c) rate of the reaction when [NO] = 5×10^{-3} M and [O] = 7×10^{-3} M.

Now you substitute these values in the above equation to get the rate:

$$\text{rate} = 3.1 \times 10^4 [NO]^2 [O_2] / M^2.s$$
$$= 3.1 \times 10^4 (5 \times 10^{-3} M)^2 (7 \times 10^{-3} M) / M^2.s$$
$$= 5.4 \times 10^{-3} M/s$$

Next , Concentration as a Function of Time from the rate and rate law equations

Integrated Rate Law for a First-Order Reaction

$$A \longrightarrow \text{product(s)}$$

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

Calculus can be used to derive an **integrated** rate law.

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

$[A]_t$ concentration of A at time t

$[A]_0$ initial concentration of A

Using: $\ln\left(\frac{x}{y}\right) = \ln(x) - \ln(y)$

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

$$y = mx + b$$

Integrated Rate Law for a First-Order Reaction

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

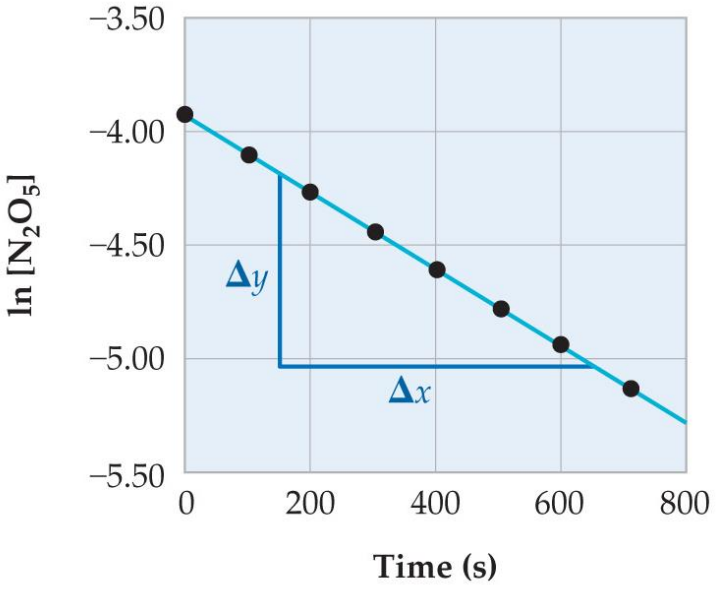
$$\text{rate} = k[N_2O_5]$$

Slope = $-k$

Calculate the slope:

$$\frac{-5.02 - (-4.17)}{650\ \text{s} - 150\ \text{s}} = -0.0017\frac{1}{\text{s}}$$

$$k = 0.0017\frac{1}{\text{s}}$$



Half-Life of a First-Order Reaction

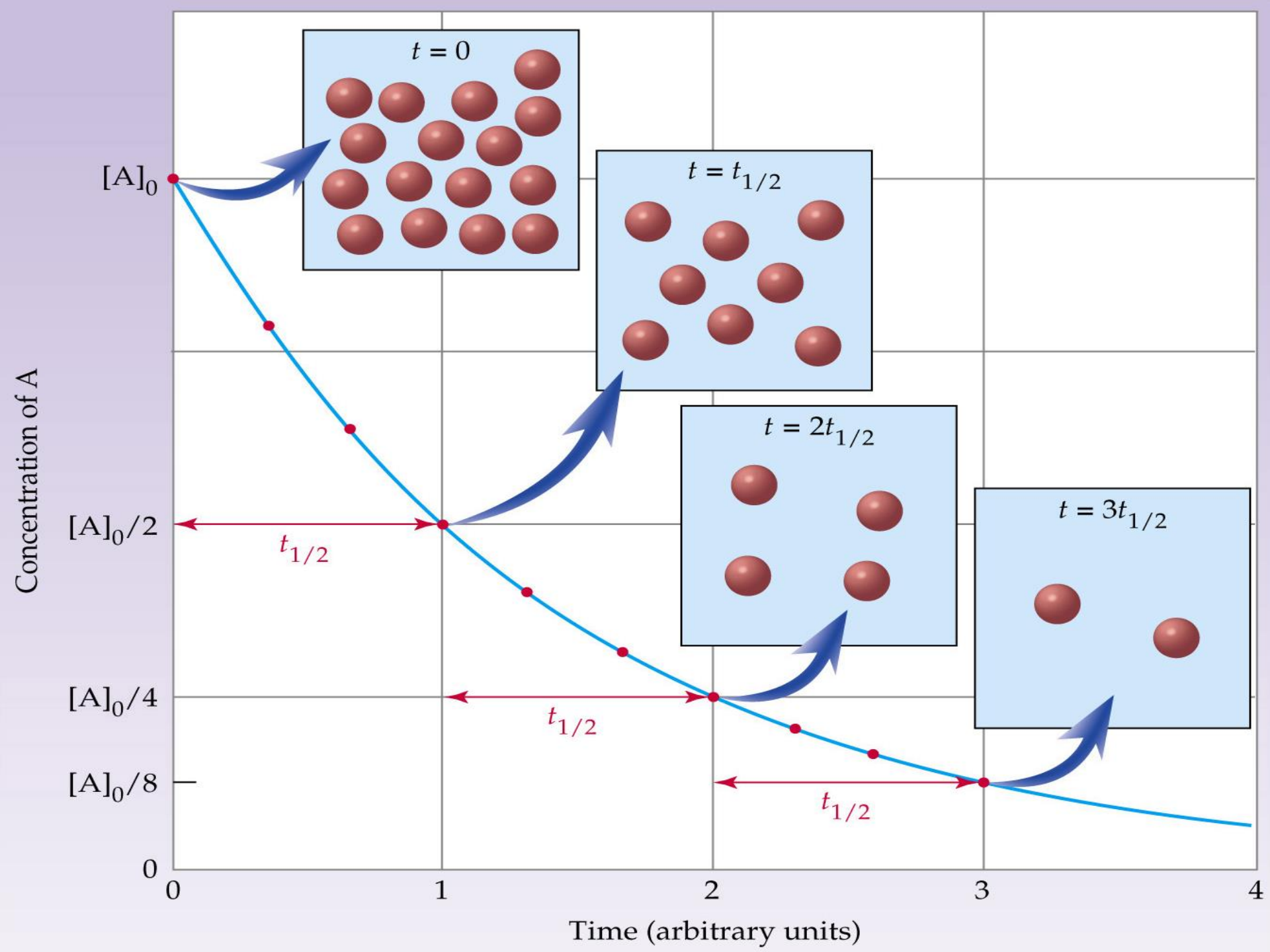
Half-Life: The time required for the reactant concentration to drop to one-half of its initial value

