Chemical Kinetics-1

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Ref:Zumdahl; Chemistry 8 th edition

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).

$$A \longrightarrow B$$

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

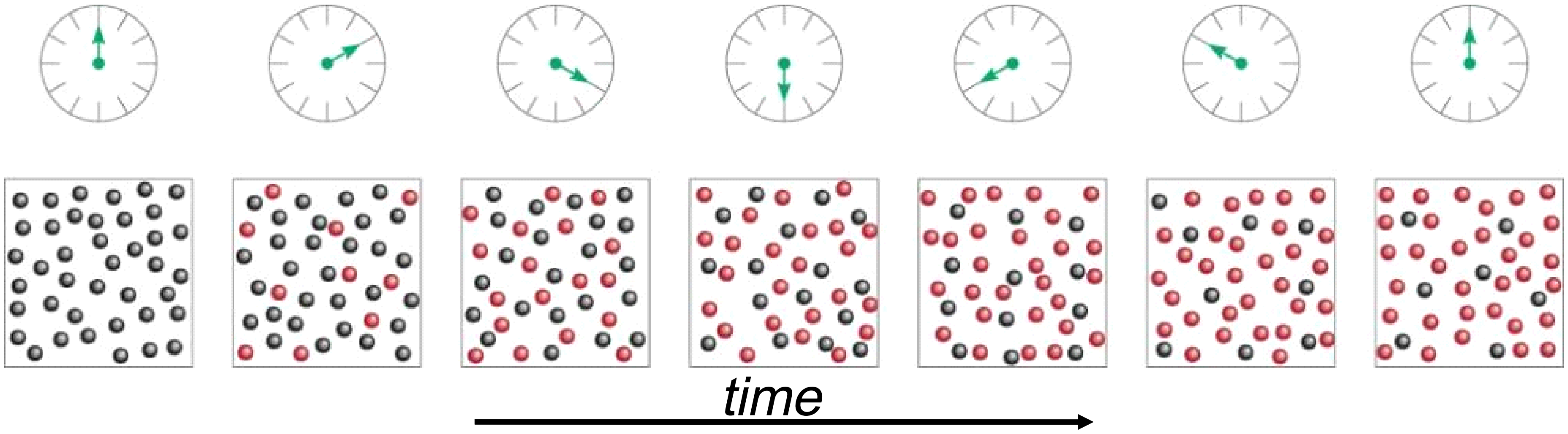
$\Delta[A]$ = change in concentration of A over time period Δt

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

$\Delta[B]$ = change in concentration of B over time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.

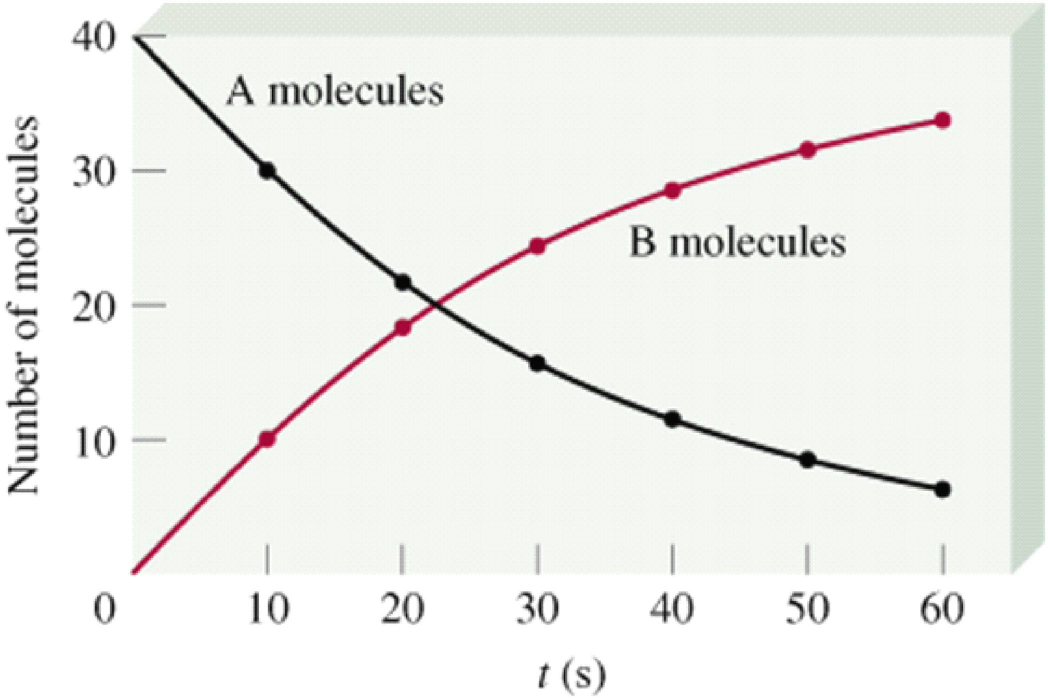
$A \longrightarrow B$



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

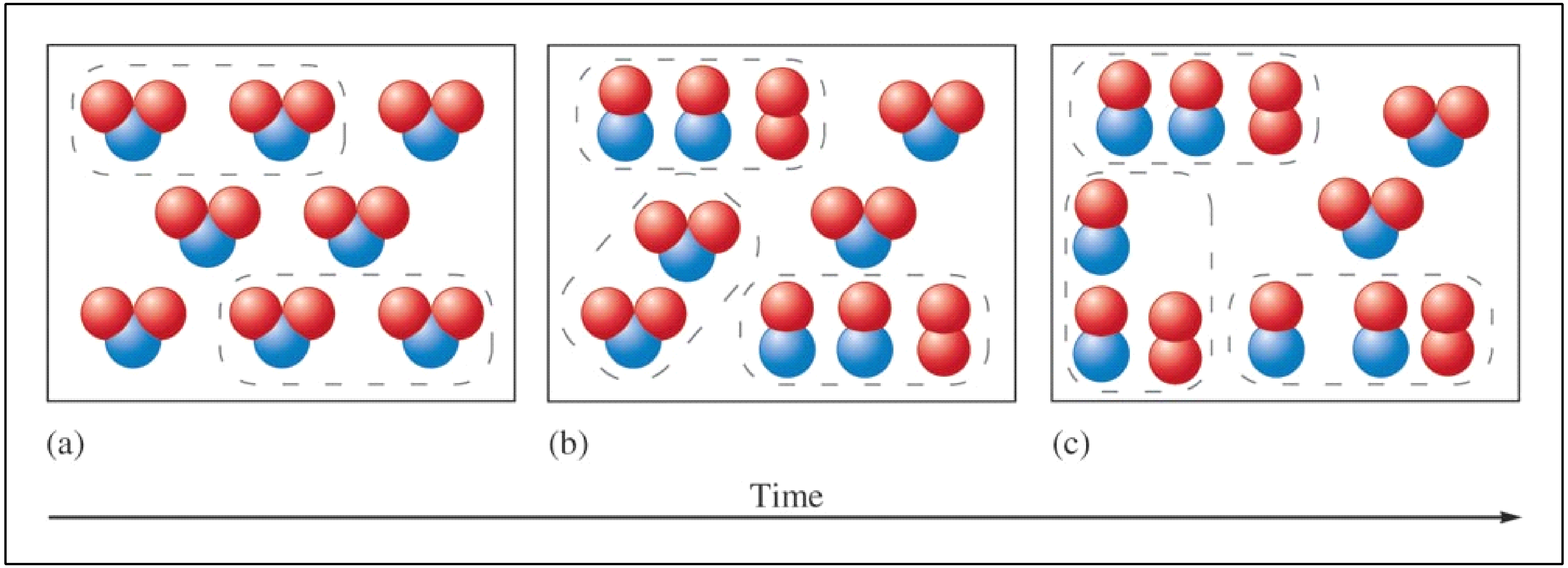
$$= -\frac{[A]_{\text{final}} - [A]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

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



Reaction Rate

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



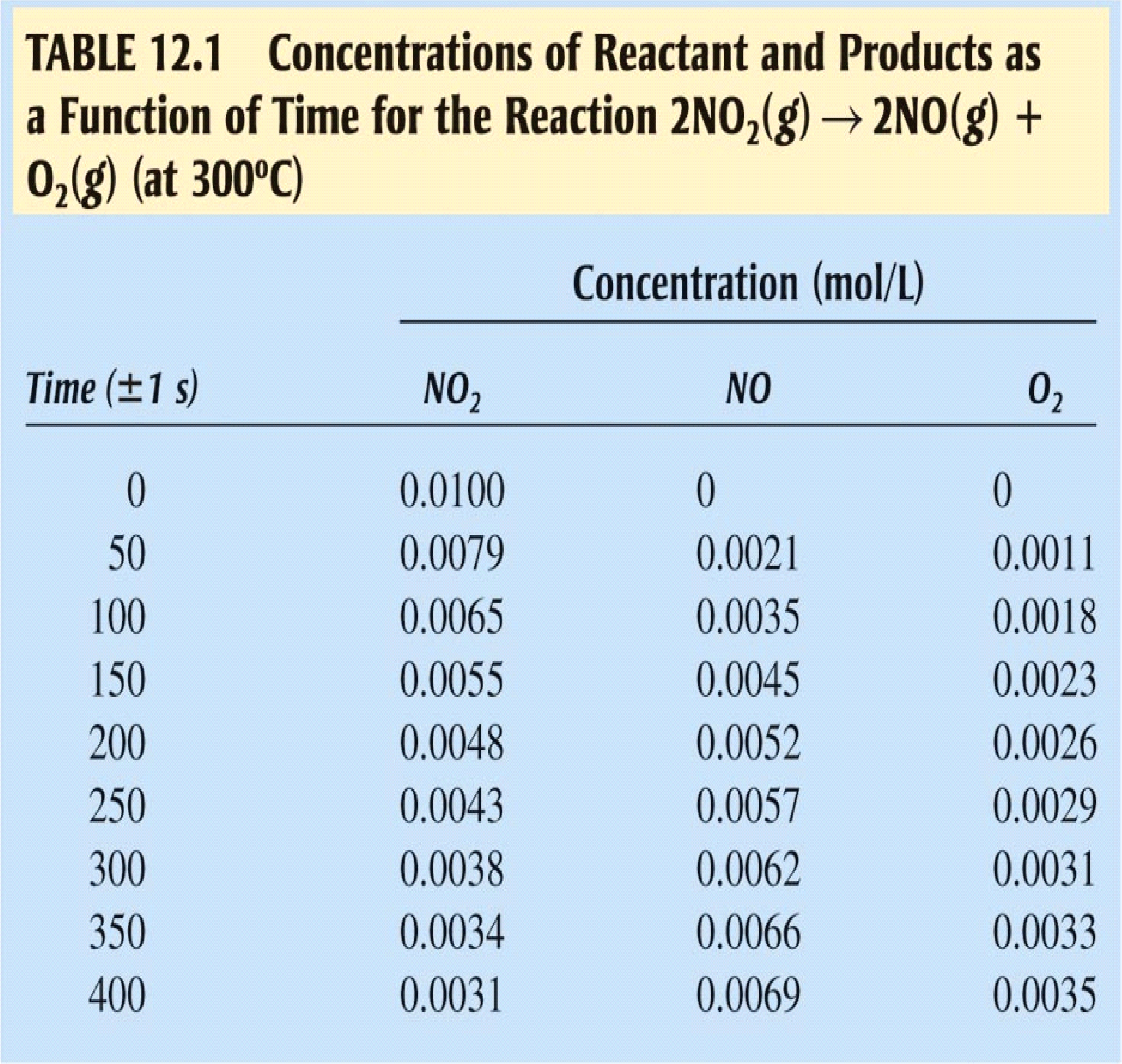


TABLE 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ (at 300°C)

