

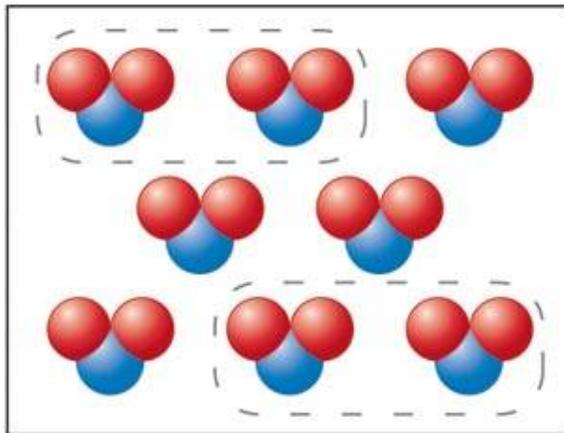
Chemical Kinetics

DR.S. ANAND GIRI

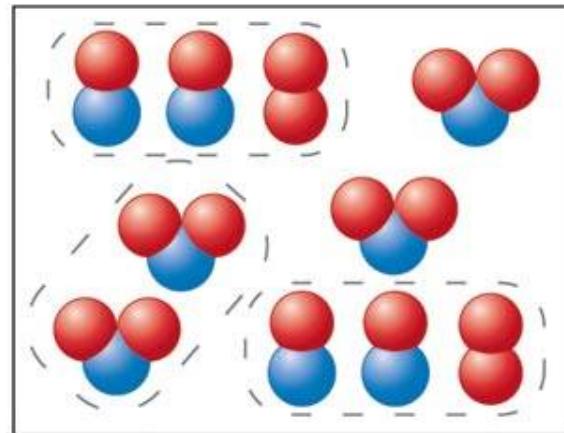
ANANLYTICAL CHEMISTRY
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Reaction Rate

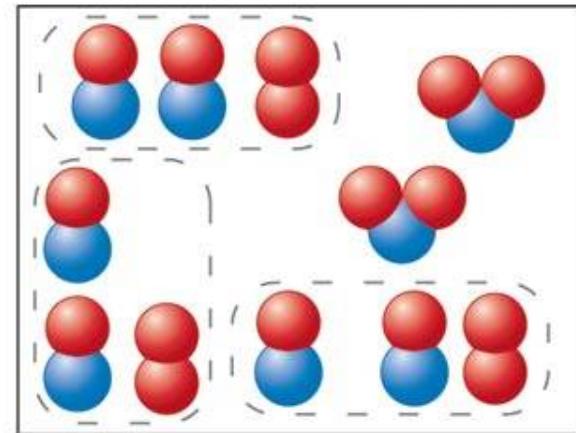
2



(a)



(b)



(c)

Time

TABLE 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$ (at 300°C)

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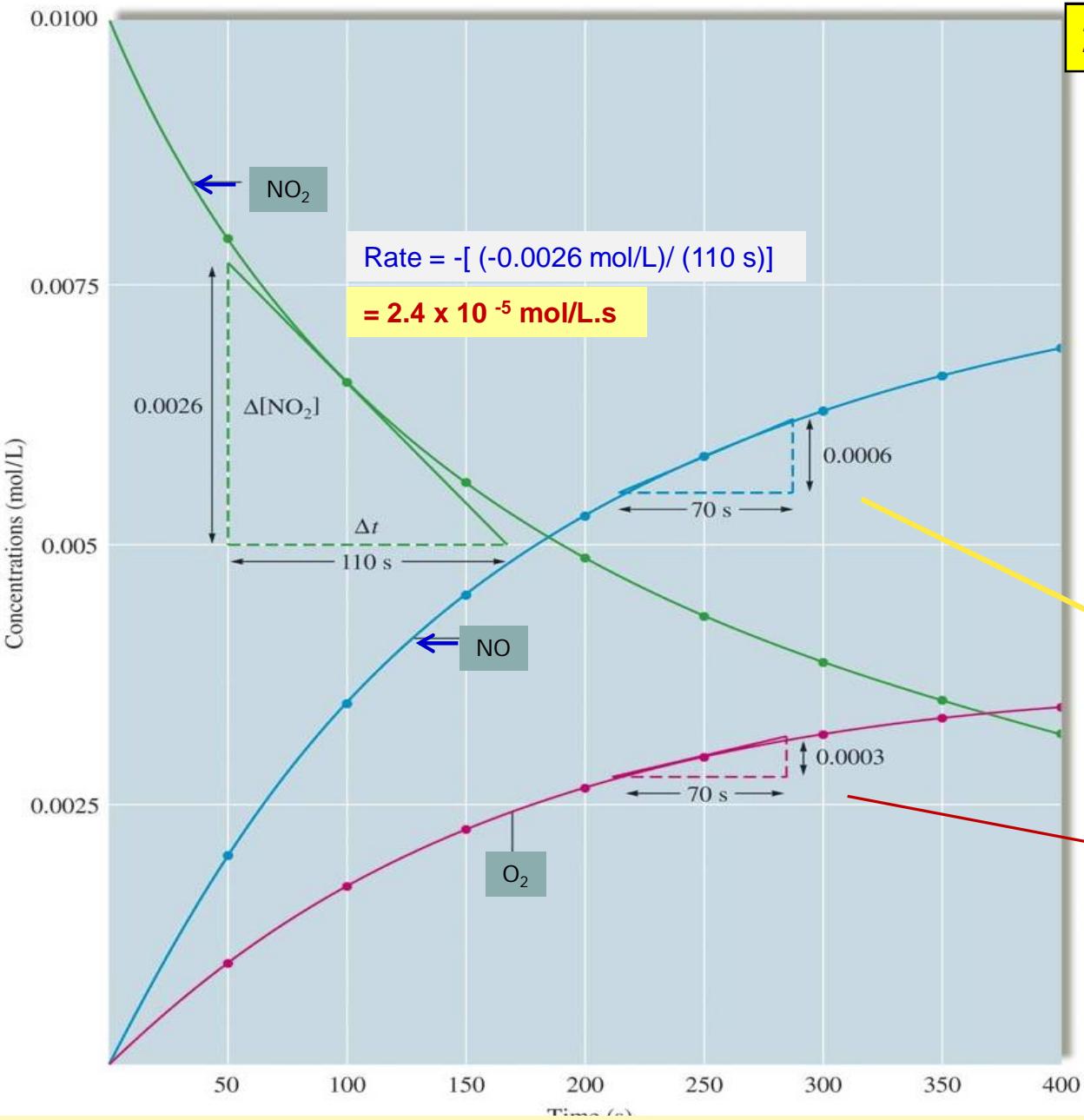
Time (± 1 s)	Concentration (mol/L)		
	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