$$A \longrightarrow \text{product(s)}$$

$$\text{rate} = k[A]$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \begin{cases} t = t_{1/2} \\ [A]_{t_{1/2}} = \dfrac{[A]_0}{2} \end{cases}$$

$$\ln\left(\frac{1}{2}\right) = -kt_{1/2} \quad \text{or} \quad t_{1/2} = \frac{0.693}{k}$$

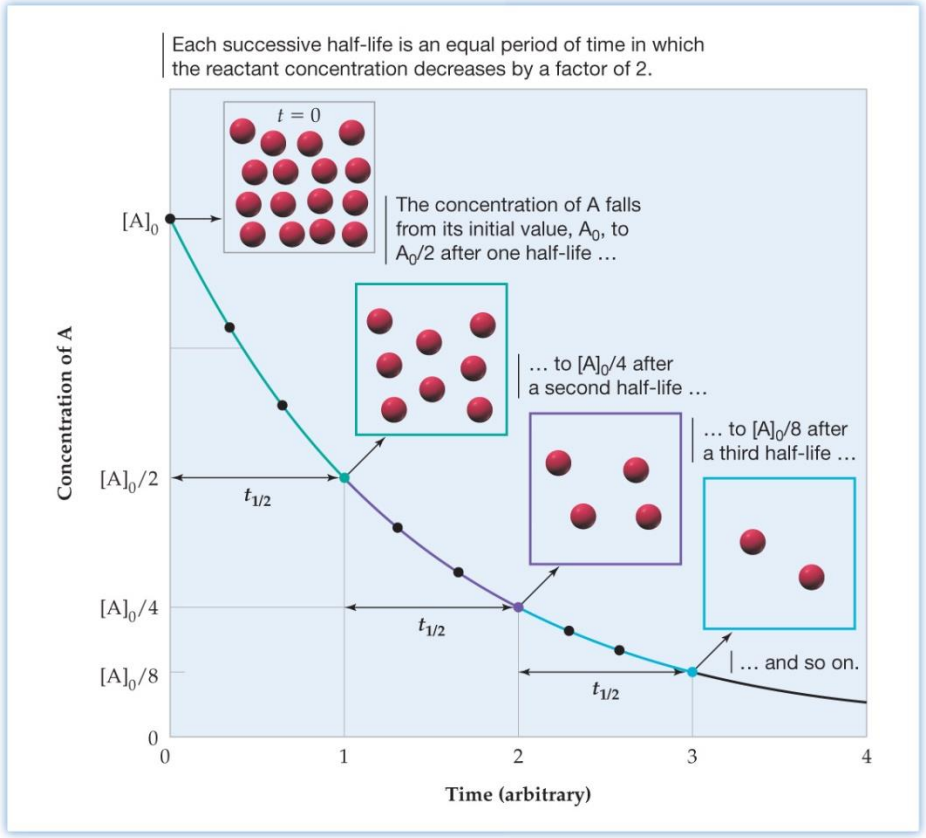

$t = 0$
$t = t_{1/2}$
$t = 2t_{1/2}$
$t = 3t_{1/2}$
$[A]_0$
$[A]_0/2$
$[A]_0/4$
$[A]_0/8$
0
$t_{1/2}$
$t_{1/2}$
$t_{1/2}$
Concentration of A
0
1
2
3
4
Time (arbitrary units)

Half-Life of a First-Order Reaction

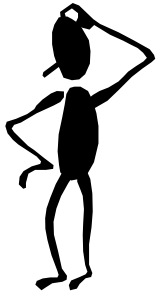
$$t_{1/2} = \frac{0.693}{k}$$

For a first-order reaction, the half-life is independent of the initial concentration.

Each successive half-life is an equal period of time.



First-Order Reactions



What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4}\ s^{-1}$?

$$t_{½} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4}\ s^{-1}} = 1200\ s = 20\ minutes$$

The reaction $2A \longrightarrow B$ is first order in A with a rate constant of $2.8 \times 10^{-2}\ s^{-1}$ at 80^0C. How long will it take for A to decrease from 0.88 *M* to 0.14 *M* ?

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

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

$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \frac{[A]_0}{[A]}}{k} = \frac{\ln \frac{0.88\ M}{0.14\ M}}{2.8 \times 10^{-2}\ s^{-1}} = 66\ s$$

Zero Order Reactions

- For a zero order reaction A → products

$$\text{Rate} = k[A]^0 = k$$

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

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

$$\text{linear} : [A] \text{ vs. } t$$

- Note that the ***half life of a zero order reaction does depend on the initial concentration*** of reactant