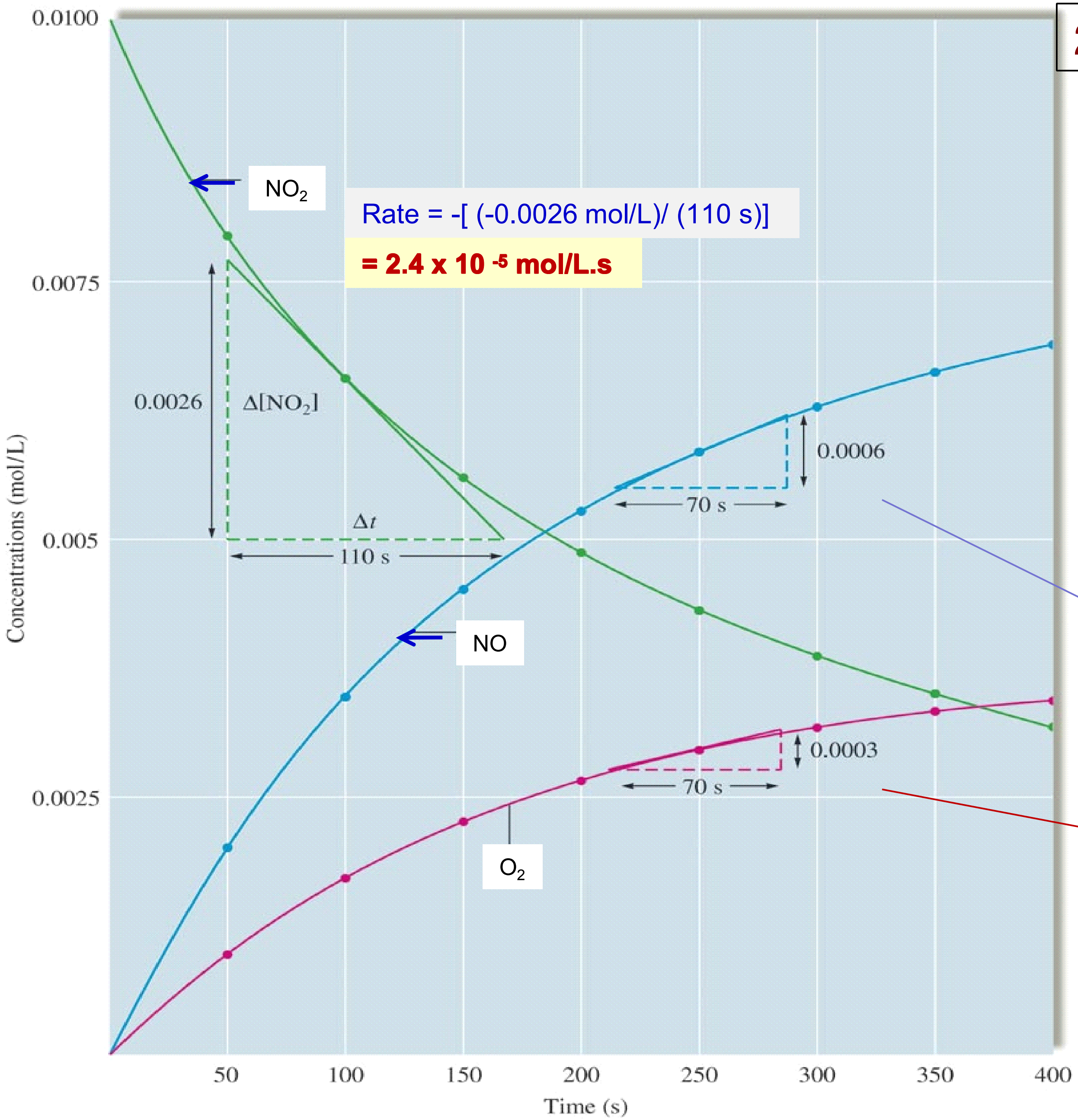
	Concentration (mol/L)		
Time (±1 s)	*NO_2*	*NO*	*O_2*
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

Results:

1. The concentration of NO_2 decreases with time.
2. The concentration of NO and O_2 increase with time

Table 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction **$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$**

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



Rate = -[(-0.0026 mol/L)/ (110 s)]

= 2.4 x 10 $^{-5}$ mol/L.s

- The curve of NO is the same as NO_2 curve except it is flipped over
- **O_2 is produced half** as
- fast as NO
- Slope of NO curve

= ($6.0\text{x}10^{-4}$ / 70)

= 8.6 x 10 $^{-6}$ mol/ L.s

Slope of O_2 curve

= ($3.0\text{x}10^{-4}$ / 70)

= 4.3 x 10 $^{-6}$ mol/ L.s

The production of NO is twice that of O_2

Fig.12.1 Starting with a Flask of Nitrogen Dioxide at 300 ^{0}C, Concentrations of NO_2, NO, and O_2 are Plotted versus Time

Rate of a Reaction

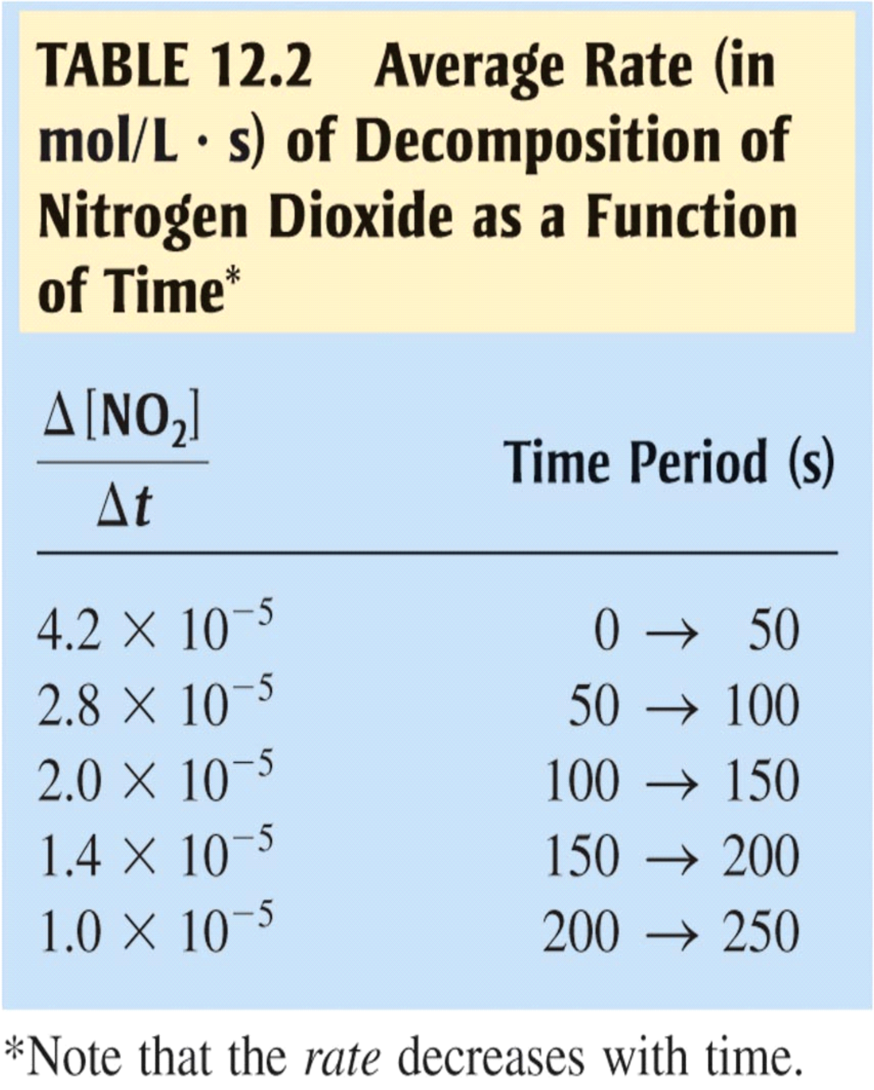


TABLE 12.2 Average Rate (in mol/L · s) of Decomposition of Nitrogen Dioxide as a Function of Time*

$\frac{\Delta[NO_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	0 → 50
2.8×10^{-5}	50 → 100
2.0×10^{-5}	100 → 150
1.4×10^{-5}	150 → 200
1.0×10^{-5}	200 → 250

*Note that the *rate* decreases with time.

Table 12.2 Average Rate (in mol/L-s) of Decomposition of Nitrogen Dioxide as a Function of Time

Slope = $\frac{\text{Change in y}}{\text{change in x}}$

$$= \frac{\Delta[NO_2]}{\Delta t}$$

but rate = - $\frac{\Delta[NO_2]}{\Delta t}$

Rate = - Slop of the tangent line

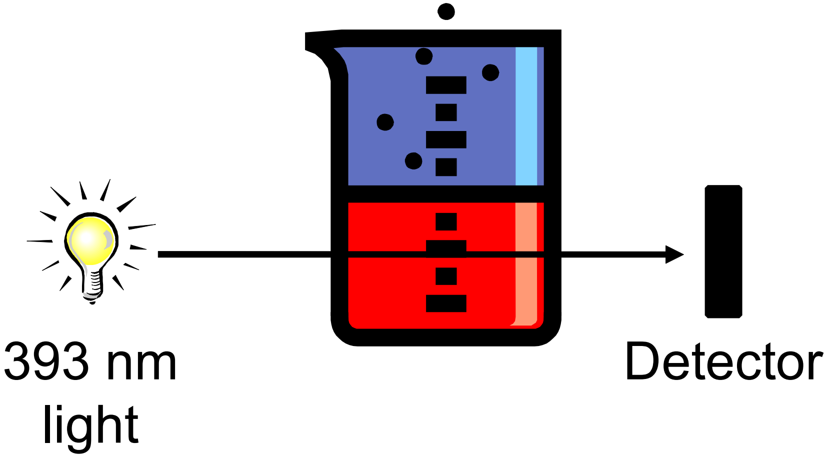
Rate = -[(-0.0026 mol/L)/ (110 s)]