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





- The curve of NO is the same as NO₂ curve except it is flipped over

- O₂ is produced half as fast as NO
- Slope of NO curve

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

$$= 8.6 \times 10^{-6} \text{ mol/L.s}$$

Slope of O₂ curve
 $= (3.0 \times 10^{-4} / 70)$

$$= 4.3 \times 10^{-6} \text{ mol/L.s}$$

The production of NO is twice that of O₂

Fig.12.1 Starting with a Flask of Nitrogen Dioxide at 300°C, Concentrations of NO₂, NO, and O₂ are Plotted versus Time

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

$\frac{\Delta[\text{NO}_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	$0 \rightarrow 50$
2.8×10^{-5}	$50 \rightarrow 100$
2.0×10^{-5}	$100 \rightarrow 150$
1.4×10^{-5}	$150 \rightarrow 200$
1.0×10^{-5}	$200 \rightarrow 250$

*Note that the *rate* decreases with time.

Rate of a Reaction

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

$$= \frac{\Delta[\text{NO}_2]}{\Delta t}$$

but rate = -
$$\frac{\Delta[\text{NO}_2]}{\Delta t}$$

Rate = - Slope of the tangent line

$$\text{Rate} = -[(-0.0026 \text{ mol/L}) / (110 \text{ s})]$$

$$= 2.4 \times 10^{-5} \text{ mol/L.s}$$

Table 12.2 Average Rate (in mol/L-s) of Decomposition of NO_2 as a Function of Time

See fig. 12.1

26/2015

TABLE 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$ (at 300°C)

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2.0×10^{-5}	$100 \rightarrow 150$
1.4×10^{-5}	$150 \rightarrow 200$
1.0×10^{-5}	$200 \rightarrow 250$

*Note that the *rate* decreases with time.

slope

$$\frac{\text{Change in } [\text{NO}_2]}{\text{Time elapsed}} = \frac{\Delta [\text{NO}_2]}{\Delta t} = \frac{[\text{NO}_2]_{t=50} - [\text{NO}_2]_{t=0}}{50 - 0}$$

$$\begin{aligned}
 &= (0.0079 \text{ mol L}^{-1} - 0.0100 \text{ mol L}^{-1}) / 50 \text{ s} \\
 &= -4.2 \times 10^{-5} \text{ mol/L · s}
 \end{aligned}$$

slope

$$\frac{\text{Change in } [\text{NO}_2]}{\text{Time elapsed}} = \frac{\Delta [\text{NO}_2]}{\Delta t}$$

$$= \frac{[\text{NO}_2]_{t=50} - [\text{NO}_2]_{t=0}}{50 - 0}$$

$$= \frac{(0.0079 \text{ mol L}^{-1} - 0.0100 \text{ mol L}^{-1})}{50 \text{ s}} \\ = -4.2 \times 10^{-5} \text{ mol L}^{-1} \cdot \text{s}^{-1}$$

But

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

$$\text{Rate} = -\frac{(0.0079 \text{ mol L}^{-1} - 0.0100 \text{ mol L}^{-1})}{50 \text{ s}} \\ = -(-4.2 \times 10^{-5} \text{ mol L}^{-1} \cdot \text{s}^{-1})$$

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The rates given in Table 1.2
are average rates over 50-second time intervals.

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the **Instantaneous Rate** : The value of the rate at a particular time can be obtained by computing the **slope of a line** tangent to the curve at that point.

Fig. 1.10 shows a tangent drawn at $t = 100$ seconds.
The *slope* of this line gives the rate at $t = 100$ seconds as follows:

$$\text{Slope of the tangent line} = - \frac{\text{Change in } y}{\text{Change in } x} = \frac{\Delta [\text{NO}_2]}{\Delta t}$$

but

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

Therefore, **Rate = - Slope of the tangent line**

instantaneous rate = rate for specific instance in time

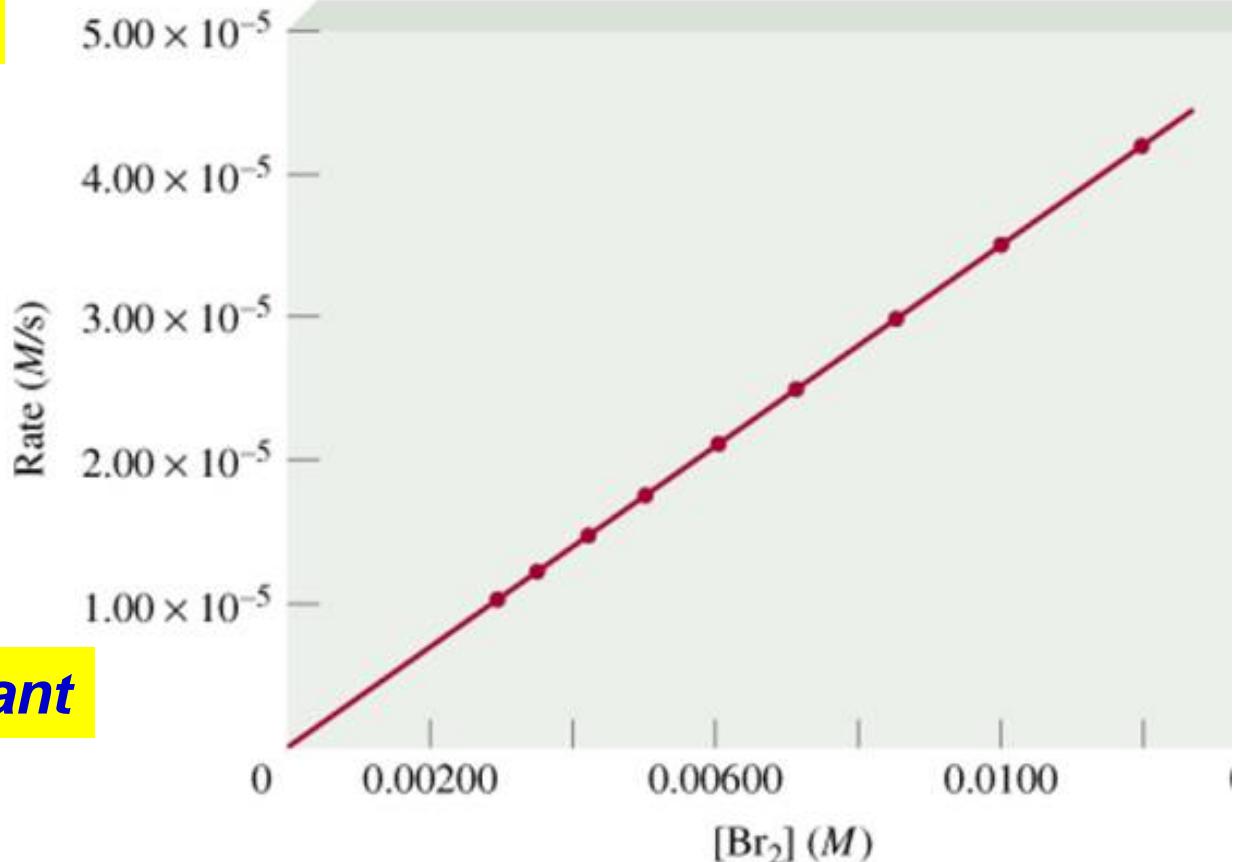
average rate = $-\frac{\Delta [\text{Br}_2]}{\Delta t}$