Second-Order Reactions

For A → products, Rate = $k[A]^2$

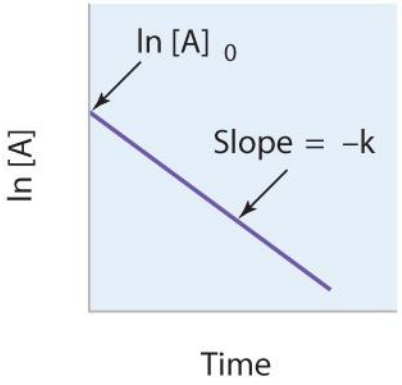
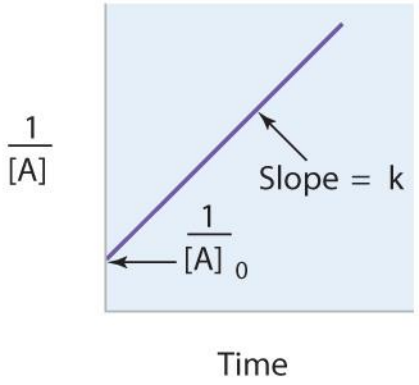
$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

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

$$\text{linear} : \frac{1}{[A]} \text{ vs. } t$$

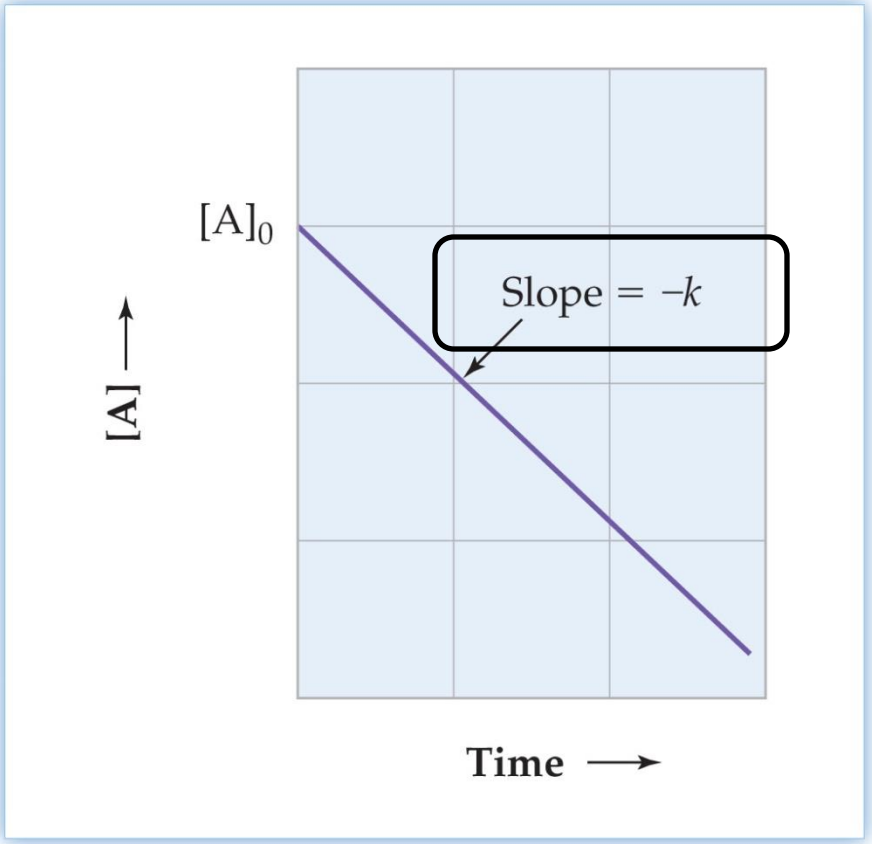
For a second order reaction, a plot of ln[A] vs. *t* is **not linear**.

TABLE 12.4 Characteristics of First- and Second-Order Reactions of the Type A → Products

	First-Order	Second-Order
Rate law	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration–time equation	$\ln [A]_t = -kt + \ln [A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Linear graph	$\ln [A]$ versus t	$\frac{1}{[A]}$ versus t
		
Graphical determination of k	$k = -(\text{Slope})$	$k = \text{Slope}$
Half-life	$t_{1/2} = \frac{0.693}{k}$ (constant)	$t_{1/2} = \frac{1}{k[A]_0}$ (not constant)

Zeroth-Order Reactions

A plot of **[A]** versus **time** gives a straight-line fit and the **slope** will be ***-k***.



EXAMPLE: The reaction

$$2\,NOBr\,(g) \rightarrow 2\,NO\,(g) + Br_2\,(g)$$

is a second order reaction with respect to NOBr.
$k = 0.810\ M^{-1}\cdot s^{-1}$ at 10^{o} C.

If $[NOBr]_o = 7.5 \times 10^{-3}$ M, how much NOBr will be left after a reaction time of 10 minutes?

SOLUTION: One can solve for the amount of NOBr after 10 minutes by substituting the given data into the integrated rate law for a second-order reaction.

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

$$\frac{1}{[NOBr]_t} = kt + \frac{1}{[NOBr]_0} \qquad (\textit{Second Order})$$

$$\frac{1}{[NOBr]_t} = (0.810\ M^{-1}\cdot s^{-1}) \times (600\ s) + \frac{1}{7.5\times10^{-3}\ M}$$

$$\frac{1}{[NOBr]_t} = 6.19\times10^{2}\ M^{-1}$$

$$[NOBr]_t = 1.6\times10^{-3}\ M$$

TABLE 11.2 **Characteristics of Zero-, First-, and Second-Order Reactions of the Form A (g) ⟶ products; [A], $[A]_0$ = conc. A at t and t = O, respectively**

Order	Rate Expression	Conc.-Time Relation	Half-Life	Linear Plot
O	rate = k	$[A]_0 - [A] = kt$	$[A]_0/2k$	[A] vs. t
1	rate = $k[A]$	$\ln\frac{[A]_0}{[A]} = kt$	$0.693/k$	ln [A] vs. t
2	rate = $k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$1/k\,[A]_0$	$\frac{1}{[A]}$ vs. t

The ***Overall Order*** of a reaction is the sum of the individual orders:

$$\text{Rate } (Ms^{-1}) = k[A][B]^{1/2}[C]^2$$

Overall order: $1 + ½ + 2 = 3.5 = 7/2$

or ***seven–halves order***

The units of a rate constant will change depending upon the overall order.

