

CHEMICAL KINETICS**Chemical Kinetics:**

- I. The study of the Rates of Chemical Reactions:
 - how fast do chemical reactions proceed to form products
- II. The study of Reaction Mechanisms:
 - the steps involved in the change from reactants to products.

I. Rates of Reactions

- Factors affecting Reaction Rates:
 1. Concentration of Reactants: Rate \propto Concentration of Reactants
 2. Presence of a Catalyst: A catalyst is a substance that increases the Reaction Rate without being consumed
 3. Temperature: Rate \propto Temperature
 4. Surface Area of Reactants: Rate \propto Surface Area of Reactants

Definition of Reaction Rate

Reaction Rate:

- increase in the molar concentration of a product per unit time

OR

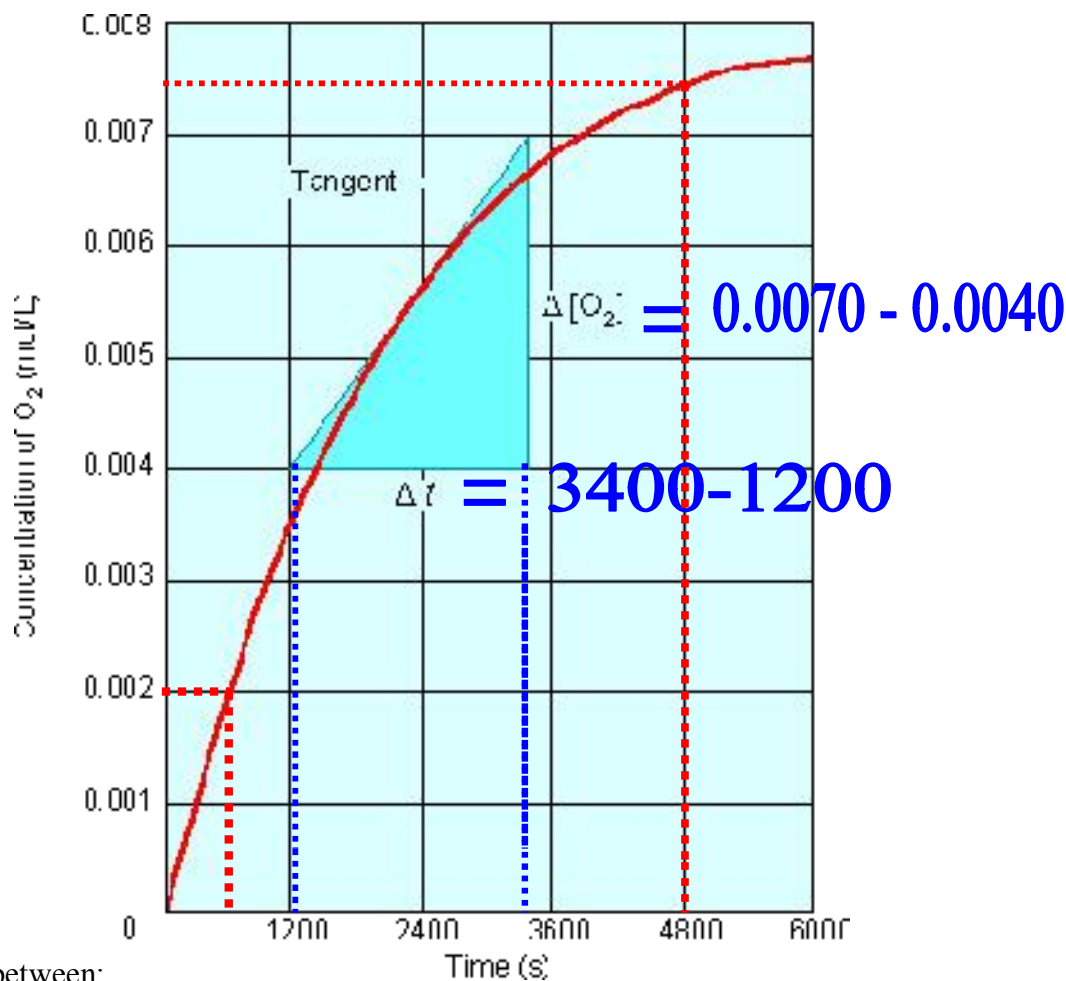
- decrease in the molar concentration of reactant per unit time

Example: $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

$$\text{Rate of formation of O}_2 = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\text{increase in the molar conc. of O}_2}{\text{time interval}}$$

- The expression above is referred to as: Average Rate over the time interval Δt

REACTION RATES



Distinguish between:

Average Rate

- Is measured over a certain period of time interval (ΔT)
- For example:

$$\text{Avg. Rate} = \frac{(0.0075 - 0.0020) \text{ mol}}{(4800 - 600) \text{ s}}$$

$$\text{Avg. Rate} = 1.3 \times 10^{-6} \text{ mol/s}$$

Instantaneous Rate

- Is the rate at a particular instant of time (during a very short time interval)
- The slope of the tangent at a particular time
- For example:

$$\text{Avg. Rate} = \frac{(0.0070 - 0.0040) \text{ mol}}{(3400 - 1200) \text{ s}}$$

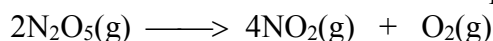
$$\text{Avg. Rate} = 1.3 \times 10^{-6} \text{ mol/s}$$

REACTION RATES
NOTE:

1. The Reaction Rate decreases as the reaction proceeds.

Reason: the concentration of reactants decreases

2. Any substance in the reaction can be used to express the Rxn. Rate



$$\text{Rate of formation of O}_2 = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\text{increase in the molar conc. of O}_2}{\text{time interval}}$$

$$\text{Rate of formation of NO}_2 = \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\text{increase in the molar conc. of NO}_2}{\text{time interval}}$$

$$\text{Rate of decomposition of N}_2\text{O}_5 = \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{\text{decrease in the molar conc. of N}_2\text{O}_5}{\text{time interval}}$$

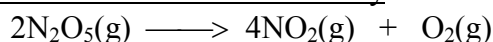
3. Reaction Rate is always positive

$$\text{(a) Rate of formation of a product} = \frac{\Delta[\text{increase in concentration of product}]}{\Delta t}$$

$$\text{(b) Rate of decomposition of a reactant} = - \frac{\Delta[\text{decrease in concentration of reactant}]}{\Delta t}$$

Since: $\Delta[\text{decrease in concentration of reactant}]$ has a negative value the Reaction Rate will be positive

4. Reaction Rate in terms of stoichiometry



Rate of decomposition of $\text{N}_2\text{O}_5 = 2 \times$ Rate of formation of O_2

OR

$$\frac{\text{Rate of decomposition of N}_2\text{O}_5}{2} = \text{Rate of formation of O}_2$$

Reason: 2 moles of N_2O_5 must decompose for the formation of 1 mole of O_2

RATE DETERMINATION

- Rate determination is done by monitoring the change in concentration of reactant or product over time.