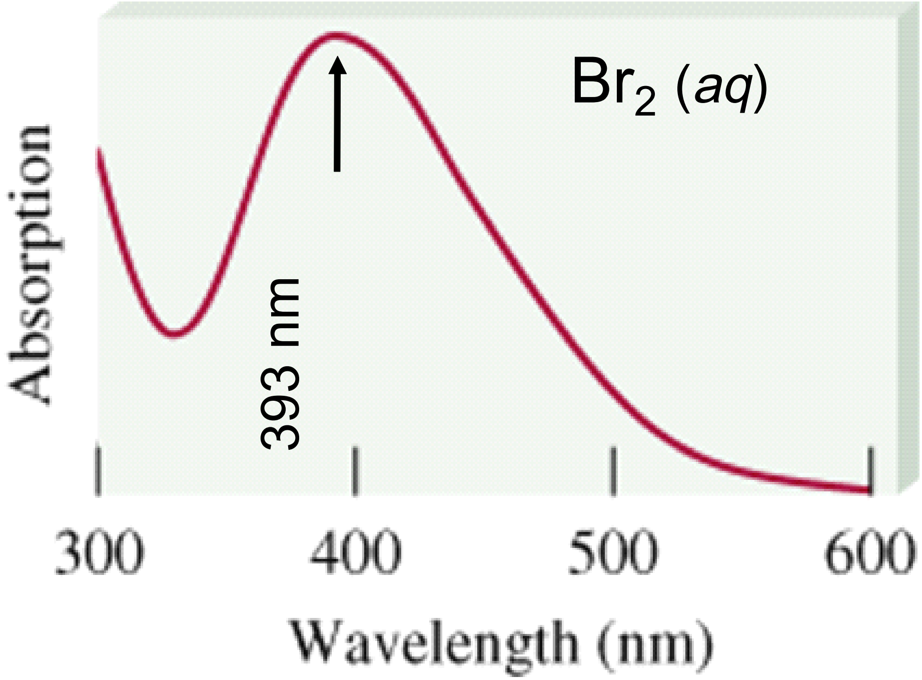
= 2.4 x 10 $^{-5}$ mol/L.s

See fig. 12.1

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

time



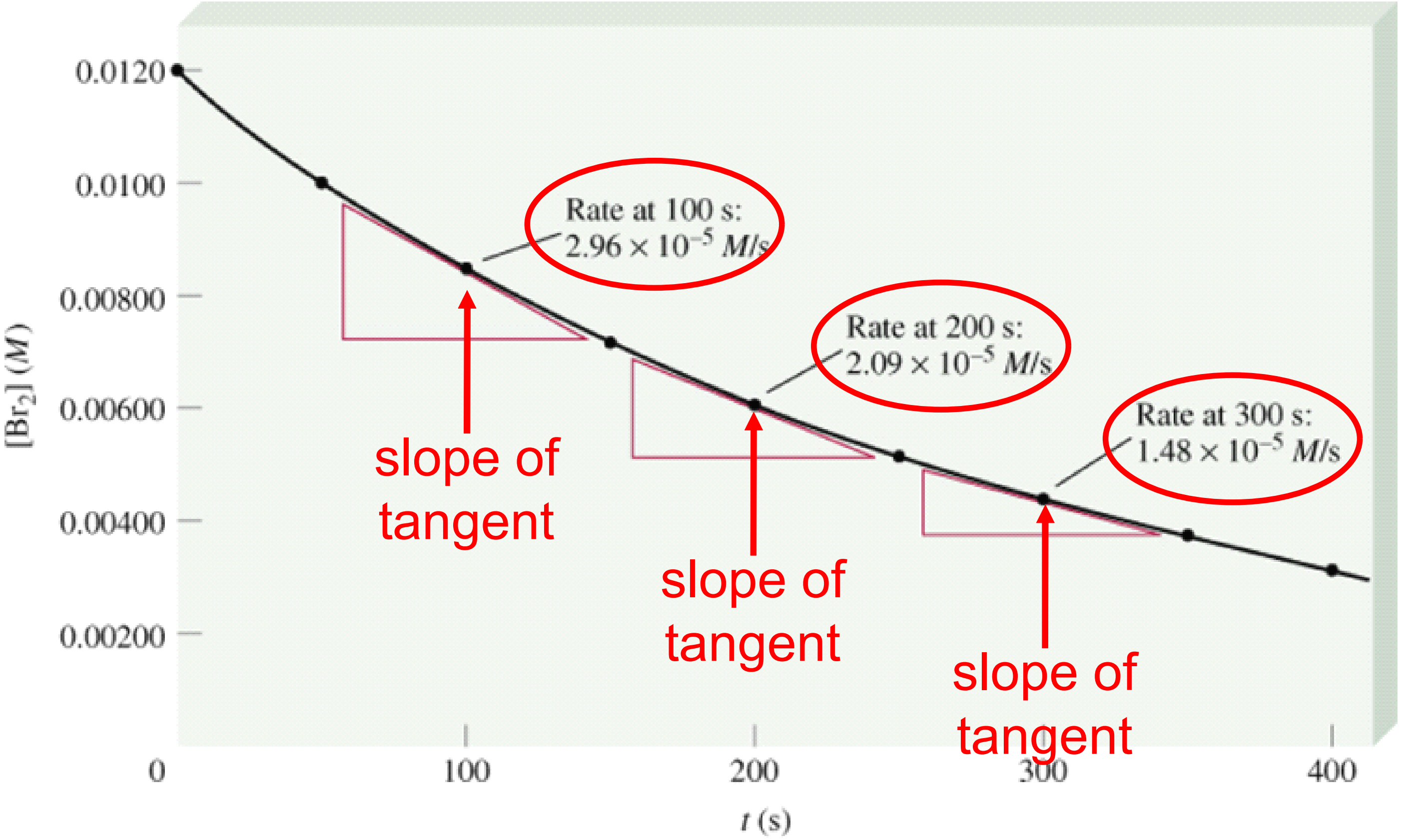


$\Delta[Br_2]$ α Δ Absorption

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

Table 13.1 Rates of the Reaction between Molecular Bromine and Formic Acid at 25°C

Time (s)	$[Br_2]$ (M)	Rate (M/s)	$k = \frac{\text{rate}}{[Br_2]}$ (s^{-1})
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}



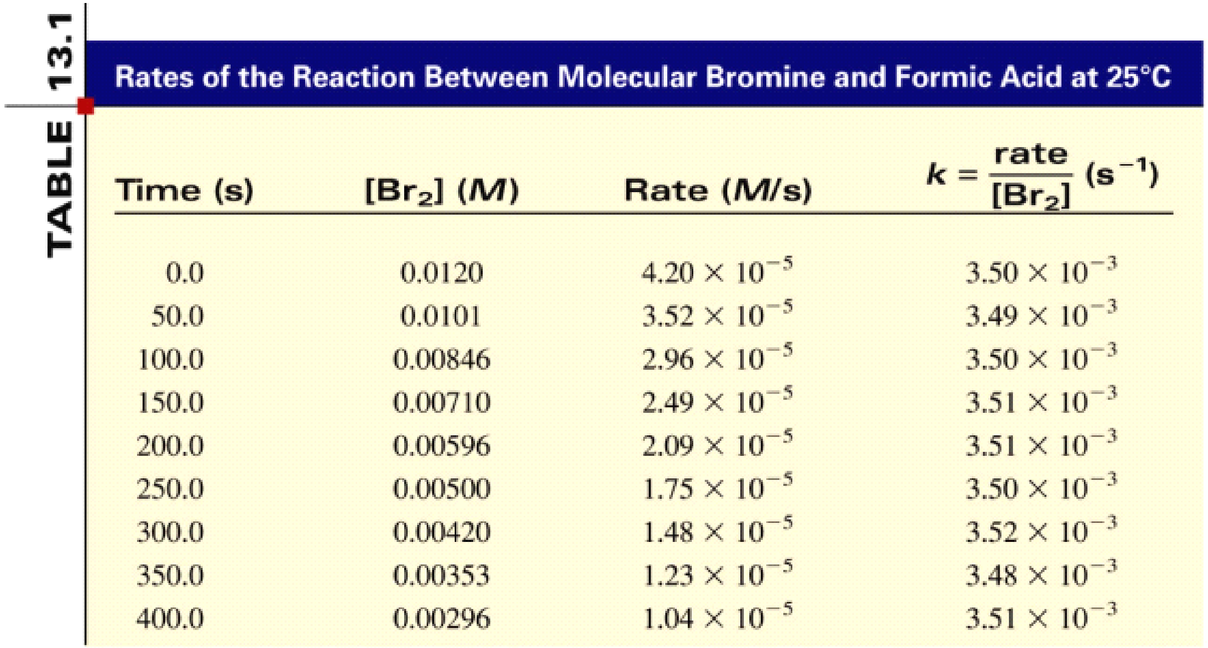
slope of tangent

slope of tangent

slope of tangent

$$\textbf{average rate} = -\frac{\Delta[Br_2]}{\Delta t} = -\frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

instantaneous rate = rate for specific instance in time



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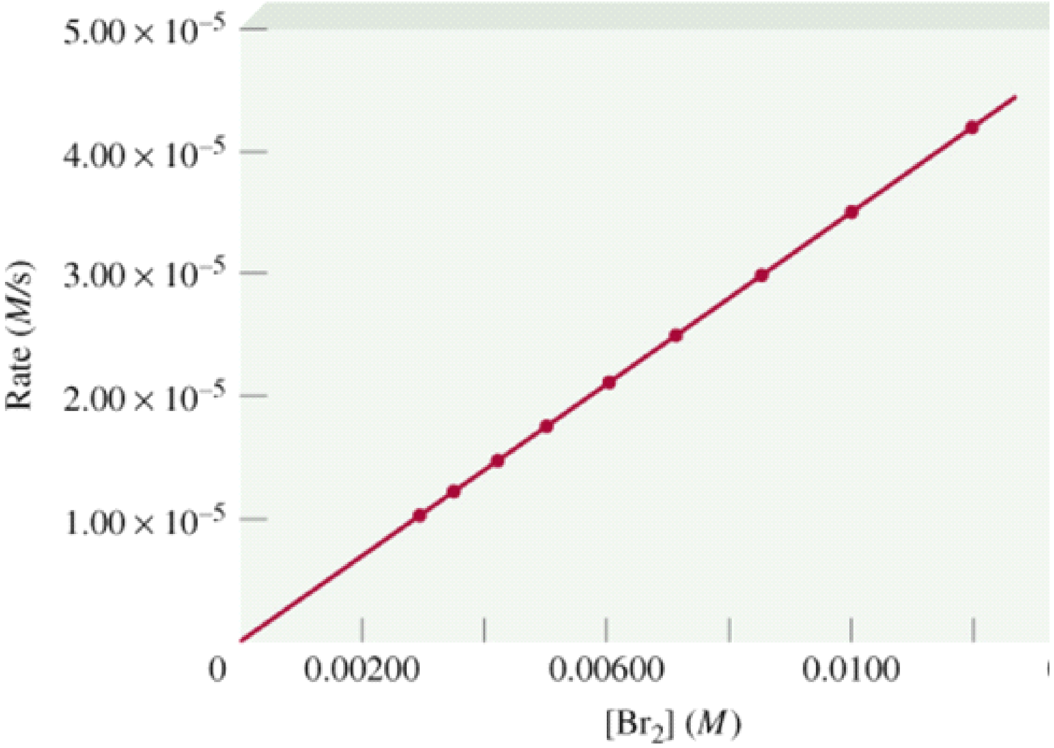