The units of rate are always M/s or Ms^{-1}

To find the units of a rate constant for a particular rate law, simply divide the units of rate by the units of molarity in the concentration term of the rate law.

$$\text{Rate } (Ms^{-1}) = k[A] \quad 1^{st} \text{ order}$$

$$k(\text{units}) = \frac{Ms^{-1}}{M} = s^{-1}$$

Rel
and

Rate Law	Order	Units of k
Rate = k	Zero	$M\,s^{-1}$
Rate = $k[A]$	First order with respect to A First order overall	s^{-1}
Rate = $k[A]^2$	Second order with respect to A Second order overall	$M^{-1}\,s^{-1}$
Rate = $k[A][B]$	First order with respect to A First order with respect to B Second order overall	$M^{-1}\,s^{-1}$
Rate = $k[A][B][C]$	First order with respect to A First order with respect to B First order with respect to C Third order overall	$M^{-2}\,s^{-1}$

*In the units of k, M represents mol L^{-1} or moles per liter.

Rules of logarithms

$\log(1) = 0$ $\quad$ $\ln(1) = 0$

$\log(10) = 1$ $\quad$ $\ln(e) = 1$

$\log(100) = 2$ $\quad$ $\ln(e^x) = x$

$\text{Log}(10^x) = x$

$\log A^x = x \log A$ $\quad$ $\ln A^x = x \ln A$

$$\log\left(\frac{A^x}{B^x}\right) = \log\left(\frac{A}{B}\right)^x = x \log\left(\frac{A}{B}\right)$$

$\log(AB) = \log A + \log B$ $\quad$ $\log\left(\frac{A}{B}\right) = \log A - \log B$

Factors for Reaction Rate A-> B

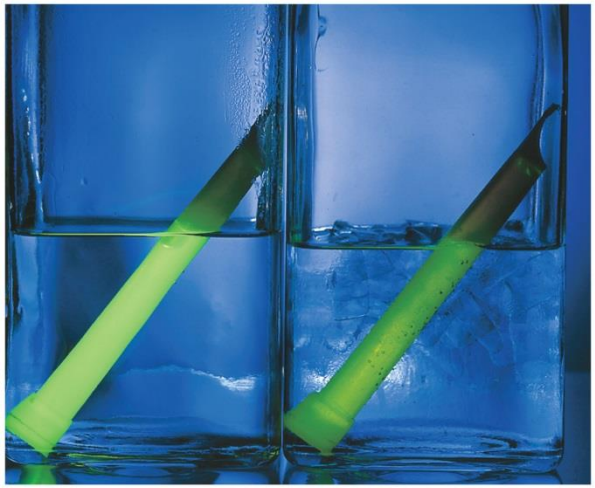
1.Concentration

- Rate = $-\Delta[A]/\Delta t$
- Rate law; Rate = $k[A]^x$

2. Temperature and Rate

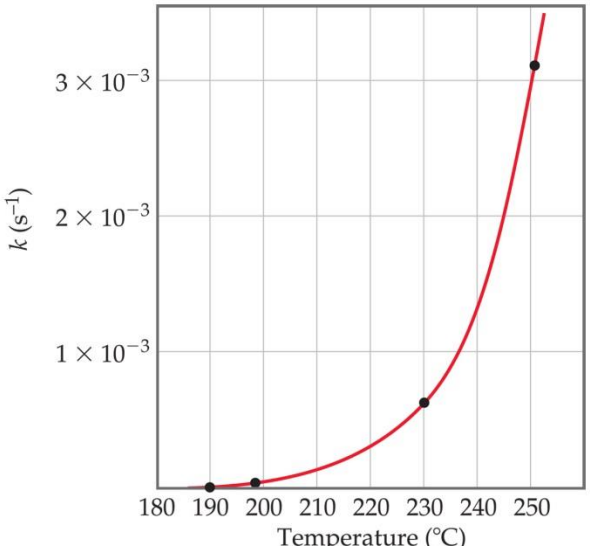
- Found in the Rate Law Constant, k

Temperature and Rate



Higher temperature Lower temperature

- Generally, as temperature increases, so does the reaction rate.
- This is because *k* ,rate constant, is temperature dependent.



Therefore one can conclude that:

$$k(T) \propto e^{f(T)}$$

Arrhenius Equation

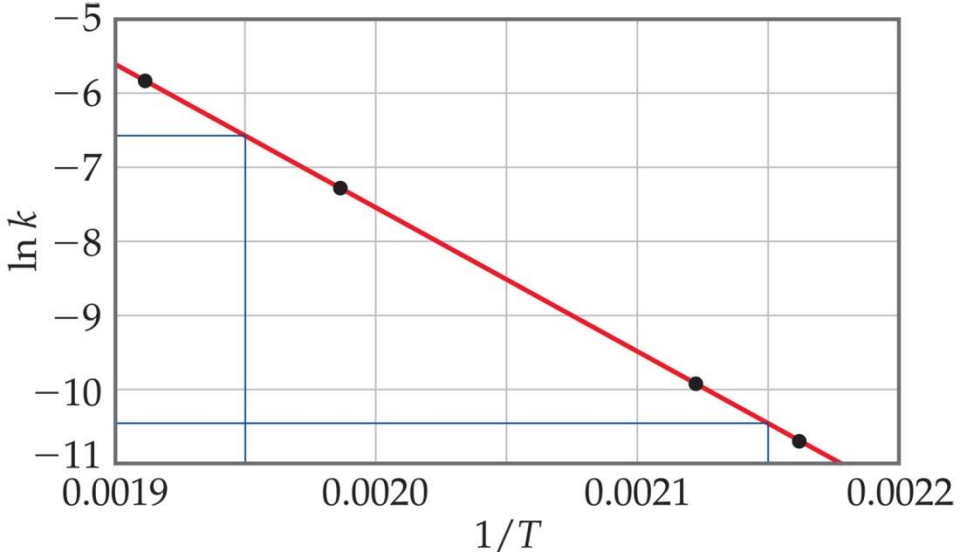
Svante Arrhenius developed a mathematical relationship between *k* and E_a:

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

The greater (Ea/RT) is;
the smaller k is;
slower reaction rate !

where *A* is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

Arrhenius Equation



Taking the natural logarithm of both sides, the equation becomes

$$ln(k) = -\frac{E_a}{RT} + lnA$$

$y = mx + b$

When *k* is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of ln *k* vs. 1/*T*.