rate $\propto [\text{Br}_2]$

rate = $k [\text{Br}_2]$

$k = \frac{\text{rate}}{[\text{Br}_2]}$ = **rate constant**

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



Reaction Rates and Rate constant



One mole of A disappears for each mole of B that is formed.

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

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

instantaneous rate = rate for specific instance in time

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

rate \propto [A]

rate = $k[A]$

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



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

Write the rate expression for the following reaction:



**Rate of decrease of concentration of CH_4
is half the concentration of O_2**

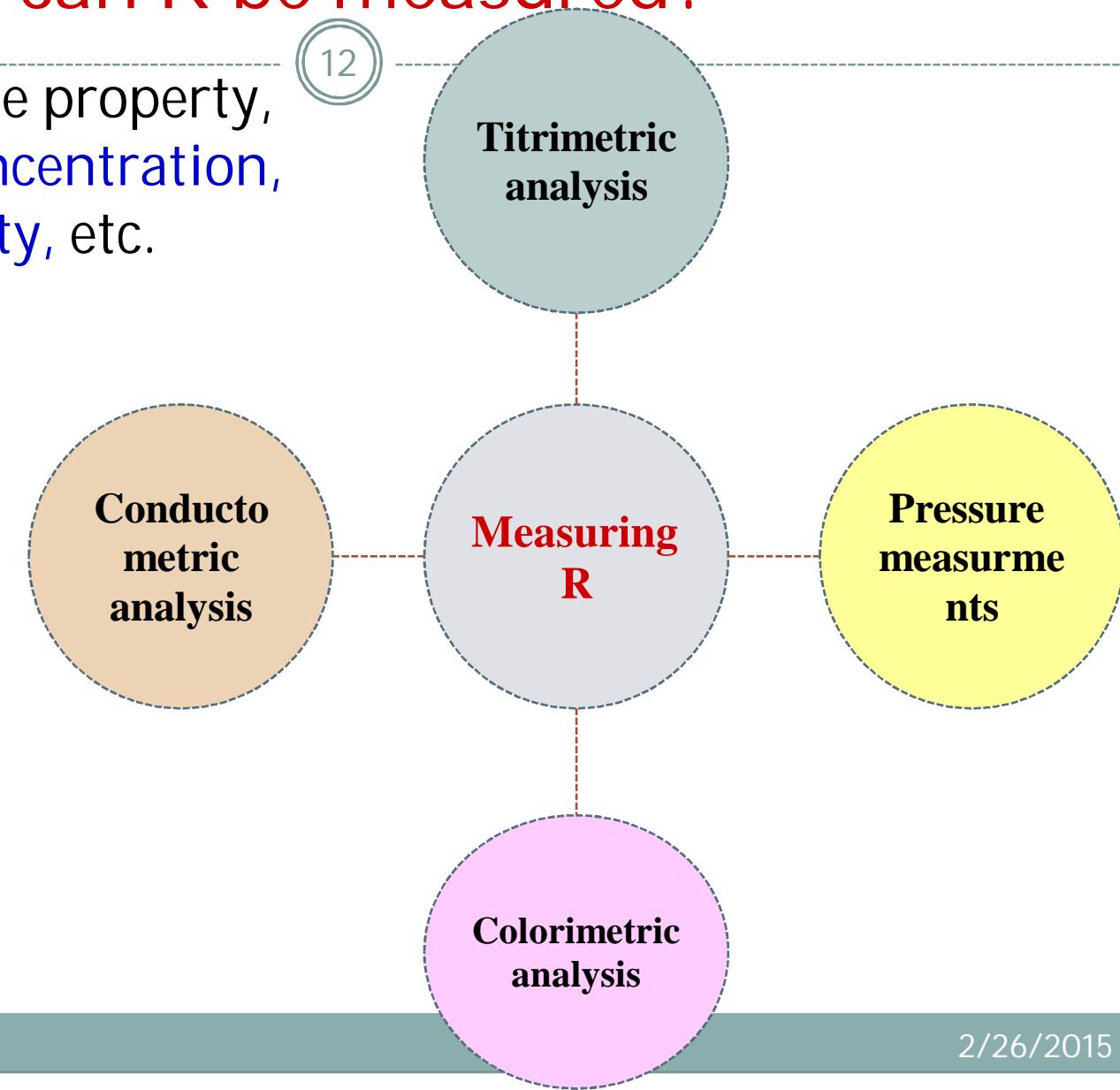
**Rate of increase of concentration of CO_2
is half the concentration of H_2O**

$$\text{rate} = - \frac{\Delta[\text{CH}_4]}{\Delta t} = - \frac{1}{2} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

How can R be measured?

- by following some property,
for example, concentration,
color, conductivity, etc.

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Rate Laws

Differential Rate Law

-Shows how the **reaction rate depends on concentration**

Integrated Rate Law

-Shows how the **concentrations depend on time**

**A rate law that
expresses how the rate depends on**

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concentration differential rate law,

but it is often simply called the **rate law**. ...