$\text{rate} \propto [Br_2]$

$\text{rate} = k\,[Br_2]$

$k = \dfrac{\text{rate}}{[Br_2]}$ = ***rate constant***

$= 3.50 \times 10^{-3}\ s^{-1}$

instantaneous rate = rate for specific instance in time

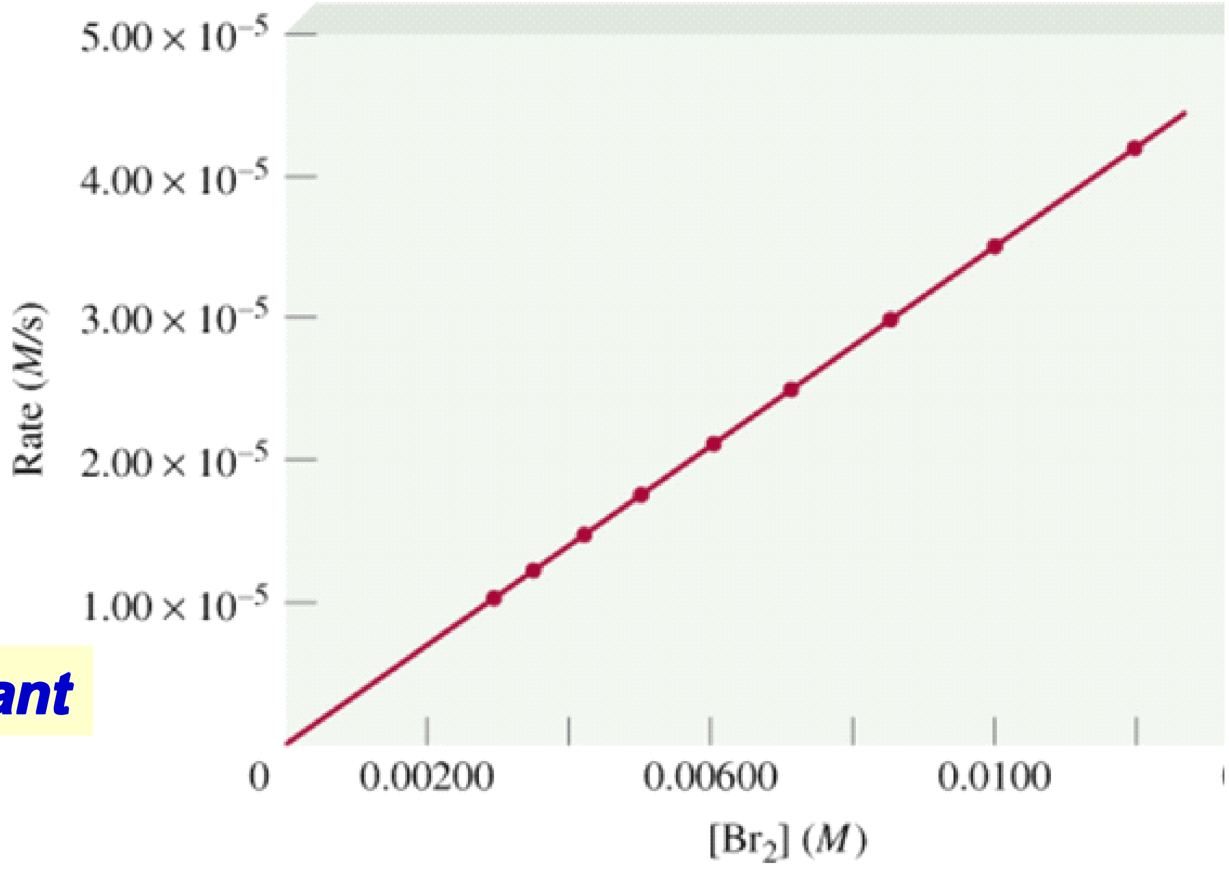
average rate $= -\frac{\Delta[Br_2]}{\Delta t}$

rate α $[Br_2]$

rate = $k\,[Br_2]$

$k = \frac{\text{rate}}{[Br_2]}$ = ***rate constant***

= $3.50 \times 10^{-3}\ s^{-1}$



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

Reaction Rates and Stoichiometry

$$2A \longrightarrow B$$

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

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

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

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

Write the rate expression for the following reaction:

$$CH_4\,(g) + \boxed{2}O_2\,(g) \longrightarrow CO_2\,(g) + \boxed{2}H_2O\,(g)$$

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

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.

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

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

reaction is ***x*th order** in A

reaction is ***y*th order** in B

reaction is **(x +y)th order overall**

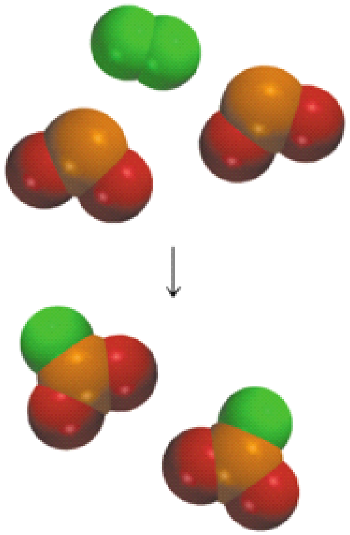
K is the reaction constant

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

$$Rate = k\,[NO_2]^{n}$$

Rate Laws

1. Rate laws are **always** determined **experimentally**.
2. Reaction order is **always** defined in terms of **reactant** (not product) concentrations.
3. **The order of a reactant is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation. It must be determined by experiment



$$F_2\,(g) + \boxed{2}ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$$\text{rate} = k\,[F_2][ClO_2]^{\boxed{1}}$$

Rate Laws

Differential Rate Law

-Shows how the reaction rate depends on concentration

Integrated Rate Law

-Shows how the concentrations depend on time

Rate Law

- Rate law will involve **only the reactants concentrations** because the reverse reaction is unimportant
- The experimental determination of either of **differential or integrated law** is sufficient because they are related
- It is important to know the **rate law** to know the **individual steps** involved in the reaction from
- the specific form of the rate law

Determining the Form of the Rate Law

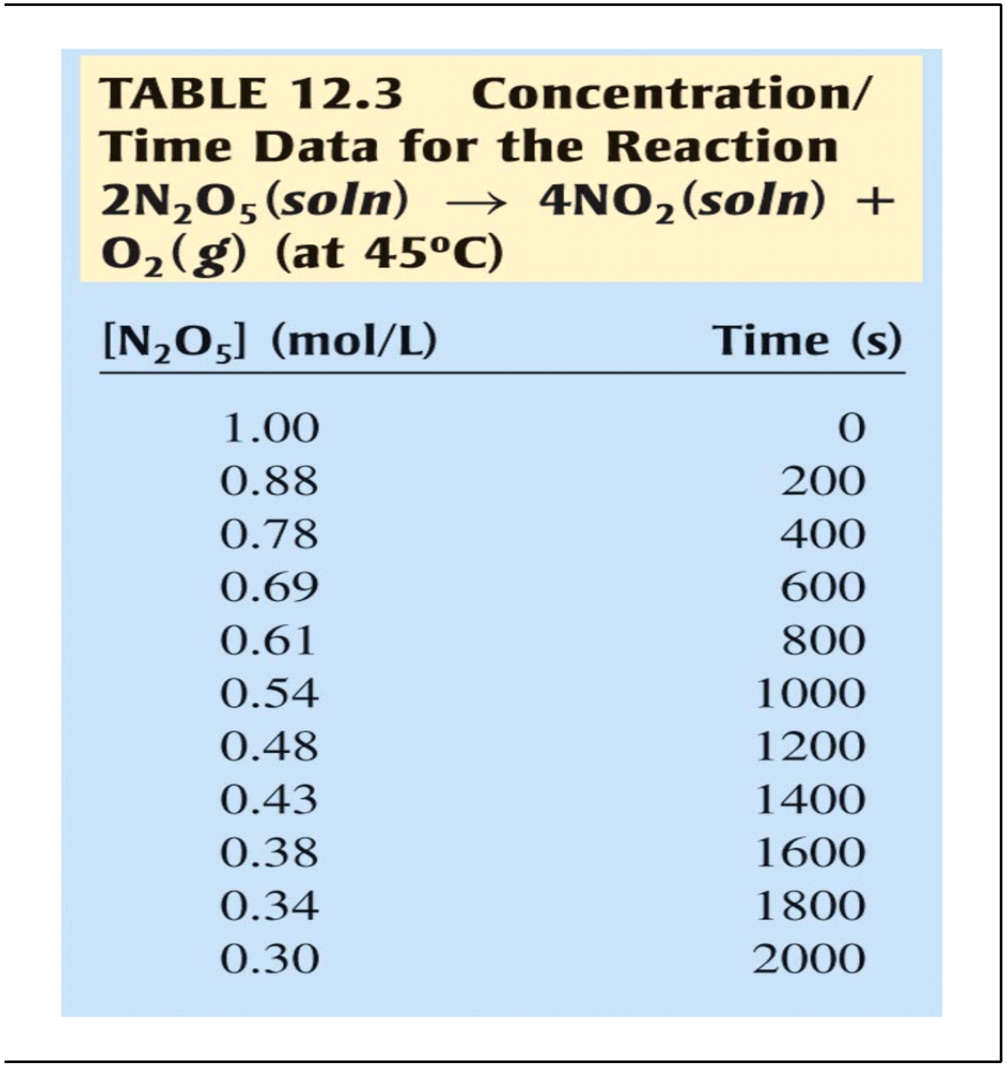
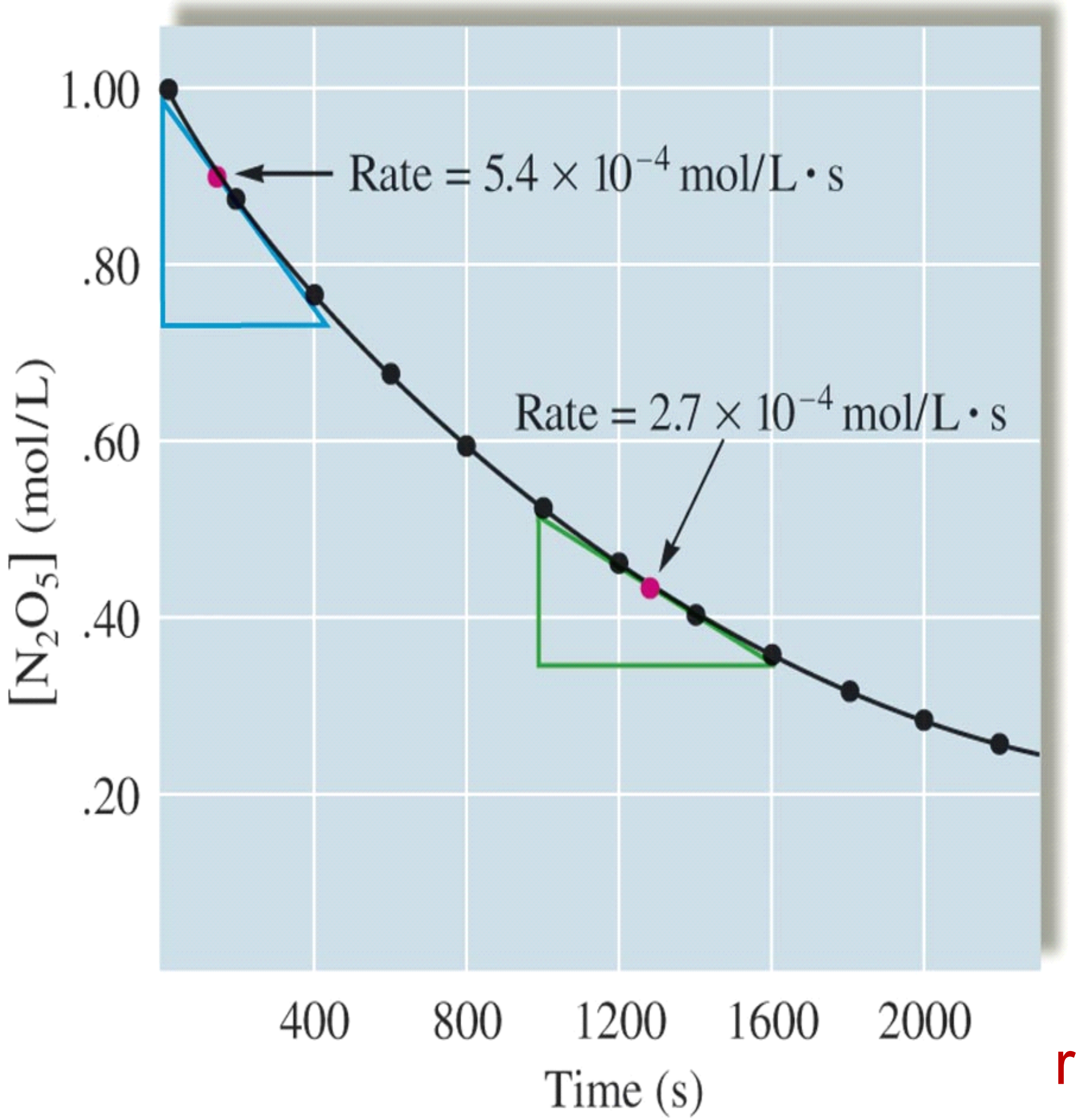