The ***Arrhenius equation*** is similar in nature and can be used for two k values and two temperatures

E_a may then be calculated

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

Example: The activation energy of a first order reaction is 50.2 kJ/mol at 25°C. At what temperature will the rate constant double?

---

(1) $k_2 = 2k_1$

(2) $$\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{2k_1}{k_1}\right) = \ln(2) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(3) $$\frac{E_a}{R} = \frac{50.2\ \text{kJ/mol} \times \frac{10^3\text{J}}{1\text{kJ}}}{8.314\frac{\text{J}}{\text{mol}\cdot\text{K}}} = 6.04\times10^3\text{K}$$

(4) $$\ln(2) = 0.693 = 6.04\times10^3\text{K} \times \left(\frac{1}{298\text{K}} - \frac{1}{T_2}\right)$$

A 10°C change of temperature doubles the rate!!

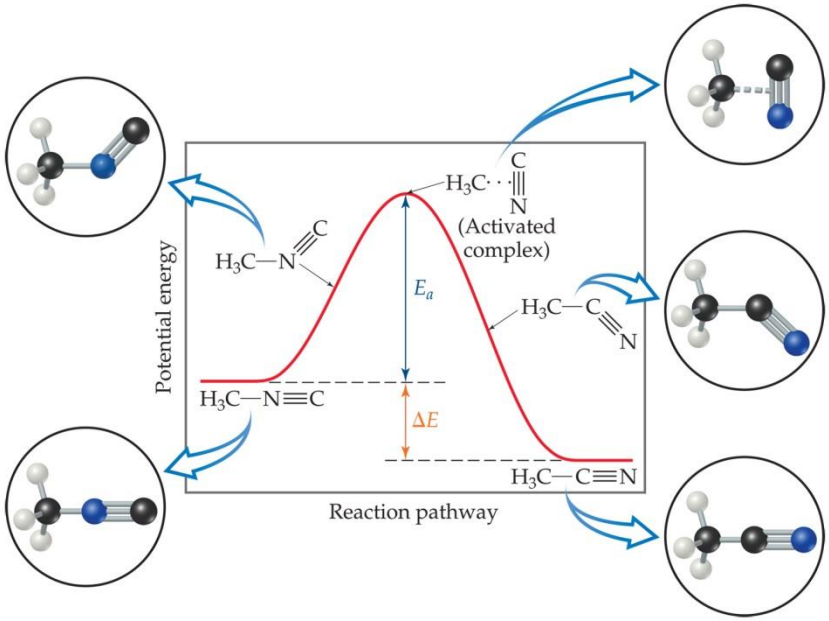
(5) $$\frac{1}{T_2} = 3.24\times10^{-3}\text{K}^{-1} \longrightarrow \boxed{T_2 = 308\ \text{K}}$$

Activation Energy

- In other words, there is a minimum amount of energy required for reaction: the activation energy, E_a.
- Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.