**the rate is defined as a function of
concentration.**

A second kind of rate law,

the integrated rate law,
expresses how the *concentrations*
***depend on time*.**

**a given differential rate law is always related to a
certain type of integrated rate law, and vice versa.**

If we can conveniently measure how the rate changes as the concentrations are changed, we can **readily determine the differential (rate/concentration) rate law.**

if it is more convenient to measure the concentration as a function of time, we can determine the form of the **integrated (concentration/time) rate law.**

Example : Determine the rate law for the reaction :

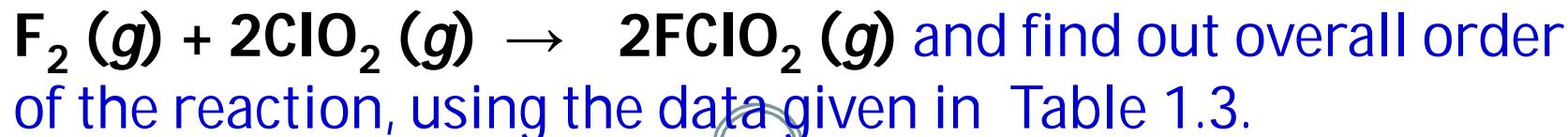


Table 1.3 : Rate Data for the Reaction between F_2 and ClO_2

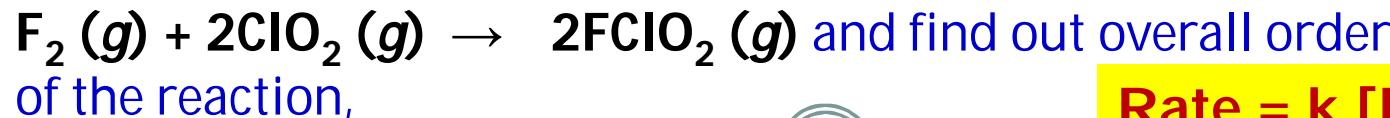
	$[F_2] (mol)$	$[ClO_2] (mol)$	<i>Initial Rate</i> ($mol\ s^{-1}$)
1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-3}

The expression for the rate law can be written as,

$$\text{Rate} = k [F_2]^x [ClO_2]^y$$

Now, we have to determine the values of **x and y** to get the actual expression of the rate law. As per the data given in the given table (Table 1.3), if $[F_2]$ is doubled keeping $[ClO_2]$ constant, the rate is doubled,

Example : Determine the rate law for the reaction :



$$\text{Rate} = k [F_2]^x [ClO_2]^y$$



Table 1.3 : Rate Data for the Reaction between F_2 and ClO_2

	$[F_2] \text{ (mol)}$	$[ClO_2] \text{ (mol)}$	<i>Initial Rate (mol s⁻¹)</i>
1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-3}

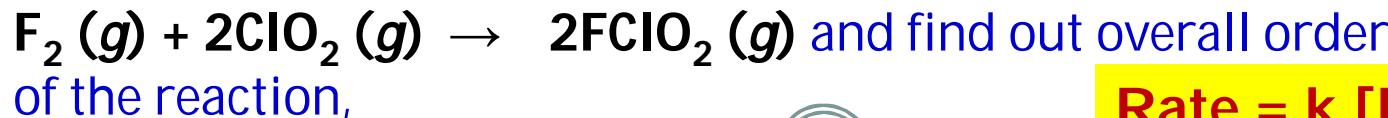
As per the data given in the given table (Table 1.3), if $[F_2]$ is doubled keeping $[ClO_2]$ constant, the rate is doubled,

$$(\text{Rate 3} / \text{Rate 1}) = \{k (0.020)^x (0.010)^y\} / \{k (0.010)^x (0.010)^y\}$$

$$= (2.4 \times 10^{-3} / 1.2 \times 10^{-3}) = \{ (0.020)^x \} / \{ (0.010)^x \}$$

$$2 = 2^x \quad \text{Therefore, } x = 1.$$

Example : Determine the rate law for the reaction :



$$\text{Rate} = k [F_2]^x [ClO_2]^y$$

Table 1.3 : Rate Data for the Reaction between F_2 and ClO_2

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1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-3}

When $[ClO_2]$ is increased four times with $[F_2]$ remaining the same, the rate is increased to four times its initial value.

$$\frac{\text{(Rate 2 / Rate 1)}}{=} = \frac{\{k (0.010)^x (0.040)^y\}}{\{k (0.010)^x (0.010)^y\}}$$

$$= (4.8 \times 10^{-3} / 1.2 \times 10^{-3}) = \{ (0.040)^y \} / \{ (0.010)^y \}$$

4 = 4^y Therefore, $y = 1$. And the rate law is:

The overall order of the reaction is **(1+1), i.e., 2.**

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



Experiment	$[\text{S}_2\text{O}_8^{2-}]$	$[\text{I}^-]$	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}

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}]^x [\text{I}^-]^y$$

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

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

Double $[\text{S}_2\text{O}_8^{2-}]$, rate doubles (experiment 2 & 3)

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



Experiment	$[\text{S}_2\text{O}_8^{2-}]$	$[\text{I}^-]$	Initial Rate (M/s)
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3	0.16	0.017	2.2×10^{-4}

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}]^x [\text{I}^-]^y$$

$$y = 1 \quad x = 1$$

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

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

Double $[\text{S}_2\text{O}_8^{2-}]$, rate doubles (experiment 2 & 3)

$$\frac{\text{Rate-3}}{\text{Rate-2}} = \frac{2.2 \times 10^{-4}}{1.1 \times 10^{-4}} = 2 \quad \frac{[\text{S}_2\text{O}_8^{2-}]}{[\text{S}_2\text{O}_8^{2-}]} = \frac{0.16}{0.08} = 2 \quad x=1$$

$$\text{rate} = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

$$k = \frac{\text{rate}}{[\text{S}_2\text{O}_8^{2-}][\text{I}^-]} = \frac{2.2 \times 10^{-4} \text{ M/s}}{(0.08 \text{ M})(0.034 \text{ M})} = 0.08 \text{ M}^{-1} \text{s}^{-1}$$

The Rate Law

Def: 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**.