TABLE 12.3 Concentration/Time Data for the Reaction $2N_2O_5(\mathit{soln}) \rightarrow 4NO_2(\mathit{soln}) + O_2(g)$ (at 45°C)

$[N_2O_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

To understand how a chemical reaction occurs, we need to determine experimentally **the power** to which each reactant concentration **must be raised** in the rate law

- $2N_2O_5(_{soln}) \longrightarrow 4NO_2(_{soln}) + O_2(g)$



$[N_2O_5]$	Rate (mol/L.s)
0.09 M	5.4 x10 $^{-4}$
0.045 M	2.7 x 10^{-4}

The rate of this reaction depends on the concentration of N_2O_5 to the first power

$$\text{rate} = -\frac{\Delta[N_2O_5]}{\Delta t} = k\,[N_2O_5]$$

Fig. 12.3 A Plot of the Concentration of N_2O_5 as a Function of Time for the Reaction

Method of Initial Rates

Initial Rate: the instantaneous rate determine just after the reaction begins (just after t=0)

1. To determine experimentally the instantaneous rate before the initial concentrations have changed significantly

2. The results are compared to see how the initial rate depend on **initial concentrations**
3. Finally the rate law will be determined

Determine the rate law and calculate the **rate constant** for the following reaction from the following data:

$$S_2O_8^{2-}\,(aq) + 3I^-\,(aq) \longrightarrow 2SO_4^{2-}\,(aq) + I3^-\,(aq)$$

Experiment	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-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)

$$\frac{\text{Rate-1}}{\text{Rate-2}} = \frac{2.2 \times 10^{-4}}{1.1 \times 10^{-4}} = 2 \qquad \frac{[I^-] = 0.034}{[I^-] = 0.017} = 2 \qquad \mathbf{y=1}$$

Double $[S_2O_8^{2-}]$, rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[S_2O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4}\ M/\text{s}}{(0.08\ M)(0.034\ M)} = 0.08/M{\bullet}\text{s}$$

Determine the rate law and calculate the **rate constant** for the following reaction from the following data:

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3	0.16	0.017	2.2×10^{-4}

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

$y = 1$

$x = 1$

$\textbf{rate} = k\,[S_2O_8^{2-}]\,[I^-]$

Double $[I^-]$, rate doubles (experiment 1 & 2)

Double $[S_2O_8^{2-}]$, rate doubles(experiment 2 & 3)

$$\frac{\text{Rate-3}}{\text{Rate-2}} = \frac{2.2 \times 10^{-4}}{1.1\times 10^{-4}} = 2 \quad \frac{[S_2O_8^{2-}]}{[S_2O_8^{2-}]} = \frac{0.16}{0.08} = 2 \qquad x=1$$

$\textbf{rate} = k\,[S_2O_8^{2-}]\,[I^-]$

$$k = \frac{\text{rate}}{[S_2O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4}\ M/\text{s}}{(0.08\ M)(0.034\ M)} = 0.08\ /M\text{•s}$$

$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

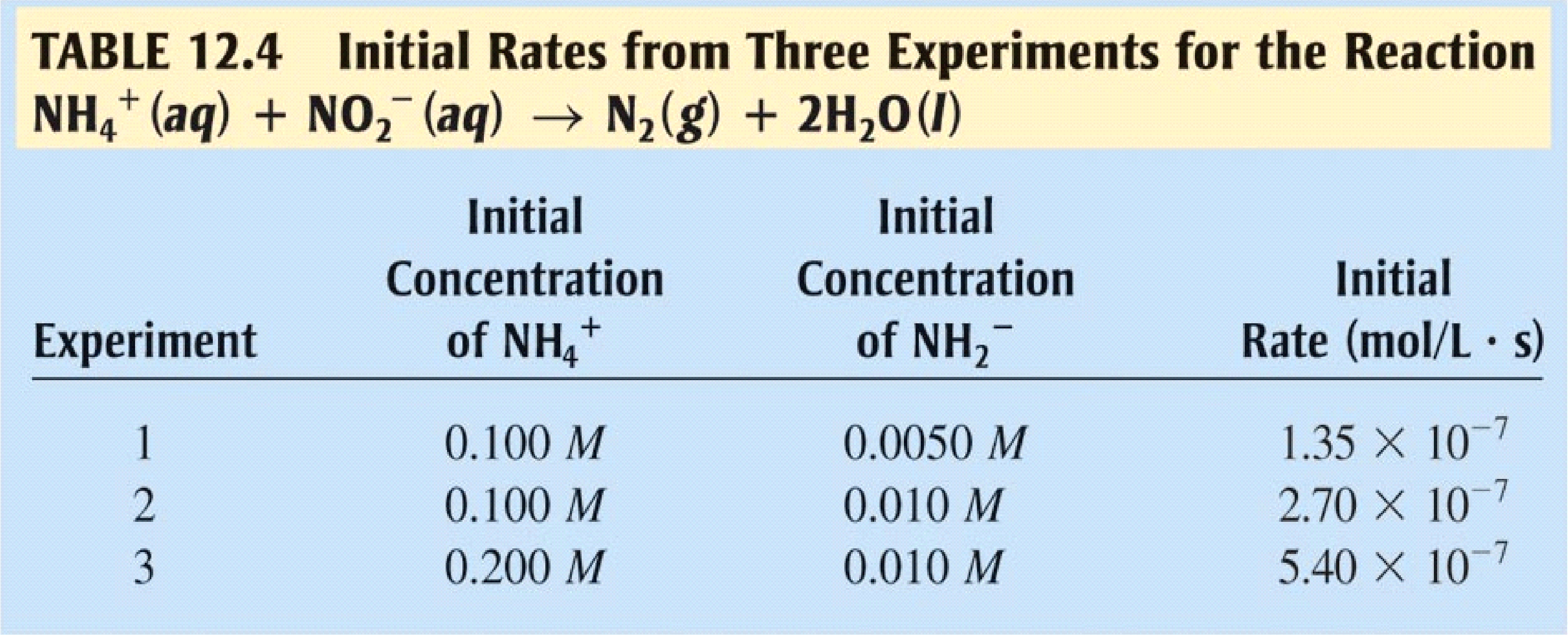


TABLE 12.4 Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NH_2^-	Initial Rate (mol/L · s)
1	0.100 *M*	0.0050 *M*	1.35×10^{-7}
2	0.100 *M*	0.010 *M*	2.70×10^{-7}
3	0.200 *M*	0.010 *M*	5.40×10^{-7}

Table 12.4 Initial Rates from Three Experiments for the Reaction $NH_4+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

$$\text{rate} = -\frac{\Delta[NH_4^+]}{\Delta t} = k\,[NH_4^+]^n[NO_2^-]^m$$

Rate 1= 1.35×10^{-7} mol/L.s =k (0.100 mol/)^n (0.005 mol/L)^m

Rate2 = 2.70×10^{-7} mol/L.s =k (0.100 mol/)^n (0.010 mol/L)^m

(Rate2/Rate1) = 2.0 =(2.0)^m m= 1

(Rate3/Rate2) =2.0 = (2.0)^n n= 1

Rate = k $[NH_4^+][NO_2^-]$

The overall reaction order = **n+m = 2**

Rate = k $[NH_4^+][NO_2^-]$

1.35×10^{-7} mol/L.s =k (0.100 mol/)(0.005 mol/L)

k = 2.7×10^{-4} L/ mol.s

Example:

The reaction between bromate ion and bromide ions in acidic aqueous solution is given by the equation below

$$BrO\text{-}_3(aq) + 5Br\text{-}(aq) + 6H^+(aq) \longrightarrow 3Br_2(l) + 3H_2O(l)$$

Find the rate law and the rate constant using the experimental data in the table below.

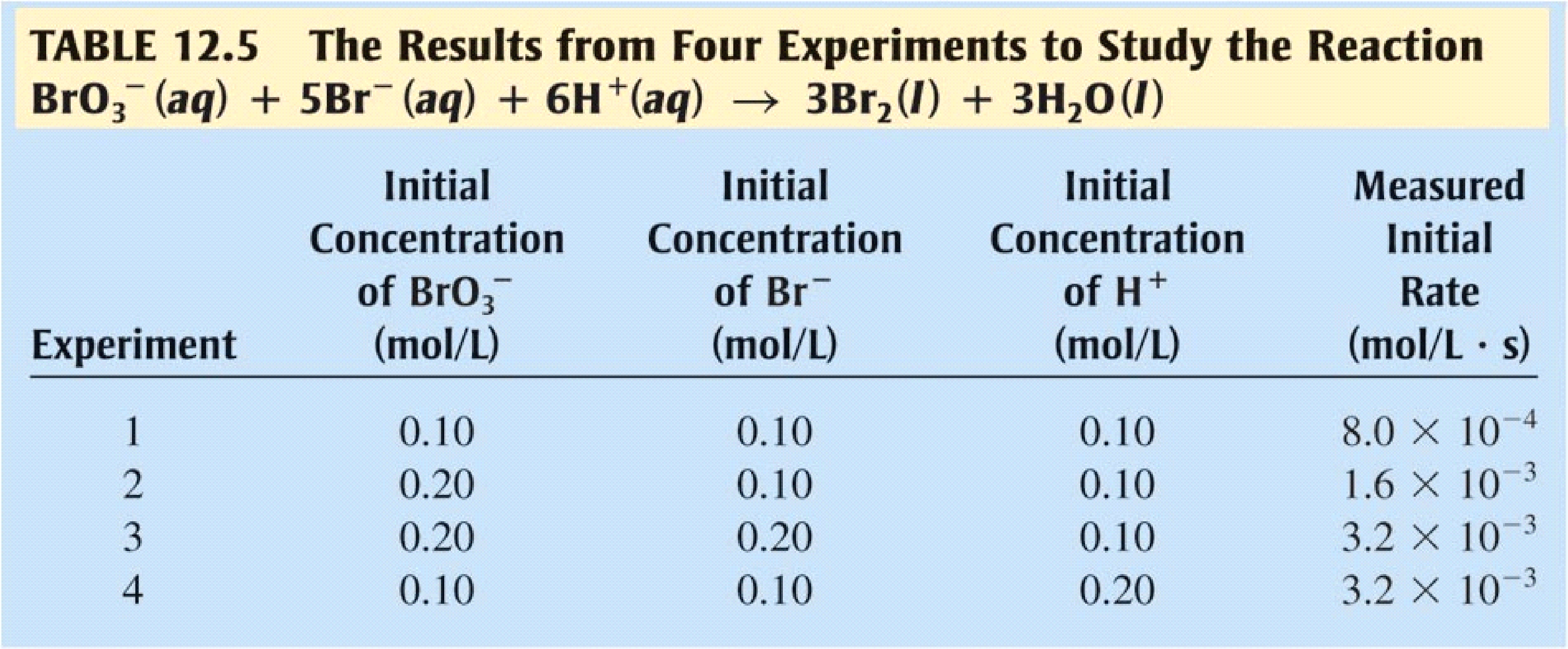
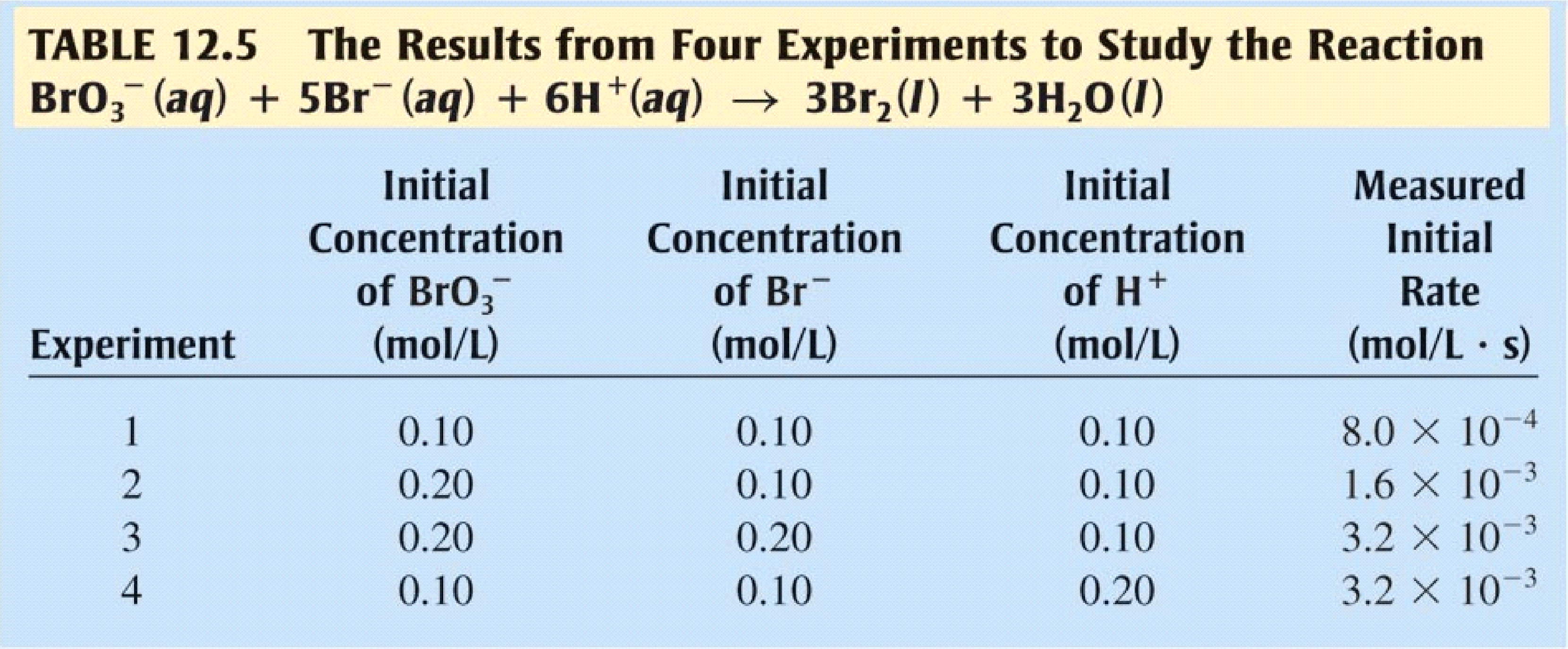