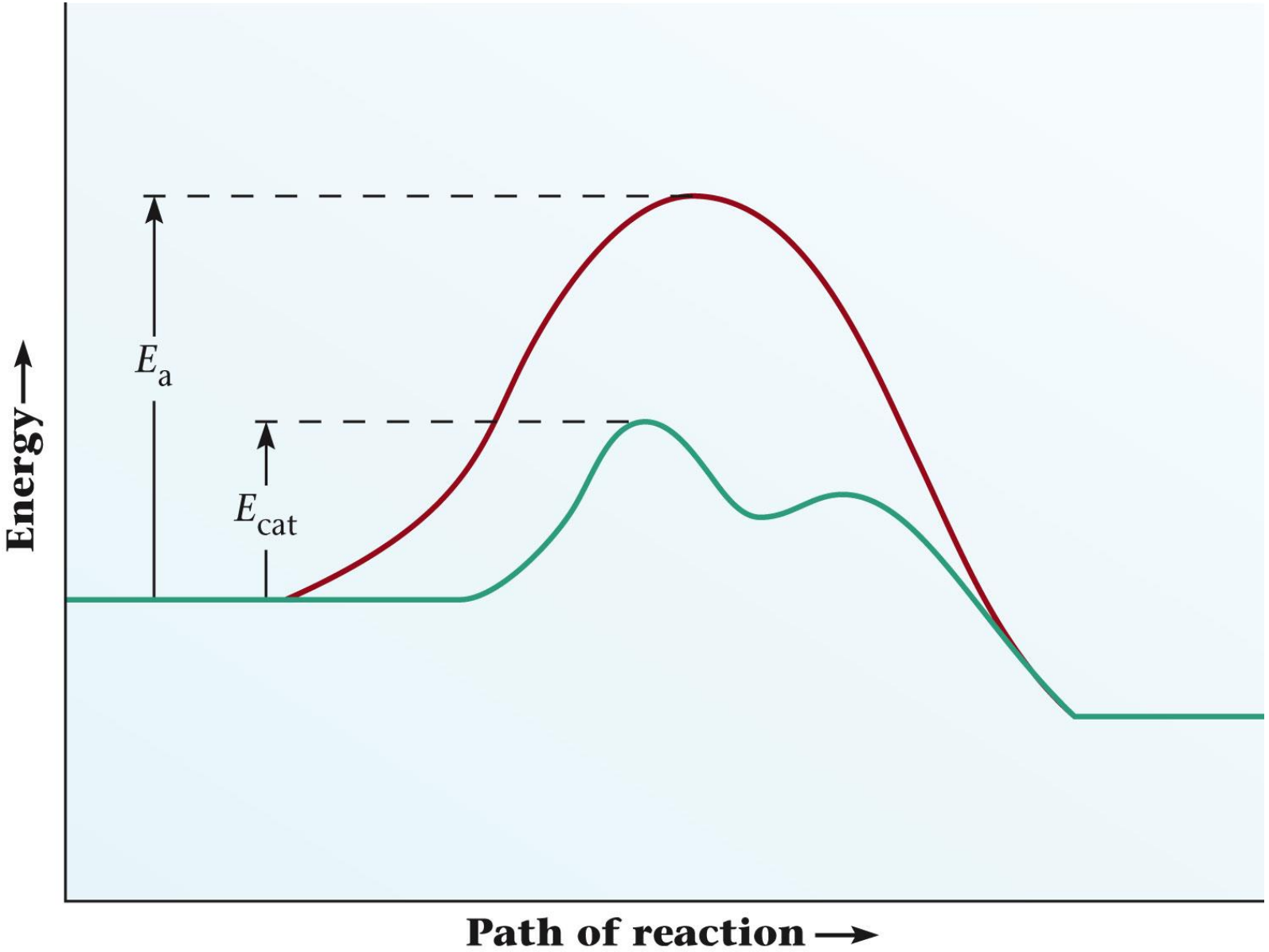
Reaction Coordinate Diagrams

- It shows the energy of the reactants and products (and, therefore, ΔE).
- The high point on the diagram is the transition state.



- The species present at the transition state is called the activated complex.
- The energy gap between the reactants and the activated complex is the activation energy barrier.

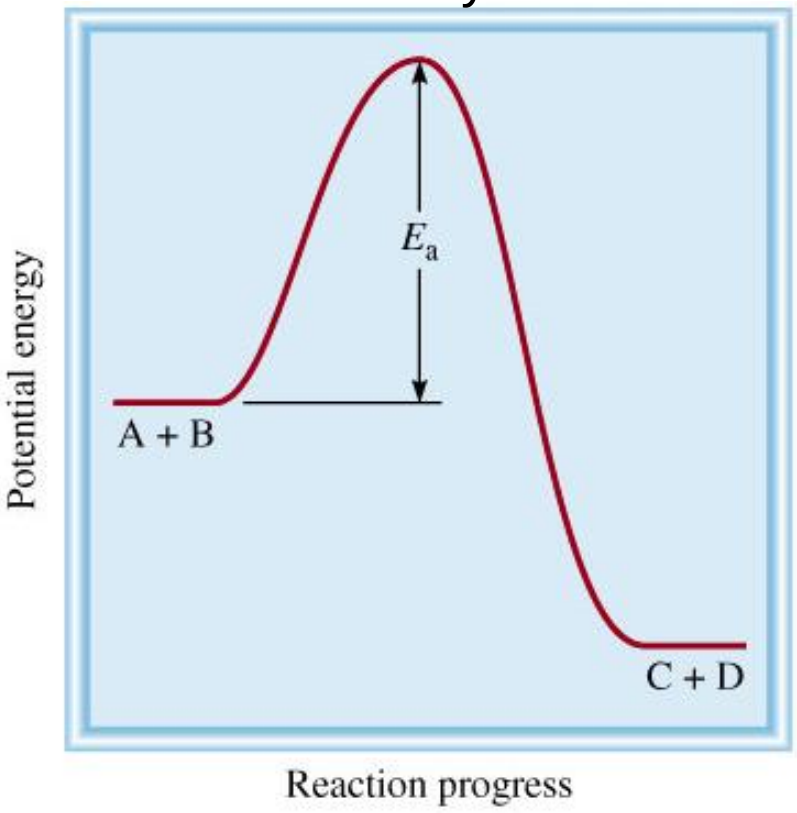
Reaction Diagram and Catalyst



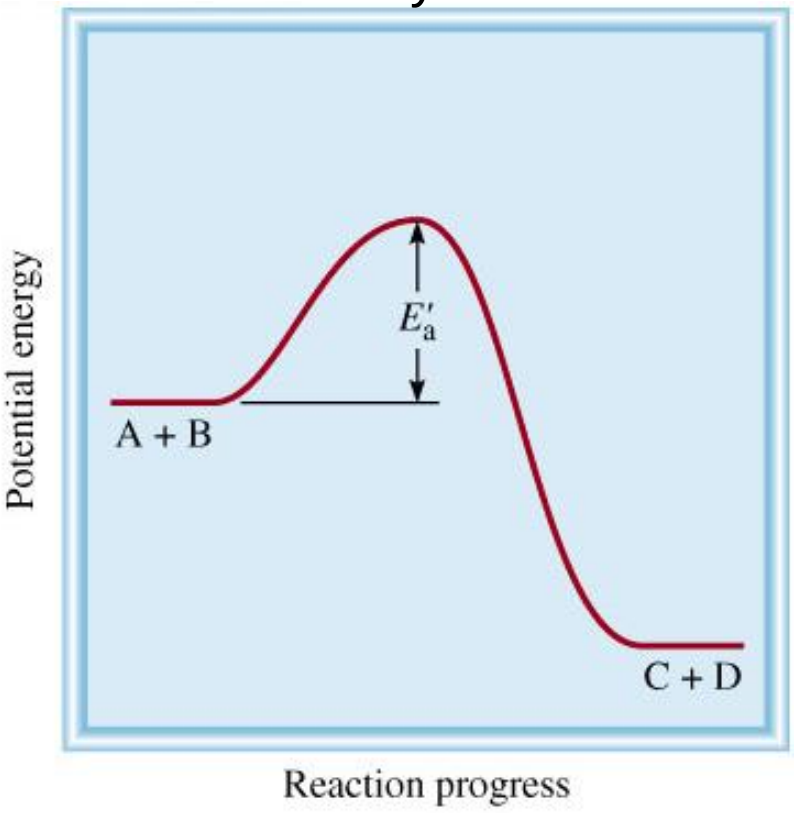
A catalyst is a substance that increases the rate of a chemical reaction without itself being consumed.