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

reaction is **xth order** in A reaction is **yth order** in B

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

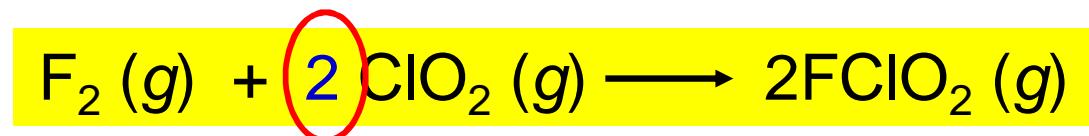
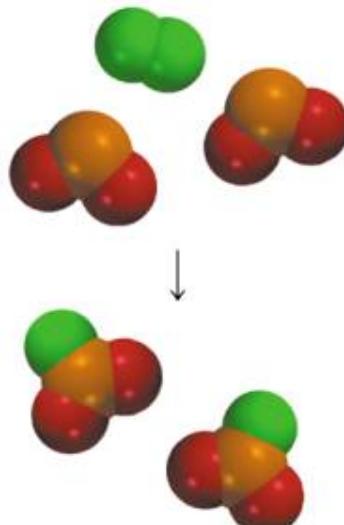
K is the reaction constant



$$\text{Rate}_{21} = k [\text{NO}_2]^n$$

Important points about the 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.
4. It must be determined by experiment



$$\text{rate} = k [F_2][\text{ClO}_2]^1$$

Rate Law

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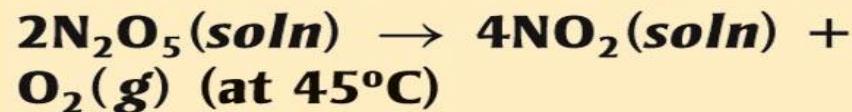
- Rate law will involve **only the reactants concentrations** because the reverse reaction is unimportant

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

Determining the Form of the Rate Law

TABLE 12.3 Concentration/Time Data for the Reaction



[N ₂ O 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



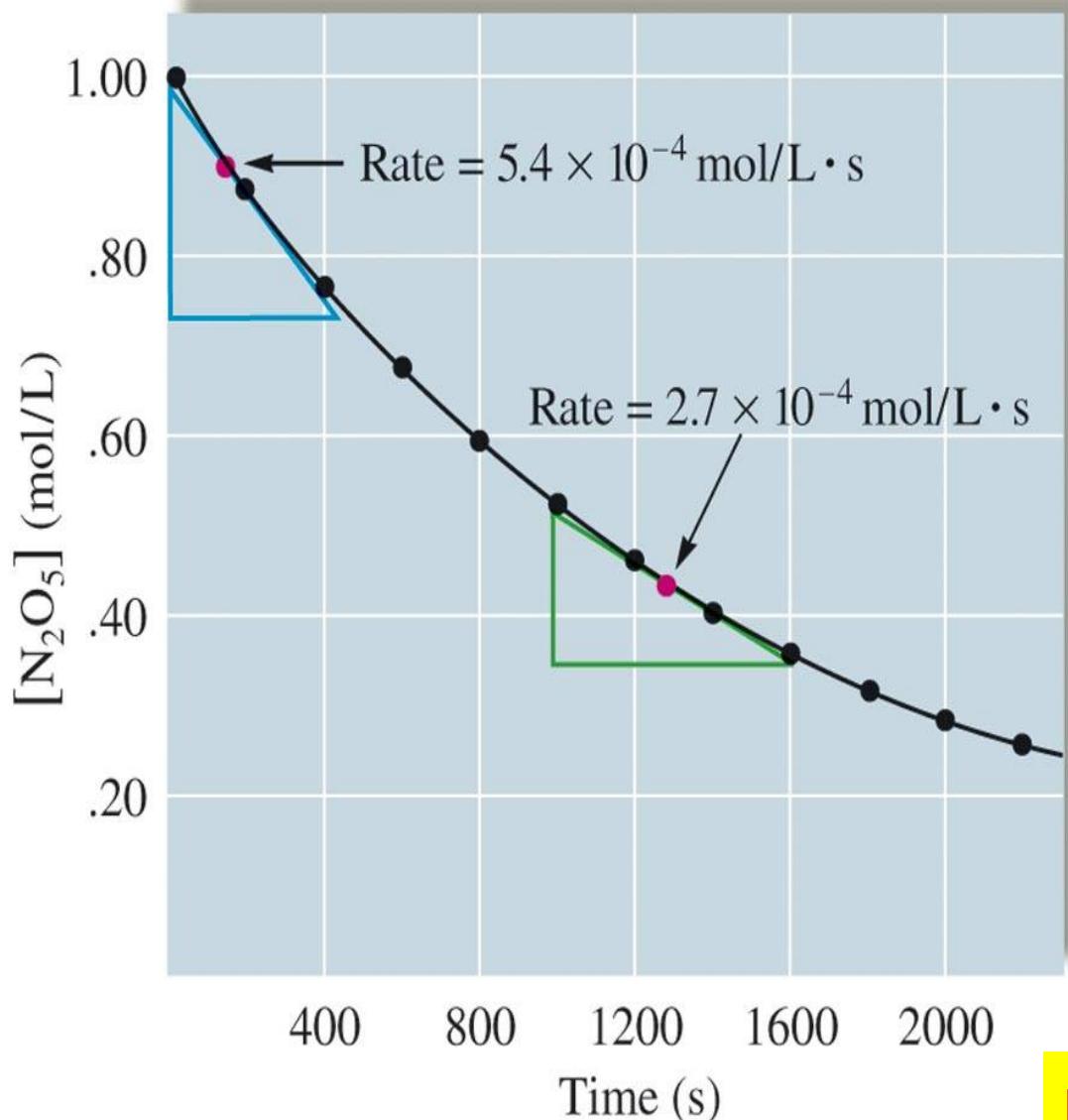
Method of **Initial Rates**

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Initial Rate: the instantaneous rate

determined 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.



$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

[N ₂ O ₅]	Rate (mol/L.s)
0.09 M	5.4 x 10 ⁻⁴
0.045 M	2.7 x 10 ⁻⁴

The rate of this reaction depends on the concentration of N₂O₅ to the first power

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]$$

Fig. 12.3 A Plot of the Concentration of N₂O₅ as a Function of Time for the Reaction



TABLE 12.4 Initial Rates from Three Experiments for the Reaction
 $\text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$

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

$$\text{rate} = k [\text{NH}_4^+]^n [\text{NO}_2^-]^m$$





$$\text{rate} = k [\text{NH}_4^+]^n [\text{NO}_2^-]^m$$

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

$$\text{Rate 2} = 2.70 \times 10^{-7} \text{ mol/L.s} = k (0.100 \text{ mol/})^n (0.010 \text{ mol/L})^m$$

$$(\text{Rate 2} / \text{Rate 1}) = 2.0 = (2.0)^m \quad m = 1$$

$$(\text{Rate 3} / \text{Rate 2}) = 2.0 = (2.0)^n \quad n = 1$$

$$\text{Rate} = k [\text{NH}_4^+] [\text{NO}_2^-]$$

The overall reaction order =

$$n+m = 2$$

$$\text{Rate} = k [\text{NH}_4^+] [\text{NO}_2^-]$$

TABLE 12.4 Initial Rates from Three Experiments for the Reaction
 $\text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_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}

$$1.35 \times 10^{-7} \text{ mol/L.s} = k (0.100 \text{ mol/}) (0.005 \text{ mol/L})$$

$$\text{Rate constant} = k = 2.7 \times 10^{-4} \text{ L/mol.s}$$

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



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
 $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$