Method:

- Withdraw samples from the reaction vessel at various times and analyze some of their physical or chemical properties that give information on the concentrations present.

Properties appropriate and easy to monitor

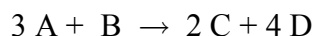
1. Color
(if product or reactant absorbs light)
3. Oxidation State
(using an electrochemical cell)
5. Volume, at constant p and T
(useful, if:
 - gaseous reactants and/or products are present, and
 - number of moles of reactants \neq number of moles of products)
6. Pressure, at constant V and T
(useful, if:
 - gaseous reactants and/or products are present, and
 - number of moles of reactants \neq number of moles of products)
7. Density
(useful if : $d(\text{reactants}) \neq d(\text{products})$)

Properties not appropriate to monitor

2. Flammability
(difficult to measure quantitatively)
4. Mass
(mass is conserved in a chemical reaction)

Examples:

1. For the hypothetical reaction shown below, write a rate expression based on each reactant and product:

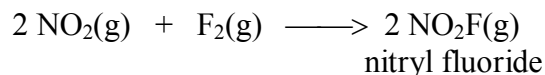


Rate based on A =

Rate based on B =

Rate based on C =

Rate based on D =

RATE LAW
Dependence of Reaction Rate on Concentration


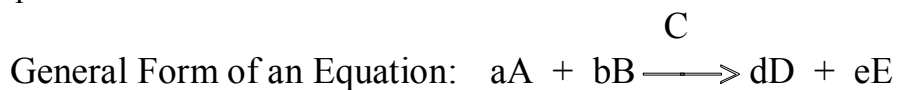
Experimental observation:

$$\text{Rate of Reaction} = k [\text{NO}_2] [\text{F}_2]$$

Meaning: - Doubling $[\text{NO}_2]$ \longrightarrow Doubles the Reaction Rate
 - Doubling $[\text{F}_2]$ \longrightarrow Doubles the Reaction Rate

RATE LAW :

- Equation that relates the Rate of Reaction to the Concentration of Reactants and Catalyst raised to various powers.



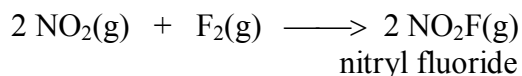
$$\text{General form for Rate Law: } \text{Rate} = k [\text{A}]^m [\text{B}]^n [\text{C}]^p$$

- | | |
|--------------------|--|
| m, n, and p | <ul style="list-style-type: none"> ➤ are frequently, but not always integers ➤ must be determined experimentally ➤ are <u>not</u> the coefficients in the balanced chemical equation |
| k | <ul style="list-style-type: none"> ➤ Rate Constant ➤ its units depend upon the form of Rate Law ➤ depends on temperature |

REACTION ORDER

I. Reaction Order with respect to a given reactant species:

- Reaction Order is the exponent of the concentration of that species in the Rate Law, as determined experimentally



Experimental observation:

- Doubling $[\text{NO}_2]$ \longrightarrow Doubles the Reaction Rate
- Doubling $[\text{F}_2]$ \longrightarrow Doubles the Reaction Rate

$$\text{Rate of Reaction} = k [\text{NO}_2]^m [\text{F}_2]^n$$

Reaction is:

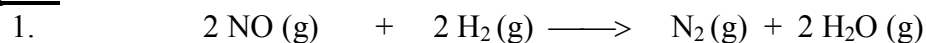
- First order with respect to NO_2 ($m=1$)
- First order with respect to F_2 ($n=1$)

II. Overall Reaction Order

- The overall reaction order is the sum of the orders of the reactant species

$$\text{Overall Reaction Order} = m + n = 1 + 1 = 2$$

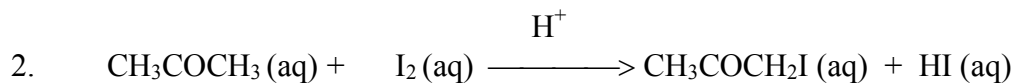
Reaction is of the Second Order Overall.

Examples:

Experimentally determined Rate Law = $k[\text{NO}]^2[\text{H}_2]$

Reaction is:

- 2nd order in NO
- 1st order in H₂
- **3rd order overall**



Experimentally determined Rate Law = $k[\text{CH}_3\text{COCH}_3][\text{H}^+]$

Reaction is:

- 1st order in CH₃COCH₃
- 0 order in I₂ (does not depend on the concentration of I₂ as long as some I₂ is present)
- 1st order in the catalyst (H⁺)
- **2nd order overall**

NOTE: Reaction Orders:

- are frequently whole numbers (1 or 2)
- may be fractional
- may be 0
- may be negative

Sample problem

Consider the reaction: $\text{Q} + \text{R} \longrightarrow \text{S} + \text{T}$

and the Rate Law: $\text{Rate} = k[\text{Q}]^0[\text{R}]^2$

You run the reaction three times, each time starting with $[\text{R}] = 2.0 \text{ M}$

For each run you change the starting concentration of Q:

- Run 1: $[\text{Q}] = 0.0 \text{ M}$
- Run 2: $[\text{Q}] = 1.0 \text{ M}$
- Run 3: $[\text{Q}] = 2.0 \text{ M}$

Rank the rate of the three reactions using each of these concentrations.

R	Q	Relative Rate
2.0 M	0.0 M	Slowest
2.0 M	1.0 M	Same Rate
2.0 M	2.0 M	

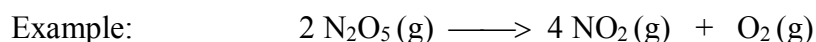
As long as there is some Q present, the Reaction Rate depends only on [R]

- The Overall Reaction Order = 2

EXPERIMENTAL DETERMINATION OF RATE LAW

- First: The Order of the reaction with respect to each reactant and catalyst must be found.