TABLE 12.5 The Results from Four Experiments to Study the Reaction $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}



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2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

$$=k\,[BrO_3^-]^n[Br^-]^m[H^+]^p$$

First-Order Reactions

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

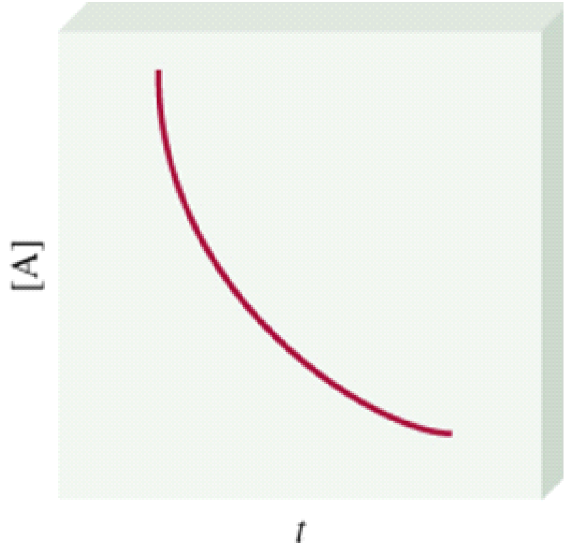
$$-\frac{\Delta[A]}{\Delta t} = k\,[A]$$

$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/s \text{ or } s^{-1}$$

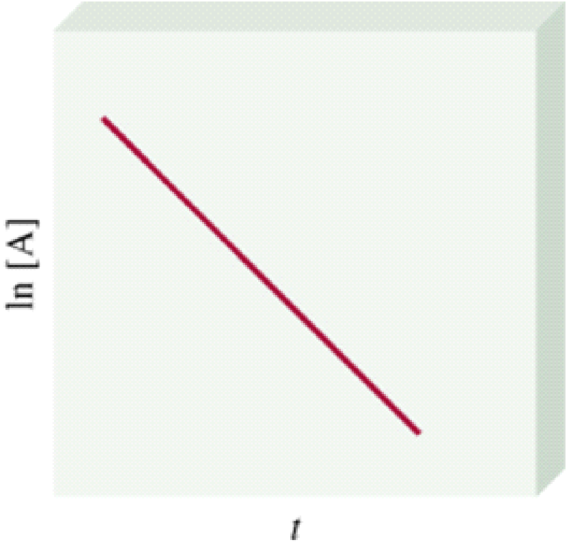
[A] is the concentration of A at any time t

$[A]_0$ is the concentration of A at time t=0

$$[A] = [A]_0 \exp(-kt)$$



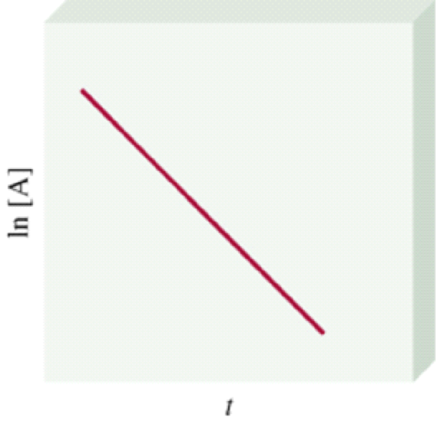
$$\ln[A] = \ln[A]_0 - kt$$



Integrated first –order rate law

1- Shows [A] depends on time, $[A]_0$ and k are known

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



2- It is of the form y= mx + b

y= ln [A]   x= t m= -k = slope

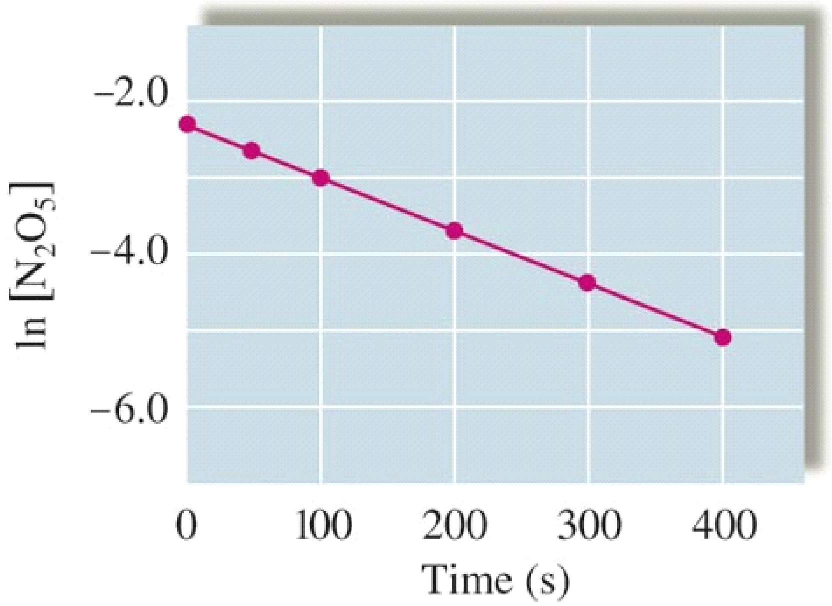
b= $\ln[A]_0$

The reaction is first order in A if a plot of ln[A] versus t is a straight line

3- The integrated first – order law can be expressed as a a ratio between [A] and [A]0

$$\ln \frac{[A]_0}{[A]} = k\,t$$

first –order rate law



$\ln[N_2O_5]$	Time (s)
−2.303	0
−2.649	50
−2.996	100
−3.689	200
−4.382	300
−5.075	400

$$\text{Slope} = \frac{\Delta y}{\Delta X} = \frac{\Delta(\ln [N2O5])}{\Delta t} = \frac{-5.075 - (-2.303)}{400 - 0\ \text{s}} = -6.93 \times 10^{-3}\ \text{s}^{-1}$$

$$K = -\text{slope} = 6.93 \times 10^{-3}\ \text{s}^{-1}$$

Calculate $[N_2O_5]$ at 150 s after the start of the reaction.

Solution

$\ln [N_2O_5] = - kt + \ln [N_2O_5]_0$

$t = 150$ s , $k = 6.93 \times 10^{-3}\ s^{-1}$ and $[N_2O_5]_0 = 0.1000$ mol/ L

$\ln [N_2O_5] = -(6.93 \times 10^{-3})(150\ s) + \ln (0.1000\ mol/\ L)$
$= -1.040 -2.303 = -3.343$

$\ln [N_2O_5]_{t\ =\ 150} = -3.343$
$[N_2O_5]_{t\ =\ 150}$ = antilog (-3.343)= 0.0353 mol/L

The reaction $2A \longrightarrow B$ is first order in A with a rate constant of $2.8 \times 10^{-2}\ s^{-1}$ at 800C.
How long will it take for A to decrease from 0.88 *M* to 0.14 *M* ?