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}

TABLE 12.5 The Results from Four Experiments to Study the Reaction
 $\text{BrO}_3^- (\text{aq}) + 5\text{Br}^- (\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial ³⁰ 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}

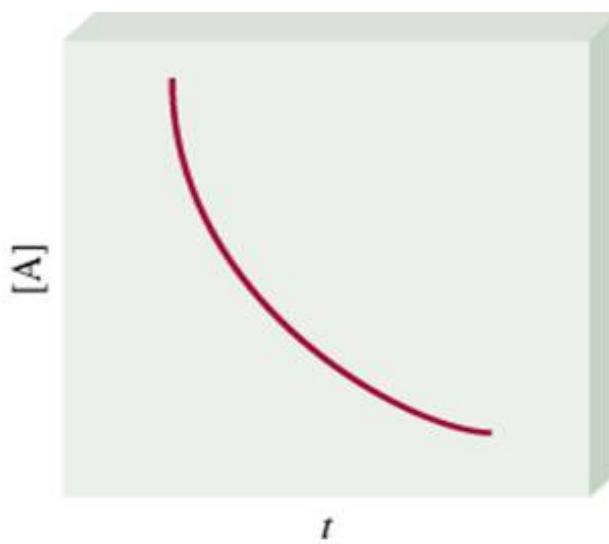
$$= k [\text{BrO}_3^-]^n [\text{Br}^-]^m [\text{H}^+]^p$$

Do exercise 12.25 to 12.28

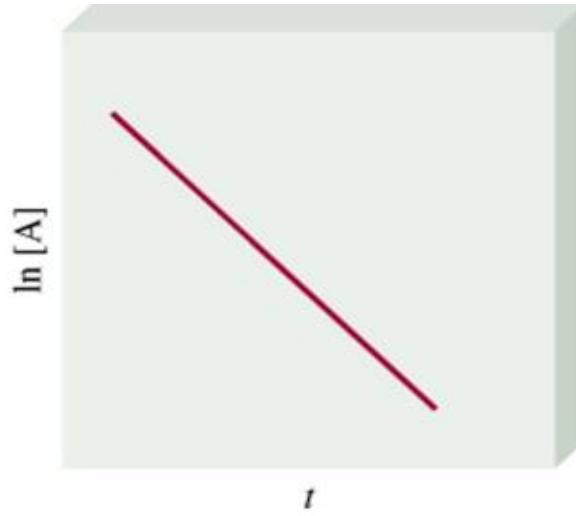
Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

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

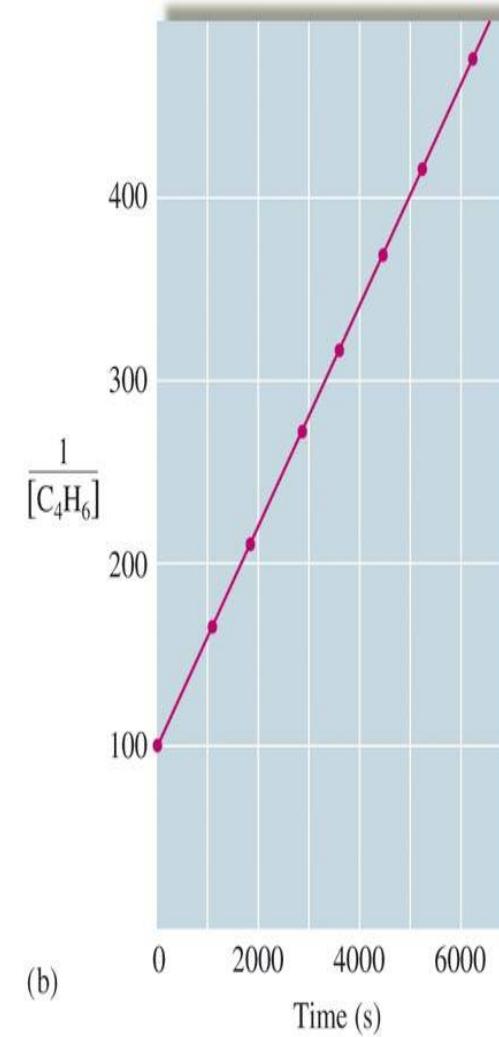
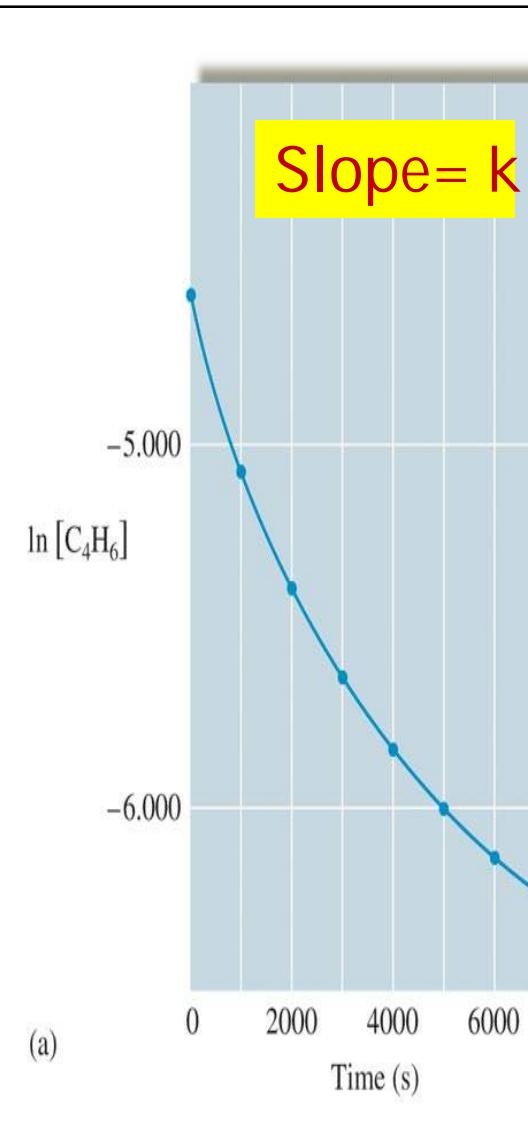
Slope = $-k$