Initial-Rate Method: - a series of experiments are done in which the initial concentrations of reactants are varied (usually doubled).
 - will yield the respective orders of reaction.



	Initial N_2O_5 Conc. (M)	Initial Rate of Disappearance of N_2O_5 (M/s)
Experiment 1	1.0×10^{-2}	4.8×10^{-6}
Experiment 2	2.0×10^{-2}	9.6×10^{-6}

Rate = $k [\text{N}_2\text{O}_5]^m$ $m = ?$ (must be determined from experimental data)

$$\frac{\text{Rate Exp. 2}}{\text{Rate Exp. 1}} = \frac{k (2)^m}{k(1)^m} = \frac{9.6 \times 10^{-6}}{4.8 \times 10^{-6}} = 2$$

Experimental: ➤ Doubling $[\text{N}_2\text{O}_5]$ doubled the rate of reaction

It follows: ➤ $m = 1$ ($2^1 = 2$)

The Reaction is: ➤ First order in N_2O_5
 ➤ First order overall

Rate = $k [\text{N}_2\text{O}_5]^1$

Rate = $k [\text{N}_2\text{O}_5]$

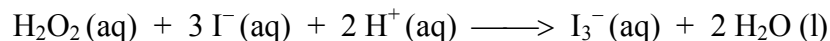
**Effect of Doubling the Initial Concentration
of Reactant on Reaction Rate**

Change in Reaction Rate	Rate is multiplied by	Reaction Order
Rate is halved	$\frac{1}{2} = 2^{-1}$	-1
Rate is the same	$1 = 2^0$	0
Rate is doubled	$2 = 2^1$	1
Rate is quadrupled	$4 = 2^2$	2

Examples:

1. Use the rate data below to

- A) determine the reaction orders with respect to $[\text{H}_2\text{O}_2]$, $[\text{I}^-]$ and $[\text{H}^+]$ and
 B) find the rate constant k for the reaction shown below:



	Initial Concentrations (M)			Initial Rate (M/s)
	$[\text{H}_2\text{O}_2]$	$[\text{I}^-]$	$[\text{H}^+]$	
Experiment 1	0.010	0.010	0.00050	1.15×10^{-6}
Experiment 2	0.020	0.010	0.00050	2.3×10^{-6}
Experiment 3	0.010	0.020	0.00050	2.30×10^{-6}
Experiment 4	0.010	0.010	0.00100	1.15×10^{-6}

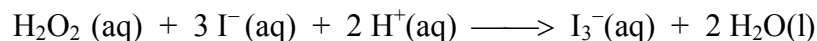
Solution

A) Compare two rate experiments in which all concentrations of reactants but one are held constant:

$[\text{H}_2\text{O}_2]$: Compare **Experiment 1** and **Experiment 2**
When $[\text{H}_2\text{O}_2]$ is doubled, the Rate is doubled
 It follows: $2^m = 2$ $m = 1$ **1st order in $[\text{H}_2\text{O}_2]$**

$[\text{I}^-]$: Compare **Experiment 1** and **Experiment 3**
When $[\text{I}^-]$ is doubled, the Rate is doubled
 It follows: $2^n = 2$ $n = 1$ **1st order in $[\text{I}^-]$**

$[\text{H}^+]$: Compare Experiment 1 and Experiment 4
When $[\text{H}^+]$ is doubled, the Rate does not change
 It follows: $2^p = 1$ $p = 0$ **0 order in $[\text{H}^+]$**



Summary: 1st order in $[\text{H}_2\text{O}_2]$
 1st order in $[\text{I}^-]$
 0 order in $[\text{H}^+]$

$$\text{RATE} = k [\text{H}_2\text{O}_2]^1 [\text{I}^-]^1 [\text{H}^+]^0$$

commonly written : **RATE = k $[\text{H}_2\text{O}_2]$ $[\text{I}^-]$**

NOTE: Reaction Orders are **not** related to the coefficients of the overall equation

B) Find the Rate Constant, k

From Experiment 1: (any other experiment could be used)

$$[\text{H}_2\text{O}_2] = 0.010 \text{ M}$$

$$[\text{I}^-] = 0.010 \text{ M}$$

$$\text{Rate} = 1.15 \times 10^{-6} \text{ M/s}$$

$$k = ?$$

$$\text{RATE} = k [\text{H}_2\text{O}_2] [\text{I}^-] \quad k = \frac{\text{Rate}}{[\text{H}_2\text{O}_2][\text{I}^-]} = \frac{1.15 \times 10^{-6} \text{ M/s}}{(0.010 \text{ M})(0.010 \text{ M})} = 1.2 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$$

2. Use the rate data below to

A) determine the rate law for the reaction $\text{A} + \text{B} \rightarrow \text{C}$, and

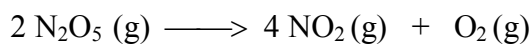
B) calculate the rate constant k, and

C) calculate the rate of reaction for experiment 4

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}
4	0.050	0.100	????

INTEGRATED RATE LAW (1ST ORDER REACTION)
Concentration – Time Equations for First Order Reactions

- are derived from experimental data
- predict concentrations at all times



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

Using calculus:

$$\ln \frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = -kt$$

OR

$$\log \frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = \frac{-kt}{2.303}$$

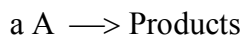
more commonly used!

$[\text{N}_2\text{O}_5]_t$: concentration at time t
 $[\text{N}_2\text{O}_5]_0$: concentration at time 0

These equations can be used to calculate:

- concentration of $[\text{N}_2\text{O}_5]$ at any time,
- the time it takes for $[\text{N}_2\text{O}_5]$ to decrease to a particular value

In General:



Assuming First Order Rate Law:

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

Differential Rate Law:

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

Integrated Rate Law:

$$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$$

OR

$$\log \frac{[\text{A}]_t}{[\text{A}]_0} = \frac{-kt}{2.303}$$

Example 1:

Sulfuryl chloride, SO_2Cl_2 , decomposes when heated:



- In an experiment, the initial concentration of SO_2Cl_2 was 0.0248 M
- The Rate Constant is $2.2 \times 10^{-5} \text{ s}^{-1}$. The Reaction is first order.
- What is the concentration of SO_2Cl_2 after 2.5 hours?