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

$$[A]_0 = 0.88\ M$$

$$[A] = 0.14\ M$$

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

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

First-Order Reactions

The ***half-life, $t_{½}$,*** is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$t_{½} = t$ when $[A] = [A]_0/2$ $\qquad$ $\ln [A] = -kt + \ln [A]_0$

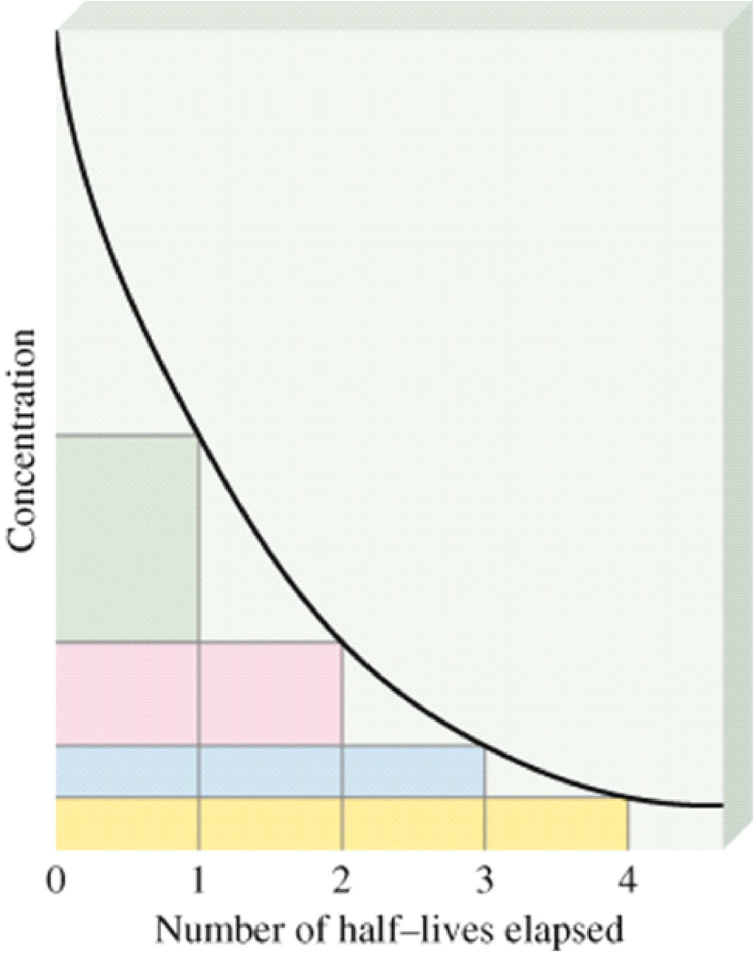
$$t_{½} = \frac{\ln \dfrac{\cancel{[A]}_0}{\cancel{[A]}_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

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

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

How do you know decomposition is first order?

units of k (s^{-1})



First-order reaction

$$A \longrightarrow \text{product}$$

# of half-lives	$[A] = [A]_0/n$
1	2
2	4
3	8
4	16

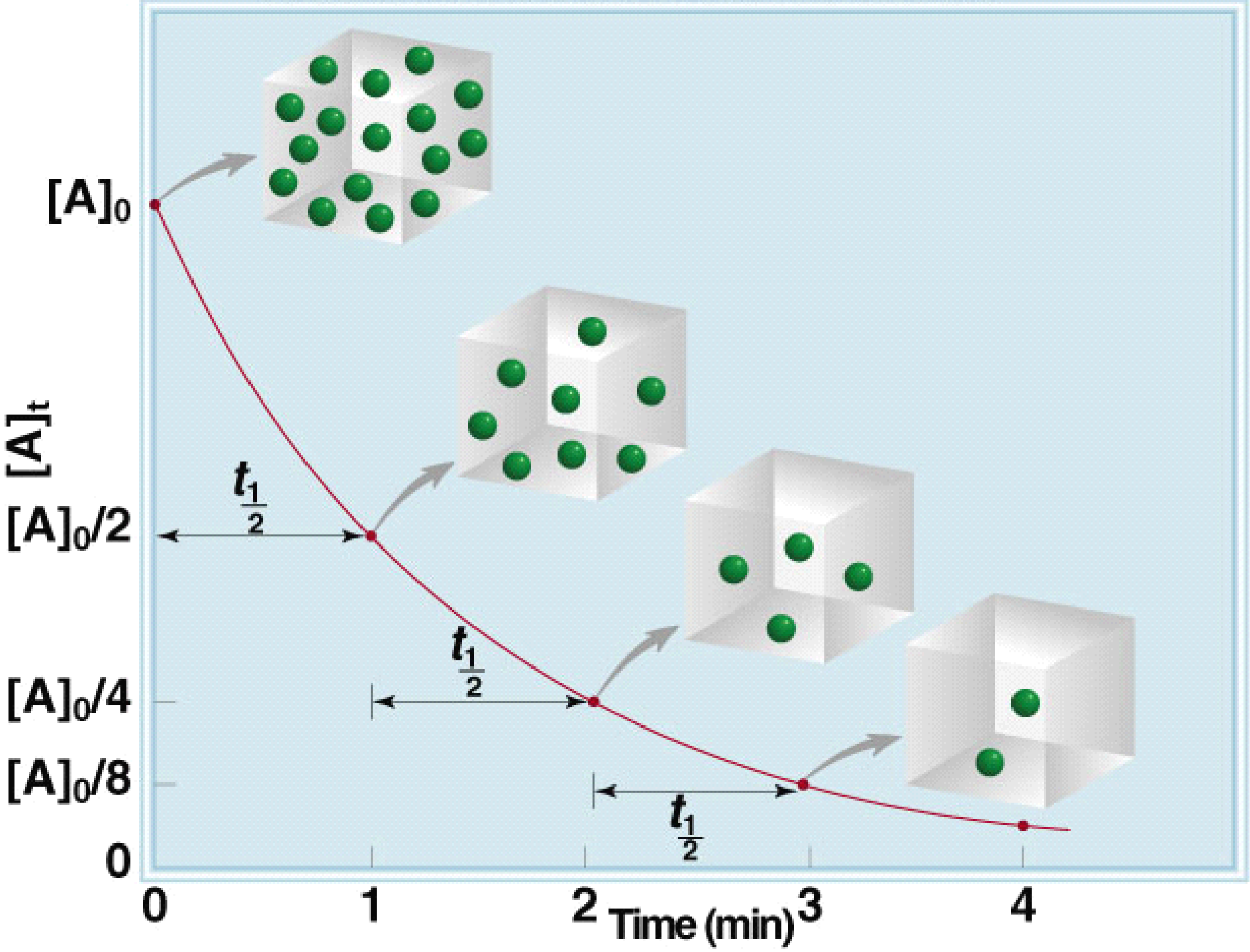
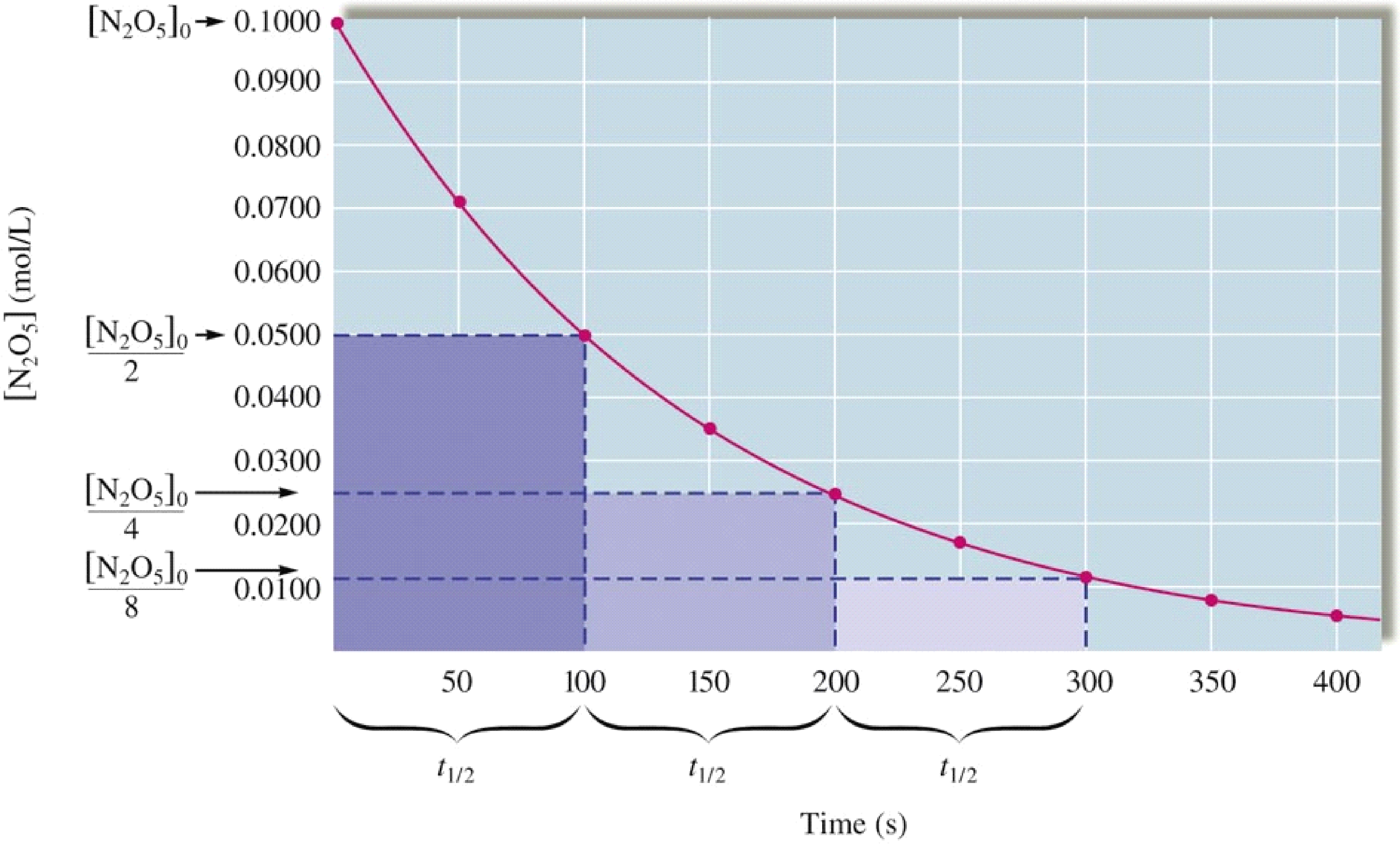

[A]$_0$
[A]$_t$
[A]$_0$/2
[A]$_0$/4
[A]$_0$/8
0
$t_{\frac{1}{2}}$
$t_{\frac{1}{2}}$
$t_{\frac{1}{2}}$
0
1
2
Time (min)
3
4

Figure 5 A Plot of [N_2O_5] versus Time for the Decomposition Reaction of N_2O_5



A certain first-order reaction has a half life of 20.0 minutes.

a. Calculate the rate constant for the reaction.
b. How much time is required for this reaction to be 75% complete?

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20.0 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

$$\ln \frac{[A]_0}{[A]} = k\,t \qquad \frac{[A]}{[A]_0} \times 100\% = 25\ \% \qquad \frac{[A]}{[A]_0} = 0.25 \qquad \frac{[A]_0}{[A]} = 4.0$$

$$\ln \frac{[A]_0}{[A]} = k\,t \qquad \ln(4.0) = (3.47 \times 10^{-2} \text{ min}^{-1})t$$

$t = 40.$ min

Second-Order Reactions

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

$$k = \frac{\text{rate}}{[A]^2} = \frac{M/s}{M^2} = 1/M\bullet s \qquad -\frac{\Delta[A]}{\Delta t} = k\,[A]^2$$

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

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

$[A]_0$ is the concentration of A at time t=0

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

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

Determining Rate Law

Butadiene reacts to form its dimer according to the equation

$$2\,C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

The data were collected as shown in the table in page 544 in Zumdahl.

a. Is the reaction first order or second order

b. What is the value of the rate constant

c. What is the half life.