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



Slope = k



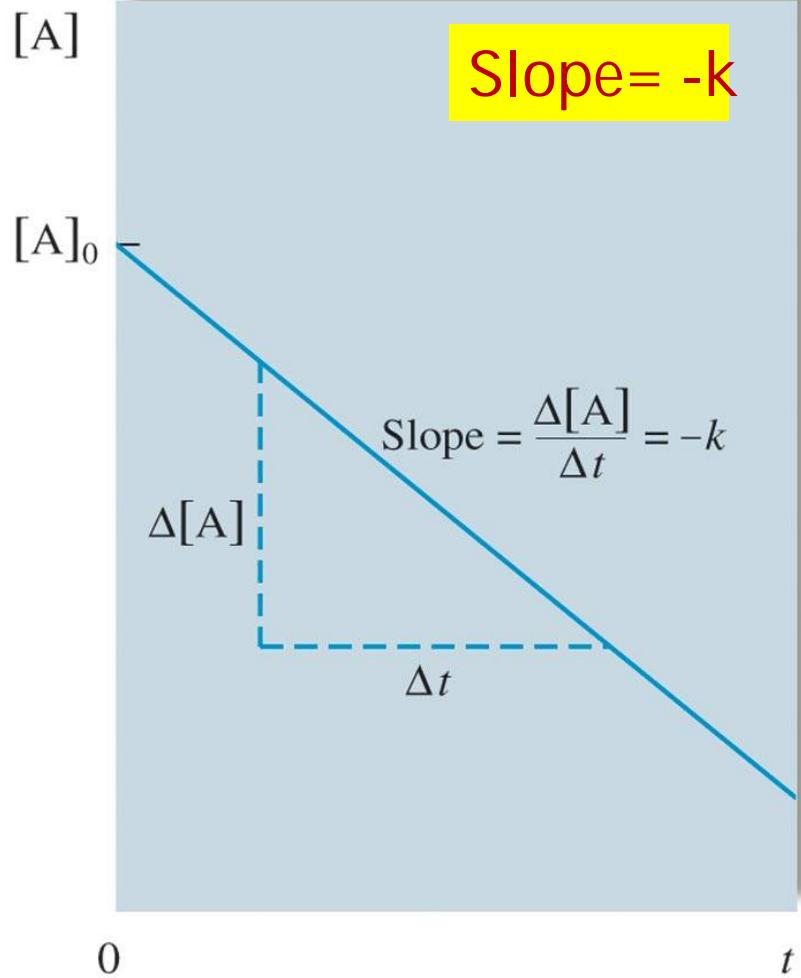


Figure 12.7 A Plot of $[A]$ versus t for a Zero-Order Reaction

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

$$2\text{N}_2\text{O}(g) \longrightarrow 2\text{N}_2(g) + \text{O}_2(g)$$

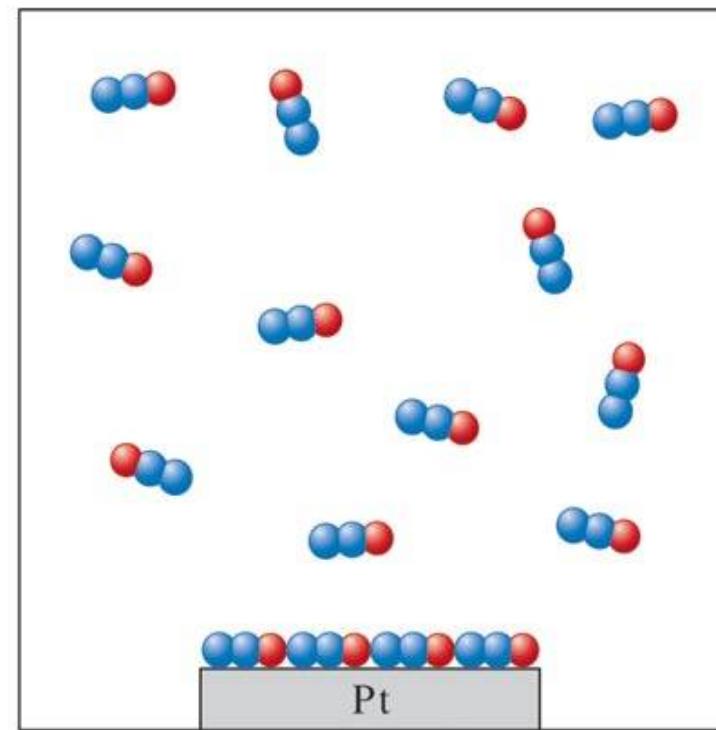
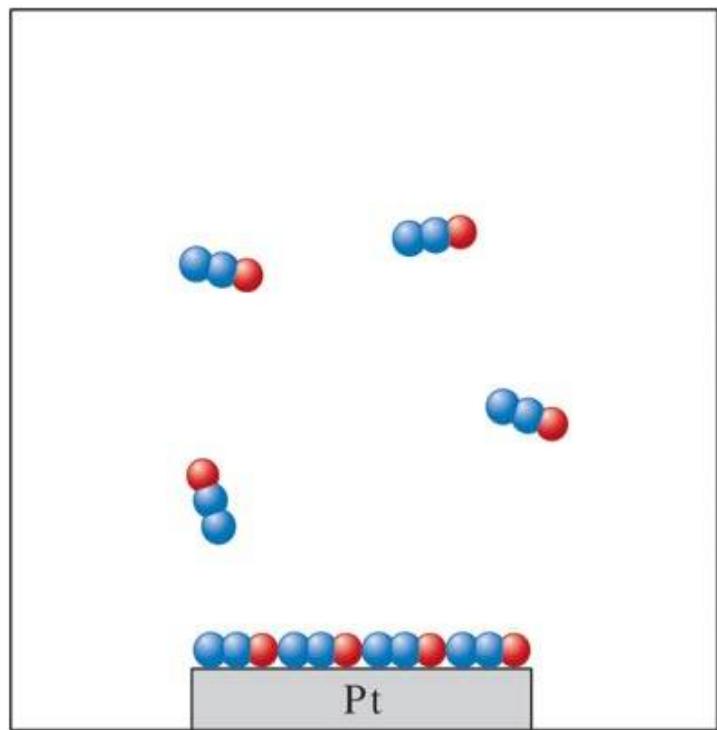
For example, the decomposition reaction occurs **on a hot platinum surface**. When the platinum surface is completely covered with N_2O molecules, **an increase in the concentration of N_2O has no effect on the rate**, since **only those N_2O molecules on the surface can react**. Under these conditions, **the rate is a constant**