$$[\text{A}]_0 = 0.0248 \text{ M} \qquad k = 2.2 \times 10^{-5} \text{ s}^{-1} \qquad t = 2.5 \text{ h (9000 s)}$$

$$\log \frac{[\text{A}]_t}{[\text{A}]_0} = \frac{-kt}{2.303} \qquad \log \frac{[\text{SO}_2\text{Cl}_2]_t}{[\text{SO}_2\text{Cl}_2]_0} = \frac{-kt}{2.303}$$

$$\log \frac{[\text{SO}_2\text{Cl}_2]_t}{[\text{SO}_2\text{Cl}_2]_0} = \frac{-(2.2 \times 10^{-5} \text{ s}^{-1})(9000 \text{ s})}{2.303} = -0.086$$

Take antilogarithms of both sides;

$$\frac{[\text{SO}_2\text{Cl}_2]_t}{[\text{SO}_2\text{Cl}_2]_0} = 0.82 \qquad [\text{SO}_2\text{Cl}_2]_t = (0.82) \times [\text{SO}_2\text{Cl}_2]_0$$

$$[\text{SO}_2\text{Cl}_2]_t = (0.82)(0.0248 \text{ M}) = \mathbf{2.0 \times 10^{-2} \text{ M}}$$

Significant Figures, Logs and Antilogs

Find log of (3.6×10^{-12})

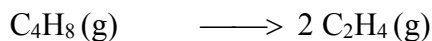
$$\log(3.6 \times 10^{-12}) = -11.44$$

Given: -11.44, find antilog:

$$\text{Antilog} = 10^{-11.44} = 3.6 \times 10^{-12}$$

Example 2:

Cyclobutane, C₄H₈ decomposes, when heated to give ethylene:



- The reaction is first order.
- In an experiment, the initial concentration of C₄H₈ was 0.00150 M.
- After heating at 450°C for 455 seconds, this was reduced to 0.00119 M.
- What was the concentration of C₄H₈ after a total of 827 seconds?

$$[\text{C}_4\text{H}_8]_0 = 0.00150 \text{ M} \quad [\text{C}_4\text{H}_8]_{455} = 0.00119 \text{ M} \quad [\text{C}_4\text{H}_8]_{827} = ?$$

a) Calculate rate constant (k) for the reaction:

$$\log \frac{[\text{C}_4\text{H}_8]_{455}}{[\text{C}_4\text{H}_8]_0} = \log \frac{0.00119 \text{ M}}{0.00150 \text{ M}} = -\frac{k (455 \text{ s})}{2.303} = -197.57 \text{ k}$$

$$\log 0.7933 = -197.57 \text{ k}$$

$$-0.10054 = -197.57 \text{ k}$$

$$\text{k} = 5.089 \times 10^{-4} \text{ s}^{-1}$$

b) Calculate concentration of C₄H₈ at 827 s:

$$\log \frac{[\text{C}_4\text{H}_8]_{827}}{[\text{C}_4\text{H}_8]_0} = -\frac{k (t)}{2.303} = -\frac{(5.089 \times 10^{-4} \text{ s}^{-1})(827 \text{ s})}{2.303} = -0.1827$$

Taking the antilog of both sides:

$$\frac{[\text{C}_4\text{H}_8]_{827}}{[\text{C}_4\text{H}_8]_0} = 0.6566$$

Substituting [C₄H₈]₀

$$\frac{[\text{C}_4\text{H}_8]_{827}}{0.00150 \text{ M}} = 0.6566$$

$$[\text{C}_4\text{H}_8]_{827} = 9.85 \times 10^{-4} \text{ M}$$

HALF-LIFE ($t_{1/2}$) OF A FIRST ORDER REACTION

- Half-life is the time it takes for the reactant concentration to decrease to one-half of its initial value.

$$\log \frac{[A]_t}{[A]_0} = \frac{-k t}{2.303}$$

In one half-life ($t_{1/2}$): $[A]_t = \frac{1}{2} [A]_0 \implies \log \frac{\frac{1}{2} [A]_0}{[A]_0} = \frac{-k (t_{1/2})}{2.303}$

$$-0.301 = \frac{-k (t_{1/2})}{2.303} \implies t_{1/2} = \frac{0.301 \times 2.303}{k}$$

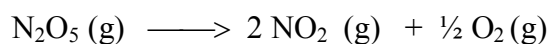
$$t_{1/2} = \frac{0.693}{k}$$

NOTES:

- Half-Life does not depend on the initial concentration, $[A]_0$
- The half-life is the same at any time during the reaction

Example:

Dinitrogen pentoxide, decomposes when heated in carbon tetrachloride solvent:



The rate law is first order in N_2O_5 with a rate constant of $6.2 \times 10^{-4} \text{ min}^{-1}$.

- (a) What is the half-life for this reaction?

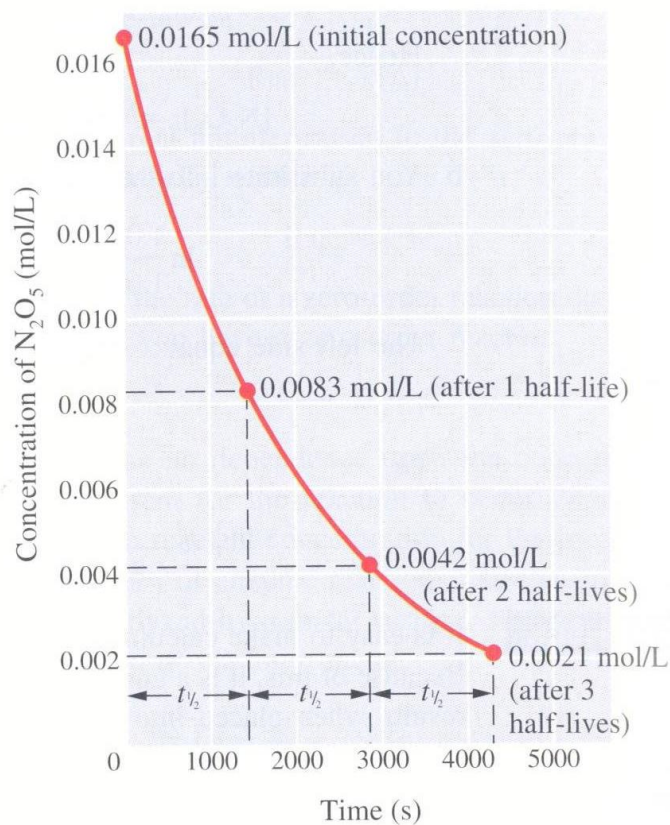
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.2 \times 10^{-4} \text{ min}^{-1}} = 1118 \text{ min} = 1.1 \times 10^3 \text{ min}$$