$$k = A \cdot \exp(-E_a / RT) \qquad E_a \downarrow \qquad k \uparrow$$

Uncatalyzed



Catalyzed



$$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$$

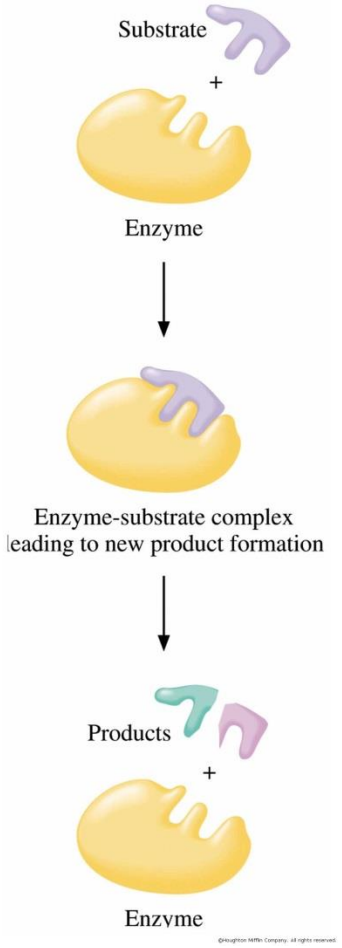
$$E_a' < E_a$$

Homogeneous and Heterogeneous Catalysts

- **Homogeneous catalyst**: catalyst existing in the same phase as the reactants.
- **Heterogeneous catalysis**: catalyst existing in a different phase than the reactants.
  - The previous section gave an example of a homogeneous catalyst since the catalyst Br_2 was in the same phase as the hydrogen peroxide.
- The catalytic hydrogenation of ethylene is an example of a heterogeneous catalysis reaction:

$$H_2C=CH_2(g)+H_2(g)\xrightarrow{Pt}H_3C-CH_3(g)$$

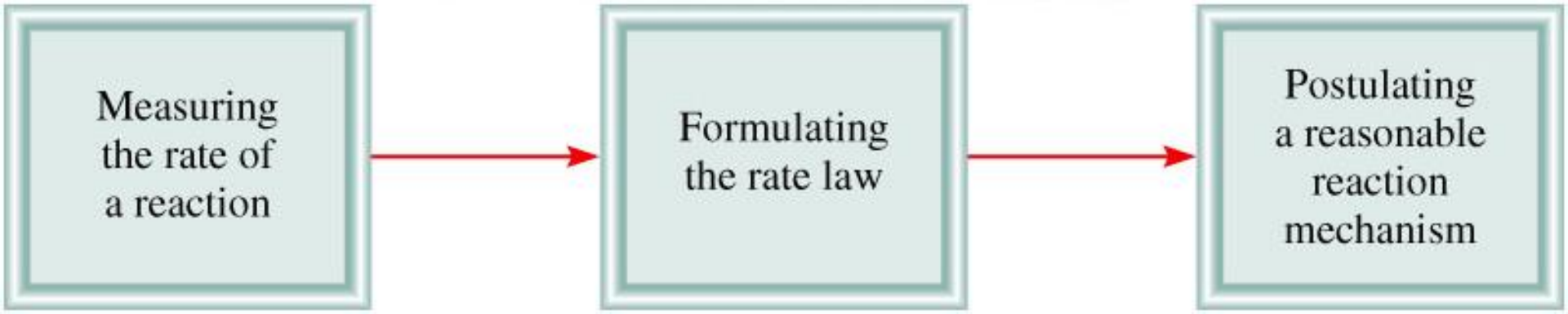
- **ENZYMES** (biological catalysts)
  - They are proteins (large organic molecules that are composed of amino acids).
  - Slotlike active sites. The molecule fits into this slot and reaction proceeds. Poisons can block active site or reduce activity by distorting the active site.



Factors that Influence the Rate of Reaction

- Concentration of reactants ,
- Types of reactions
- Temperature
- Presence of a catalyst
- Reaction mechanism

Sequence of Steps in Studying a Reaction Mechanism



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 ***reaction mechanism***.

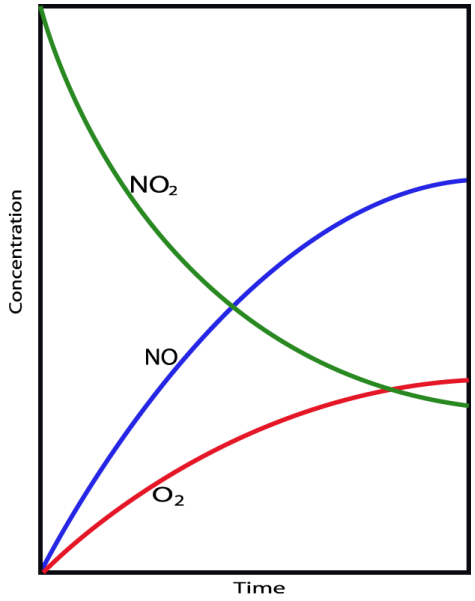
$$2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2\ (g)$$

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: $2NO + O_2 \longrightarrow 2NO_2$



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.