Figure 12.8 The Decomposition Reaction

$$2\text{N}_2\text{O}(g) \longrightarrow 2\text{N}_2 + \text{O}_2(g)$$

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takes Place on a Platinum Surface



	Order		
Rate Law:	Zero	First	Second
Integrated Rate Law:	$\text{Rate} = k$	$\text{Rate} = k[\text{A}]$	$\text{Rate} = k[\text{A}]^2$
	$[\text{A}] = -kt + [\text{A}]_0$	$\ln[\text{A}] = -kt + \ln[\text{A}]_0$	$\frac{1}{[\text{A}]} = kt - \frac{1}{[\text{A}]_0}$
Plot Needed to Give a Straight Line:	$[\text{A}]$ versus t mol/L .s.	$\ln[\text{A}]$ versus t	L/mol.s $\frac{1}{[\text{A}]}$ versus t
Half-Life:	$\text{Slope} = -k$ $t_{1/2} = \frac{[\text{A}]_0}{2k}$	$\text{Slope} = -k$ $t_{1/2} = \frac{0.693}{k}$	Units of k (s⁻¹) $\text{Slope} = k$ $t_{1/2} = \frac{1}{k[\text{A}]_0}$

Q.1. What is the half-life of N_2O if it decomposes with a rate constant of $5.7 \times 10^{-4} \text{ s}^{-1}$?

Q.2. Butadiene reacts to form its dimer according to the equation:



the plot of $1/[\text{C}_4\text{H}_6]$ versus time was a straight line and the
 $k = \text{slope} = 6.14 \times 10^{-2} \text{ L/mol.s}$

What is the half-life for the reaction of this experiment?

Q.3 The decomposition of ethanol ($\text{C}_2\text{H}_5\text{OH}$) on an alumina (Al_2O_3)



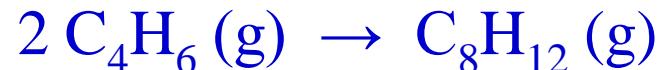
Surface was studied at 600 K. Concentration versus time data were collected for this reaction, **and a plot of $[\text{A}]$ versus time resulted in a straight line with a slope of $-4.00 \times 10^{-5} \text{ mol/L.s}$**

- a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- b. If the initial concentration of $\text{C}_2\text{H}_5\text{OH}$ was $1.25 \times 10^{-2} \text{ M}$, calculate the half-life for this reaction.

Q.1. What is the half-life of N_2O if it decomposes with a rate constant of $5.7 \times 10^{-4} \text{ s}^{-1}$?

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

Q.2. Butadiene reacts to form its dimer according to the equation:

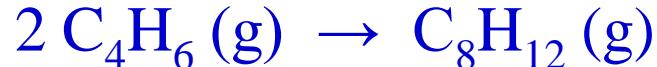


the plot of $1/[\text{C}_4\text{H}_6]$ versus time was a straight line and the

$$k = \text{slope} = 6.14 \times 10^{-2} \text{ L/mol.s}$$

What is the half-life for the reaction of this experiment?

Q.2. Butadiene reacts to form its dimer according to the equation:



the plot of $1/[\text{C}_4\text{H}_6]$ versus time was a straight line and the
 $k = \text{slope} = 6.14 \times 10^{-2} \text{ L/mol.s}$

What is the half-life for the reaction of this experiment?

Solution:

The expression for the half-life of a second-order reaction is

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

In this case $k = 6.14 \times 10^{-2} \text{ L/mol.s}$ (from part b) and
 $[A]_0 = [\text{C}_4\text{H}_6]_0 = 0.01000 \text{ M}$ (the concentration at $t = 0$). Thus

$$t_{1/2} = \frac{1}{(6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s})(1.000 \times 10^{-2} \text{ mol/L})} = 1.63 \times 10^3 \text{ s}$$

The initial concentration of C_4H_6 is halved in 1630 s.

Q.3 The decomposition of ethanol (C_2H_5OH) on an alumina (Al_2O_3)



Surface was studied at 600 K. Concentration versus time data were collected for this reaction, **and a plot of [A] versus time resulted in a straight line with a slope of $-4.00 \times 10^{-5} \text{ mol/L s}$.**

- Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- If the initial concentration of C_2H_5OH was $1.25 \times 10^{-2} M$, calculate the half-life for this reaction.

SOLUTION:

This is a **zero order reaction** as a plot of [A] versus time resulted in a straight line. And $k = -(\text{slope}) = -(-4.00 \times 10^{-5}) \text{ mol/L s}$.

$$k = 4.00 \times 10^{-5} \text{ mol/L s}$$

The rate law is given by
integrated rate law as

$$\begin{aligned} \text{rate} &= k \\ [A] &= [A]_0 - kt \end{aligned}$$

Q.3 The decomposition of ethanol (C_2H_5OH) on an alumina (Al_2O_3)



Surface was studied at 600 K. Concentration versus time data were collected for this reaction, **and a plot of $[A]$ versus time resulted in a straight line with a slope of $-4.00 \times 10^{-5} \text{ mol/L s}$.**

- Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- If the initial concentration of C_2H_5OH was $1.25 \times 10^{-2} M$, calculate the half-life for this reaction.**

. Solution

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

Given $k = 3.60 \times 10^{-2} \text{ M}^{-1} \text{ s}$ and $[A]_0 = 2.80 \times 10^{-3} M$,

So

$$\begin{aligned} t_{1/2} &= 1 / 3.60 \times 10^{-2} \text{ M}^{-1} \text{ s} \times 2.80 \times 10^{-3} M, \\ &= 1 / 10.08 \times 10^{-5} = 0.0992 \times 10^5 = 9.92 \times 10^3 \text{ s.} \end{aligned}$$

Q.4. A certain reaction has the following general form:



At a particular temperature and $[A]_0=2.80 \times 10^{-3} M$, concentration versus time data were collected for this reaction, and **a plot of $1/[A]$ versus time resulted in a straight line** with a slope value of $+3.60 \times 10^{-2} \text{ L/mol.s}$.

Calculate the half-life for this reaction.

Solution:

Calculate the half-life for this reaction.

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

Given $k= 3.60 \times 10^{-2} \text{ M}^{-1} \cdot \text{s}$ and $[A]_0=2.80 \times 10^{-3} M$,

So

$$t_{1/2} = 1 / 3.60 \times 10^{-2} \text{ M}^{-1} \cdot \text{s} \times 2.80 \times 10^{-3} M,$$

$$= 1 / 10.08 \times 10^{-5} = 0.0992 \times 10^5 = \mathbf{9.92 \times 10^3 \text{ s.}}$$