- (b) How long would it take for the concentration of N_2O_5 to decrease to 25 % of its initial value?

$$t_{25\% \text{ left}} = t_{1/4 \text{ left}} = 2 \times t_{1/2} = 2 (1.1 \times 10^3 \text{ min}) = 2.2 \times 10^3 \text{ min}$$

- (c) How long would it take for the concentration of N_2O_5 to decrease to 12.5 % of its initial value?

$$t_{12.5\% \text{ left}} = t_{1/8 \text{ left}} = 3 \times t_{1/2} = 3 (1.1 \times 10^3 \text{ min}) = 3.3 \times 10^3 \text{ min}$$



- In each half-life the concentration of the reactant is halved.
- First half-life: concentration changes from 0.016 M to 0.008 M (1440 s)
- Second half-life: concentration changes from 0.008 M to 0.004 M (2880 s)
- Third half-life: concentration changes from 0.004 M to 0.002 M (4320 s)
- **Half-life of first order reactions is independent of time**

Concentration (M)	Decrease in Concentration	Time Elapsed (s)	Number of Half-lives Elapsed
0.0120	0	0	0
0.0060	50%	1300	1
0.0030	25%	2600	2
0.0015	12.5%	3900	3
0.00075	6.25%	5200	4

In General:

Concentration	Time	Number of Half-lives
A_0	0	0
$\frac{1}{2} A_0 = 50\% A_0$	$t_{1/2}$	1
$\frac{1}{4} A_0 = 25\%$	$t_{1/4}$	2
$\frac{1}{8} A_0 = 12.5\%$	$t_{1/8}$	3
$\frac{1}{16} A_0 = 6.25\%$	$t_{1/16}$	4

GRAPHING FIRST ORDER REACTIONS

- The order of a reaction can be determined by graphing the experimental data.
- The experimental data are plotted by
 1. First assuming a first-order reaction,
 2. Second, assuming a second-order reaction,
 3. Third, assuming a third-order reaction, and so on.
- The graph which best fits the experimental data gives the order of a reaction.

- First order Rate Law:

$$\log \frac{[A]_t}{[A]_0} = \frac{-k t}{2.303}$$

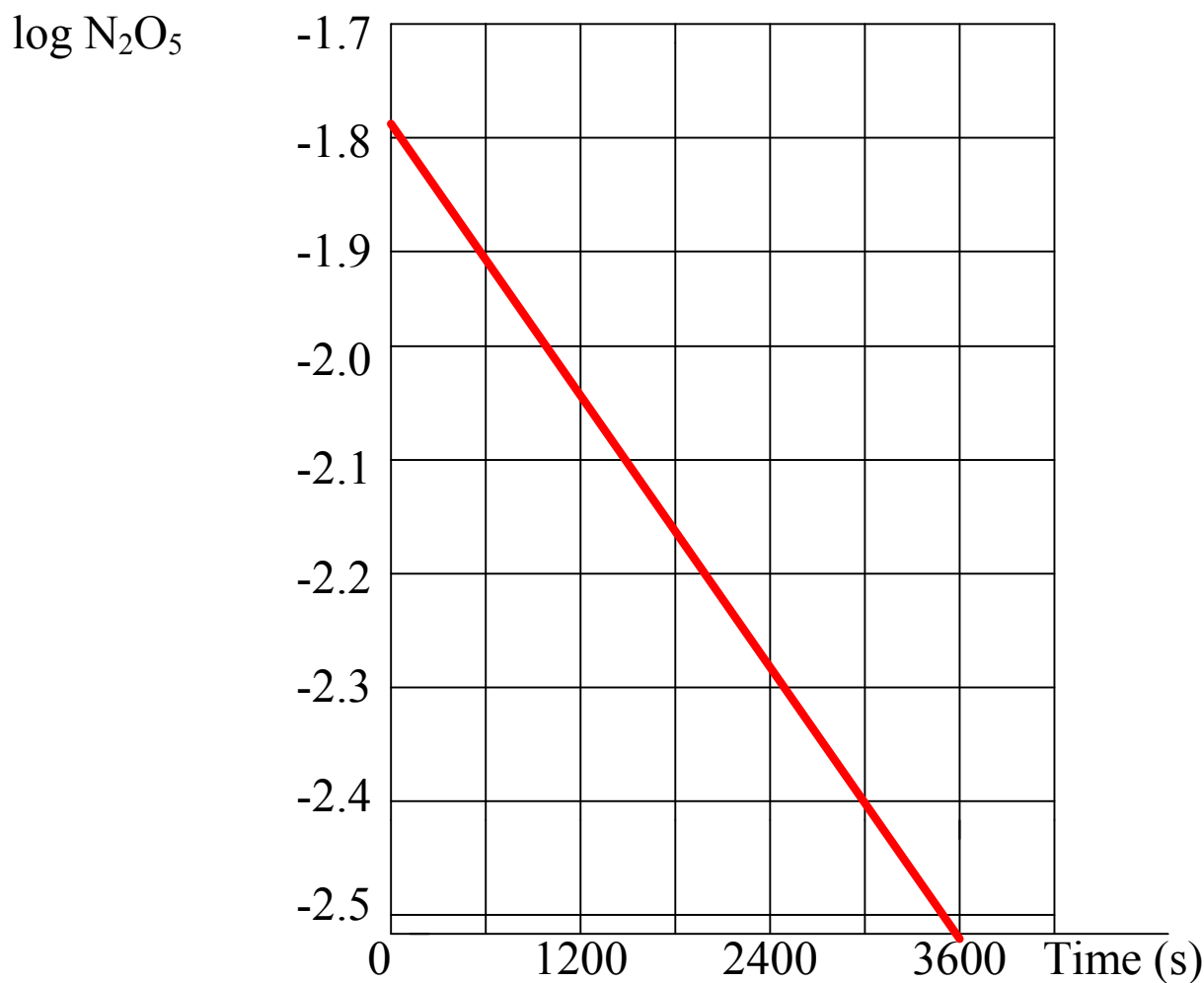
- This equation may be rewritten:

$$\log [A]_t = \left(\frac{-k t}{2.303} \right) + \log [A]_0 \quad (\text{This is the equation of a straight line})$$

$$\log [A]_t = \left(\frac{-k}{2.303} \right) t + \log [A]_0 \quad y = mx + b$$

- A plot of **log [A]** (y) versus **time** (x) should give a straight line for a first order reaction.