Elementary step 1: $NO + NO \longrightarrow N_2O_2$

\+ Elementary step 2: $N_2O_2 + O_2 \longrightarrow 2NO_2$

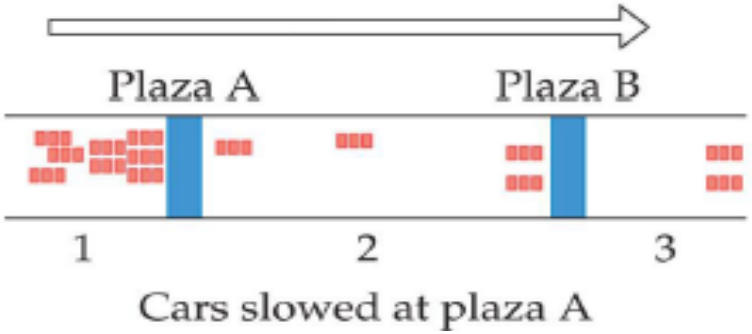
Overall reaction 1+ 2: $2NO + O_2 \longrightarrow 2NO_2$

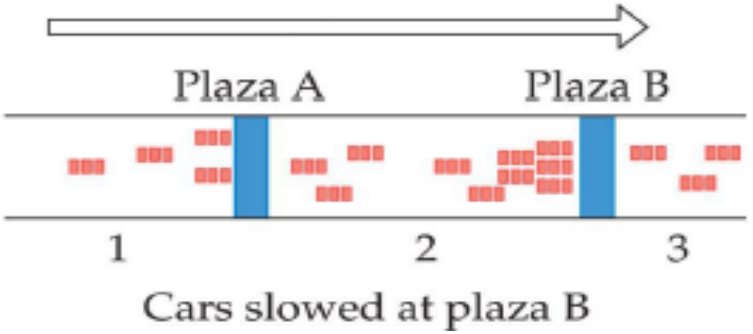
The molecularity of ***a reaction*** is the number of molecules reacting in an elementary step.

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

Mechanism Involving Multiple Steps

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, rate-determining step.



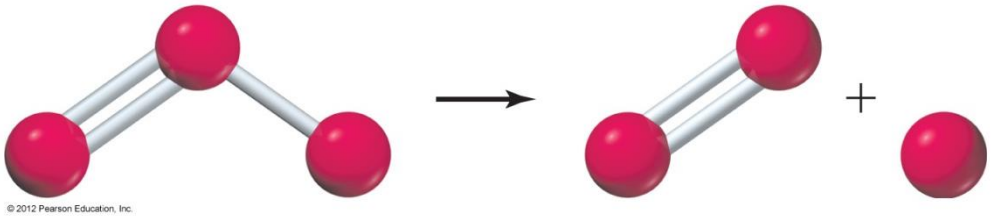


The ***rate-determining step*** is the slowest step in the sequence of steps leading to product formation.

Reaction Mechanisms-Molecularity

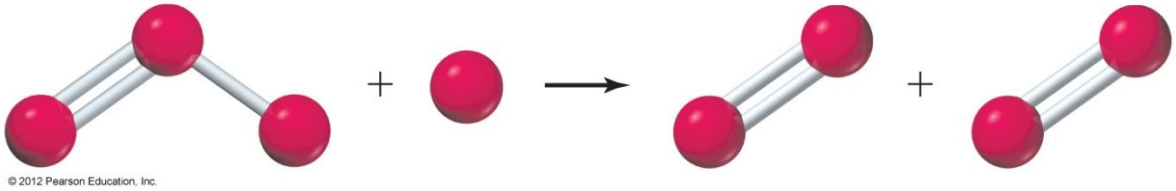
Unimolecular Reaction

$$O_3^*(g) \longrightarrow O_2(g) + O(g)$$



Bimolecular Reaction

$$O_3(g) + O(g) \longrightarrow 2O_2(g)$$



Rate Laws for Elementary Reactions

The rate law for an elementary reaction follows directly from its molecularity because an **elementary reaction is an individual molecular event.**

Unimolecular Reaction

$$O_3^*(g) \longrightarrow O_2(g) + O(g) \qquad \text{rate} = k[O_3]$$

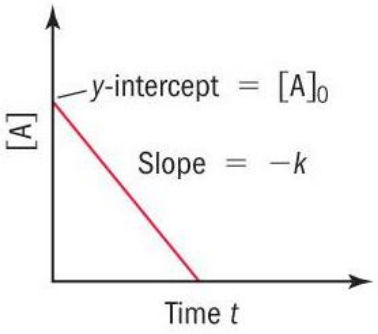
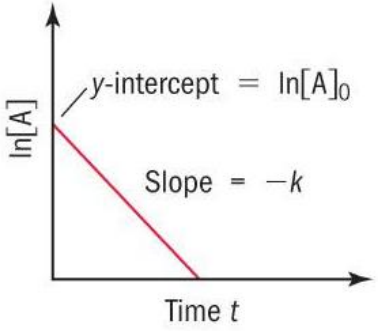
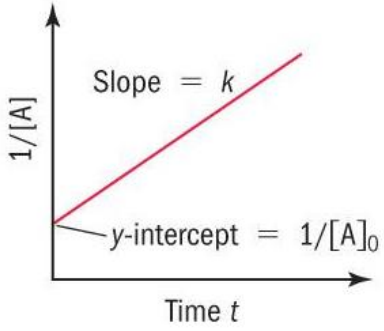
Bimolecular Reaction

$$O_3(g) + O(g) \longrightarrow 2O_2(g) \qquad \text{rate} = k[O_3][O]$$

Termolecular Reaction

$$O(g) + O(g) + M(g) \longrightarrow O_2(g) + M(g) \qquad \text{rate} = k[O]^2[M]$$

TABLE 13.2 Rate Law Summary Table

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	$\text{Rate} = k[\text{A}]^0$	$\text{M}\cdot\text{s}^{-1}$	$[\text{A}]_t = -kt + [\text{A}]_0$		$t_{1/2} = \frac{[\text{A}]_0}{2k} = \frac{1}{k}\frac{[\text{A}]_0}{2}$
1	$\text{Rate} = k[\text{A}]^1$	s^{-1}	$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0$ $\ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt$		$t_{1/2} = \frac{0.693}{k} = \frac{1}{k}(0.693)$
2	$\text{Rate} = k[\text{A}]^2$	$\text{M}^{-1}\cdot\text{s}^{-1}$	$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$		$t_{1/2} = \frac{1}{k[\text{A}]_0} = \frac{1}{k}\frac{1}{[\text{A}]_0}$