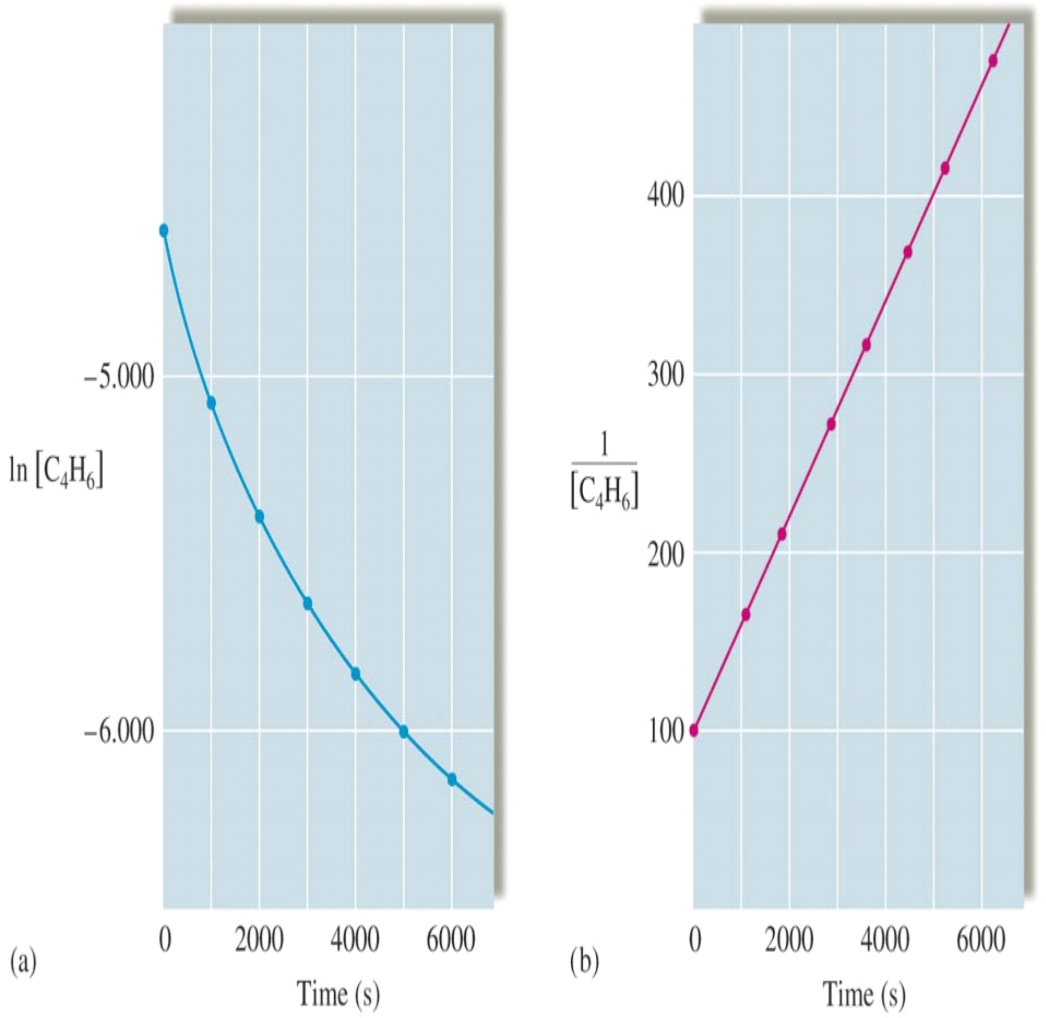


Figure 6 (a) A Plot of ln[C_4H_6] versus t (b) A Plot of 1/[C_4H_6] versus T

a. From the graphs the reaction is second order

Rate = k[C_4H_6]^2

b. Slope = k= 6.14 x 10^{-2} L/ mol.s

c.

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

$$= \frac{1}{(6.14 \times 10^{-2})(1.000 \times 10^{-2})}$$

$$= 1.63 \times 10^{3}\ s$$

Zero-Order Reactions

$\mathrm{A} \longrightarrow \text{product}$

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

$$\text{rate} = k\,[\mathrm{A}]^0 = k$$

$$k = \frac{\text{rate}}{[\mathrm{A}]^0} = M/\mathrm{s}$$

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

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

$[\mathrm{A}]$ is the concentration of A at any time t

$[\mathrm{A}]_0$ is the concentration of A at time t=0

$t_{½} = t$ when $[\mathrm{A}] = [\mathrm{A}]_0/2$

$$t_{½} = \frac{[\mathrm{A}]_0}{2k}$$

Zero-order reactions encountered when a substance such as a metal surface or an enzyme is required for the reaction to occur.

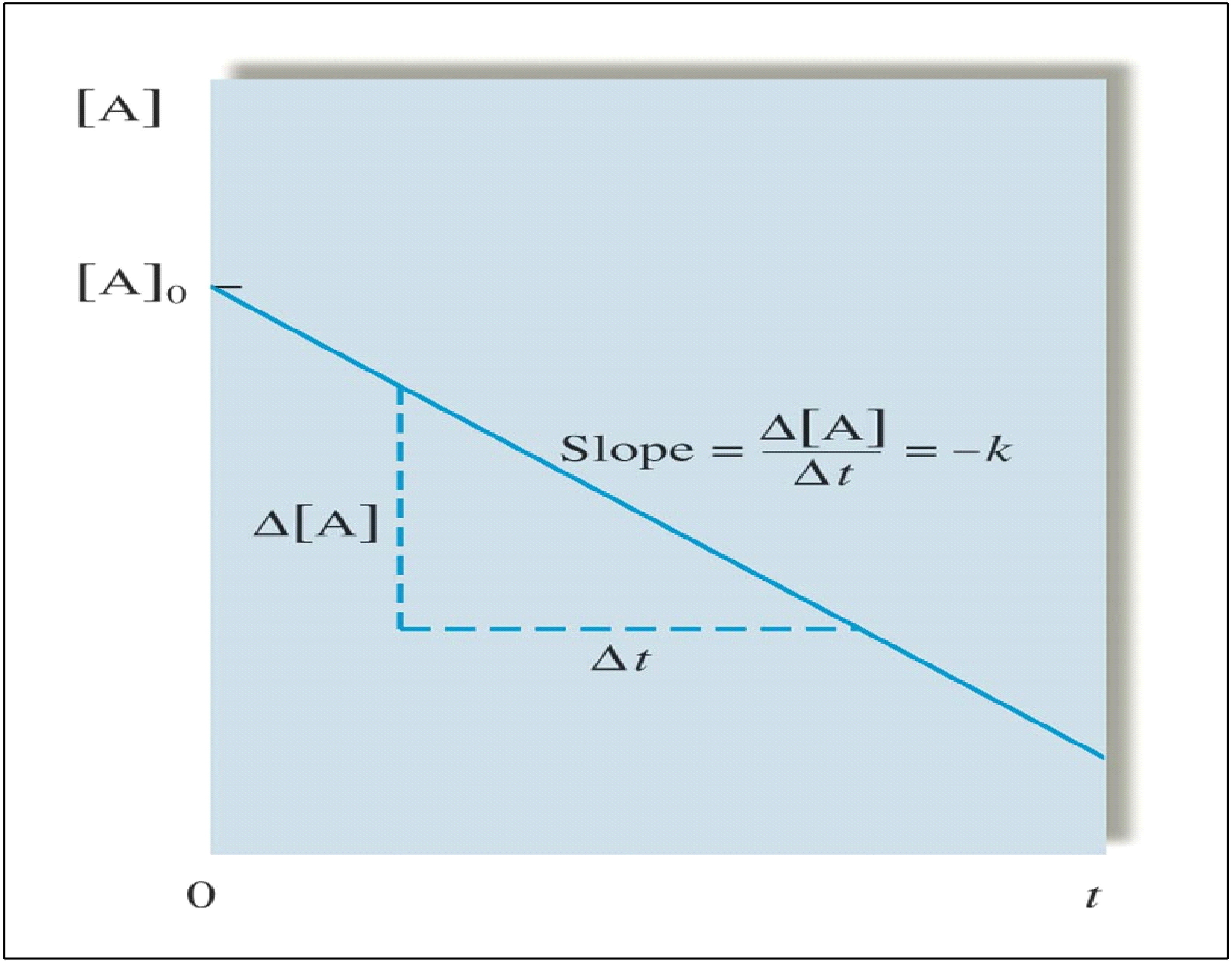
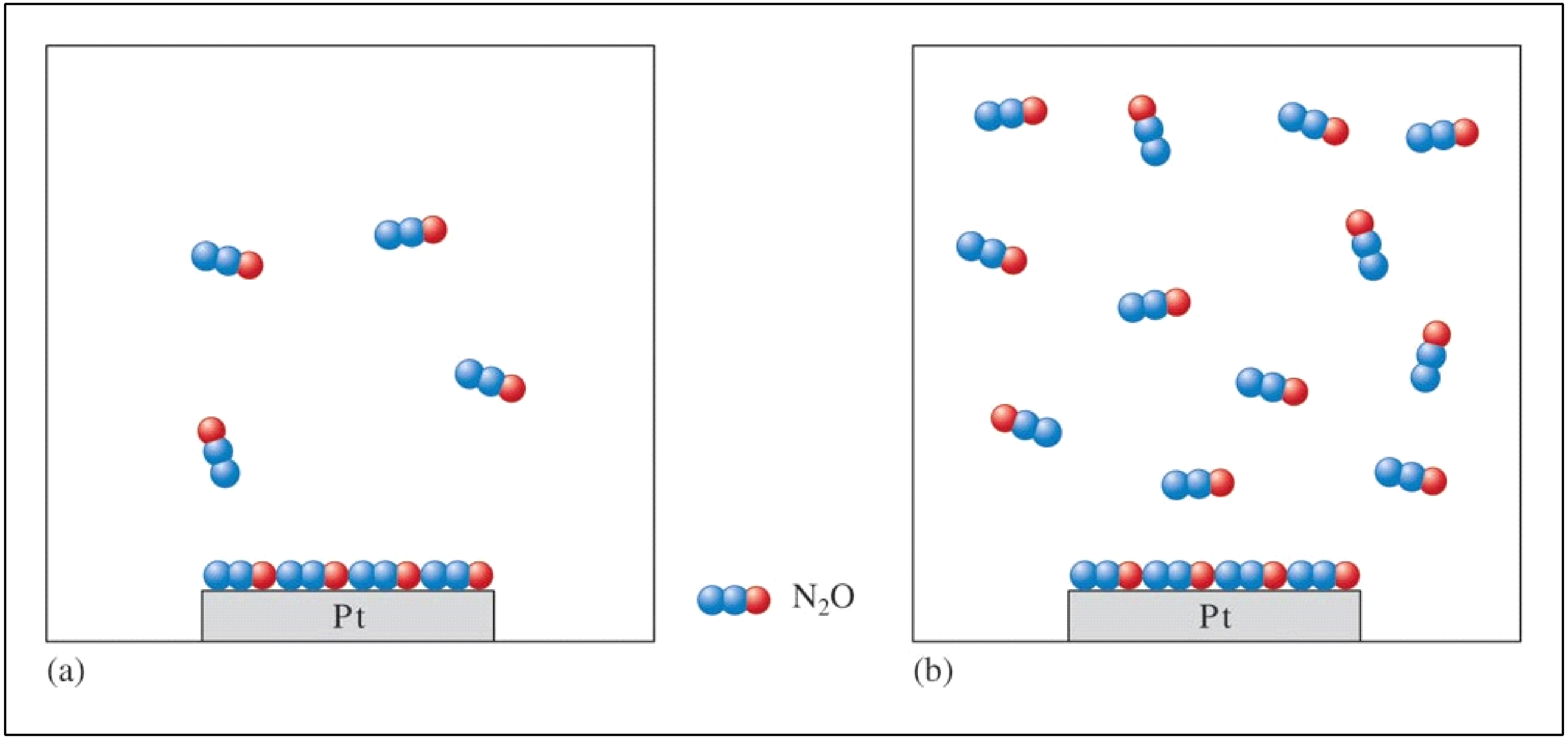


Figure 7 A Plot of [A] versus T for a Zero-Order Reaction

Figure 12.8 The Decomposition Reaction $2N_2O(g)$ $2N_2 + O_2$ (g) takes Place on a Platinum Surface



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

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