Time	[N ₂ O ₅]	log [N ₂ O ₅]
0	0.0165	-1.783
600	0.0124	-1.907
1200	0.0093	-2.032
1800	0.0071	-2.149
2400	0.0053	-2.276
3000	0.0039	-2.409
3600	0.0029	-2.538



- NOTE: The points lie on a straight line
- MEANING: The Rate Law is First Order

$$m = \text{slope of the straight line} = \frac{\Delta y}{\Delta x} = \frac{(-2.538) - (-1.783)}{(3600 - 0) \text{ s}} = \frac{-0.755}{3600 \text{ s}} = -2.10 \times 10^{-4} \text{ s}^{-1}$$

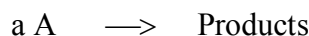
This can be used to calculate k, the Rate constant

Recall: $\log [A]_t = \left(\frac{-k t}{2.303}\right) + \log [A]_0$ $y = mx + b$

It follows:

$$m = \frac{-k}{2.303} \quad k = -2.303 (-2.10 \times 10^{-4} \text{ s}^{-1}) = 4.84 \times 10^{-4} \text{ s}^{-1}$$

INTEGRATED RATE LAW (2ND ORDER REACTION)
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Concentration – Time Equations for First Order Reactions

$$\text{Rate} = -\frac{\Delta [A]}{\Delta t} = k [A]^2$$

Differential Rate Law

By using calculus:

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

Integrated Rate Law

Example:

At 330 K:

$$k = 0.775 \text{ M}^{-1}\text{s}^{-1}$$

$$[A]_0 = 0.0030 \text{ M}$$

$$[A]_{645} = ?$$

$$\frac{1}{[A]_t} = (0.775 \text{ M}^{-1}\text{s}^{-1})(645 \text{ s}) + \frac{1}{0.0030 \text{ M}}$$

$$\frac{1}{[A]_t} = (499.9 \text{ M}^{-1}) + (333.3 \text{ M}^{-1}) = 8.3 \times 10^2 \text{ M}^{-1}$$

$$[A]_t = \mathbf{0.0012 \text{ M}}$$

HALF-LIFE ($t_{1/2}$) OF A SECOND ORDER REACTION

- Half-life is the time it takes for the reactant concentration to decrease to one-half of its initial value.

For a second order reaction: Rate = $k [A]^2$ and $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

In one half-life ($t_{1/2}$): $[A]_t = \frac{1}{2} [A]_0$ \Rightarrow $\frac{1}{0.5[A]_0} = kt + \frac{1}{[A]_0}$

$$kt_{1/2} = \frac{1}{0.5[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0} \quad \Rightarrow \quad \boxed{t_{1/2} = \frac{1}{k [A]_0}}$$

NOTES:

- Half-Life depends on the initial concentration, $[A]_0$
- Half-Life increases as reaction progresses

Example:

For a particular 2nd order reaction $k = 0.775 \text{ M}^{-1}\text{s}^{-1}$.

- a) How long does it take to the concentration to decrease from 0.0030 M to 0.0015?

For concentration to drop to half of its original value, $t = \text{half-life}$

$$t_{1/2} = \frac{1}{k [A]_0} = \frac{1}{(0.775 \text{ M}^{-1}\text{s}^{-1})(0.0030 \text{ M})} = 430 \text{ s}$$

- b) How long does it take for the concentration to be halved again?

$$t_{1/2} = \frac{1}{k [A]_0} = \frac{1}{(0.775 \text{ M}^{-1}\text{s}^{-1})(0.0015 \text{ M})} = 860 \text{ s} \quad \leftarrow \text{Twice as long}$$

GRAPHING SECOND ORDER REACTIONS

$$\begin{array}{c}
 \boxed{\frac{1}{[A]_t}} = \frac{k}{\uparrow} \frac{t}{\uparrow} + \boxed{\frac{1}{[A]_0}} \\
 \uparrow \text{y} = \text{m x} + \text{b} \\
 \text{slope} \quad \text{intercept}
 \end{array}$$

Meaning:

- A plot of $\frac{1}{[A]_t}$ (y) versus time (s) should give a straight line for a second order reaction

Strategy:

- Assume you want to find out if a particular reaction is of first or second order.
- You would need experimental data of concentrations at different times.
- Then you would plot 2 different graphs, assuming respectively 1st or 2nd order for the reaction, and using the respective rate laws.
- The graph that yields a straight line gives the correct reaction order.

Example:

Given the experimental data listed below, determine if the reaction is 1st or 2nd order, and determine the rate constant (k) for the reaction.

Time (s)	[NO ₂] ₀ (M)
0	1.00 x 10 ⁻²
60	0.683 x 10 ⁻²
120	0.518 x 10 ⁻²
180	0.418 x 10 ⁻²
240	0.350 x 10 ⁻²
300	0.301 x 10 ⁻²
360	0.264 x 10 ⁻²

Strategy:

- We must first see if the data fits the Rate Law for 1st Order Reactions. If it does, the reaction is of the 1st order
- If it does not, we must see if the data fits the Rate Law for 2nd Order. If it does, the reaction is of the 2nd order

First Order Rate Law:

$$\log [A]_t = \left(\frac{-k t}{2.303} \right) + \log [A]_0$$

Plot $\log [A]_t$ as a function of t

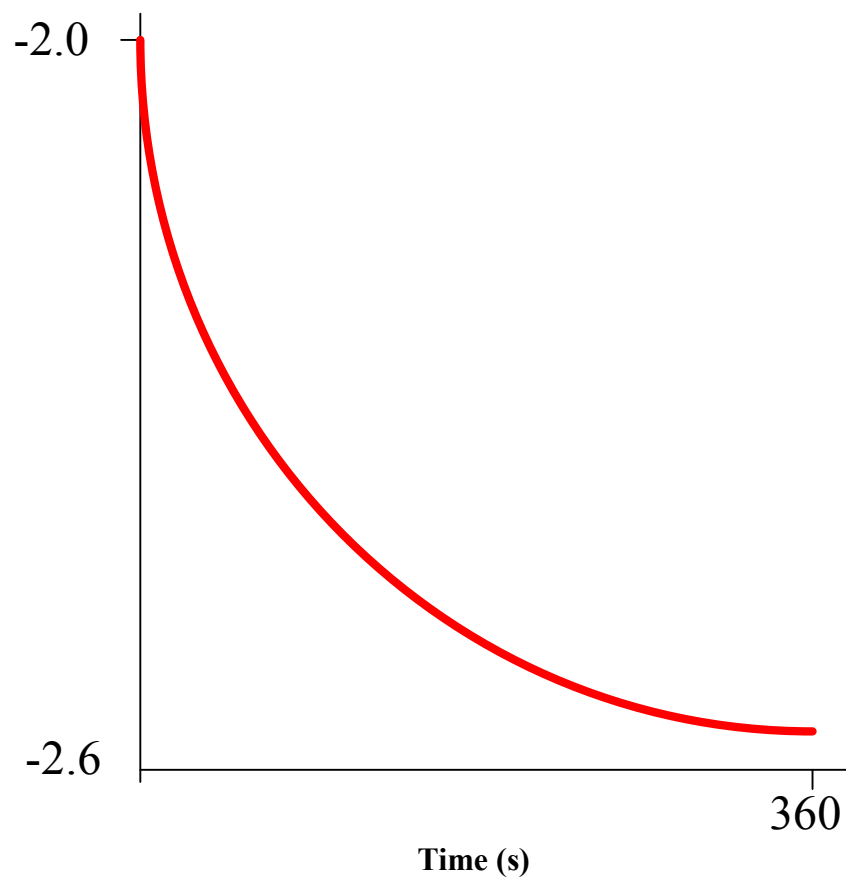
$$y = m x + b$$

Second order Rate Law

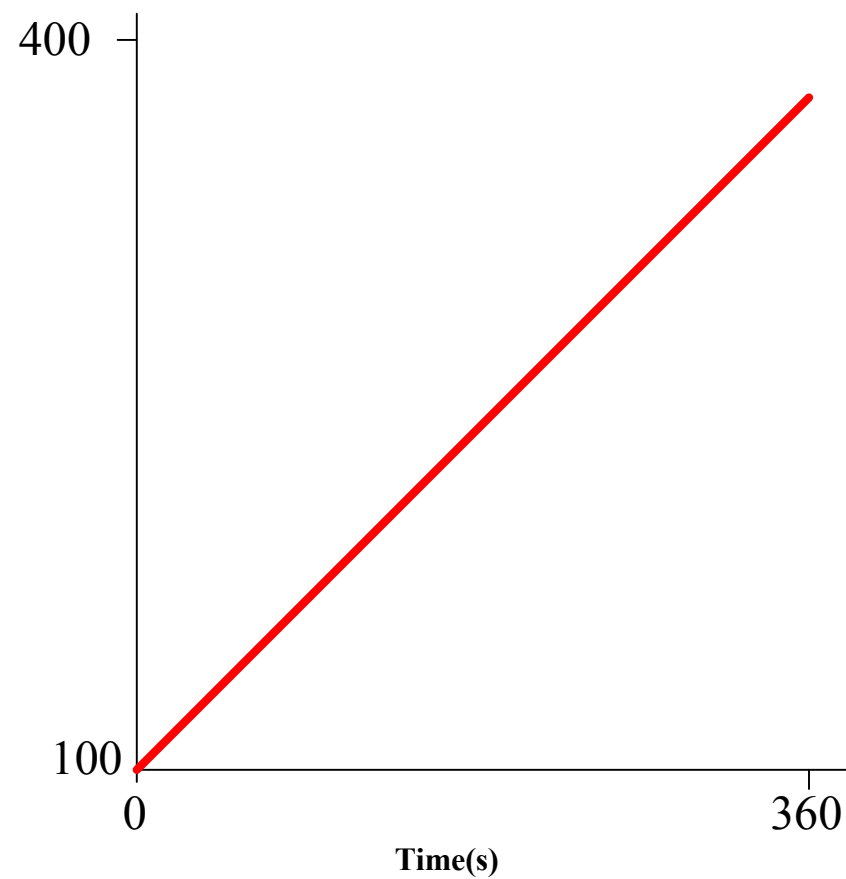
$$\frac{1}{[A]_t} = k t + \frac{1}{[A]_0}$$

Plot $1/[A]_t$ as a function of t

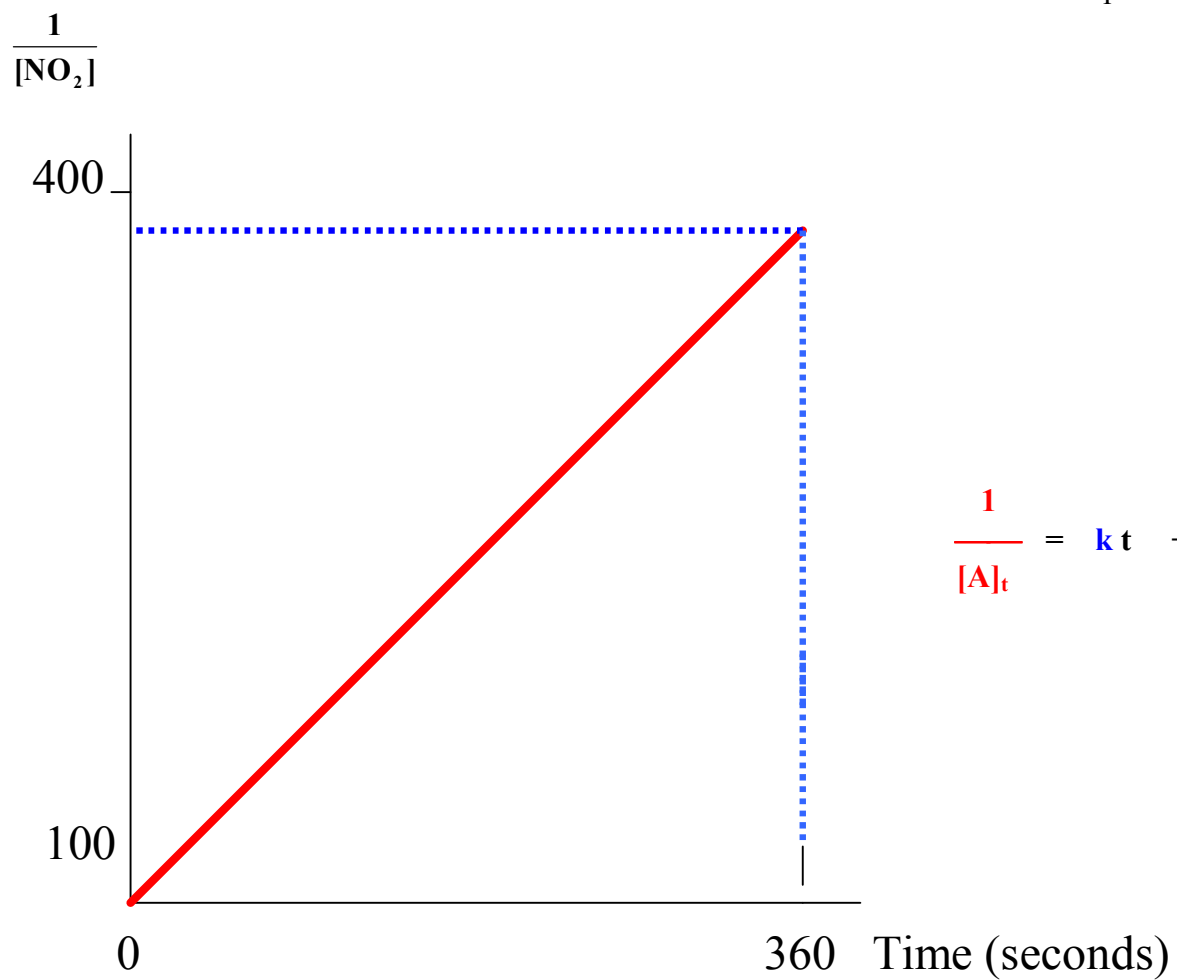
Time (s)	[NO ₂] ₀ (M)	$\log [A]_t$	$1/[A]_t$ (M ⁻¹)
0	1.00 x 10 ⁻²	-2.000	100
60	0.683 x 10 ⁻²	-2.166	146
120	0.518 x 10 ⁻²	-2.286	193
180	0.418 x 10 ⁻²	-2.379	239
240	0.350 x 10 ⁻²	-2.456	286
300	0.301 x 10 ⁻²	-2.521	332
360	0.264 x 10 ⁻²	-2.2578	379

$\log [\text{NO}_2]$ 

- Not a straight line
- Reaction is not of 1st Order

 $\frac{1}{[\text{NO}_2]}$ 

- A straight line is obtained
- **Reaction is of 2nd Order**



$$\frac{1}{[\text{A}]_t} = k t + \frac{1}{[\text{A}]_0}$$

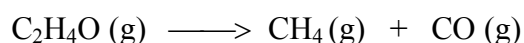
$$k = \text{slope} = \frac{\Delta y}{\Delta t} = \frac{(379 - 100) \text{ M}^{-1}}{(360 - 0) \text{ s}} = 0.775 \text{ M}^{-1} \text{ s}^{-1}$$

SUMMARY OF KINETICS EQUATIONS

Order	Rate Law	Differential Rate Law	Integrated Rate Law	Half-Life	Graphical Plot for a Straight Line
0	k	$-\frac{\Delta[A]_t}{\Delta t} = k$	$[A] = -k t + [A]_0$	$\frac{[A]_0}{2k}$	[A] vs. t
1	Rate = k [A]	$-\frac{\Delta[A]_t}{\Delta t} = k [A]$	$\log \frac{[A]_t}{[A]_0} = -\frac{kt}{2.303}$ or $\log [A]_t = \left(\frac{-k t}{2.303}\right) + \log [A]_0$	$\frac{0.693}{k}$	log [A] vs. t
2	Rate = k [A] ²	$-\frac{\Delta[A]_t}{\Delta t} = k [A]^2$	$\frac{1}{[A]_t} = k t + \frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$	$\frac{1}{[A]_0}$ vs. t

Examples:

1. Ethylene oxide, C₂H₄O(g), decomposes when heated to give methane and carbon monoxide:



The following kinetic data were observed for the reaction at 688K

	[C ₂ H ₄ O] ₀ (M)	Initial Rate (M/s)
Experiment 1	0.00272	5.57 x 10 ⁻⁷
Experiment 2	0.00544	1.11 x 10 ⁻⁶

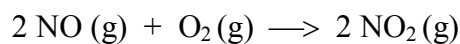
Find the Rate Law and the value of the Rate Constant.

Rate =

k =

Examples:

2. In a kinetic study of the reaction shown below, the following data were obtained for the initial rates of disappearance of NO and O₂ :



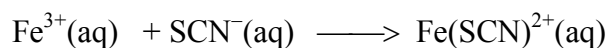
	[NO] ₀ (M)	[O ₂] ₀ (M)	Initial Rate (M/s)
Experiment 1	0.0125	0.0253	0.0281
Experiment 2	0.0250	0.0253	0.112
Experiment 3	0.0125	0.0506	0.0561

Obtain the Rate Law and the Rate Constant.

Rate =

k =

3. In the presence of excess thiocyanate ion (SCN⁻) the following reaction is 1st order with respect to Fe³⁺ with a rate constant of 1.27 s⁻¹.



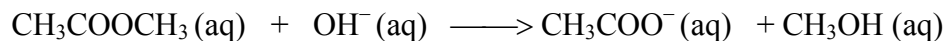
- a) What is the Half-Life in seconds?

t_{1/2} =

- b) How many seconds would be required for the initial concentration of Fe³⁺ to decrease to each of the following values? (25.0 % and 12.5 %)

- c) How many seconds are required for 90.0% of reaction to be completed?

4. Methyl acetate ($\text{CH}_3\text{COOCH}_3$) reacts in basic solution to give acetate ion (CH_3COO^-) and methanol (CH_3OH).



The overall order of reaction was determined by starting with methyl acetate, $\text{CH}_3\text{COOCH}_3$ and hydroxide ion, OH^- , at the same concentrations, so $[\text{CH}_3\text{COOCH}_3] = [\text{OH}^-] = x$.

Then $\text{Rate} = k [\text{CH}_3\text{COOCH}_3]^m [\text{OH}^-]^n = k x^{m+n}$

Determine the overall order and the value of the rate constant by plotting data assuming first- and then second-order kinetics.

Time (min)	$[\text{CH}_3\text{COOCH}_3]$ (M)		
0.00	0.01000		
3.00	0.00740		
4.00	0.00683		
5.00	0.00634		