

Chemical kinetics

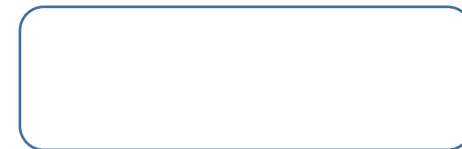
Rate (average): change in quantity in a given amount of time

$$R = \frac{\Delta Q}{\Delta t}$$

EX. Speed of a car. $v = \frac{\Delta D}{\Delta t}$

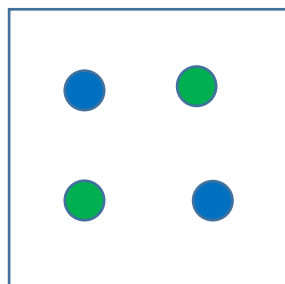
A car traveled a distance of 25 miles in 0.5 hours.

What was its average speed during that time?

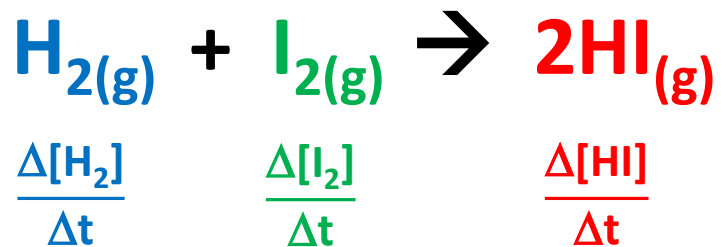


Rate of a chemical reaction

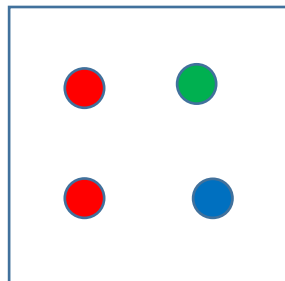
Initial (t=0s)



1.0 mole H₂
1.0 mole I₂
0 mole HI



Final (t=100s)



0.5 mole H₂
0.5 mole I₂
1.0 mole HI

$$\frac{\Delta[\text{H}_2]}{\Delta t} = \frac{[\text{H}_2]_f - [\text{H}_2]_i}{t_f - t_i} = \frac{0.5\text{M} - 1.0\text{M}}{100\text{s} - 0\text{s}} = -0.005 \frac{\text{M}}{\text{s}}$$

$$\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{\text{M}}{\text{s}}$$

$$\frac{\Delta[\text{HI}]}{\Delta t} = \frac{\text{M}}{\text{s}}$$

$$-\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \text{Rate}$$

Plotting Concentration vs. Time



$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

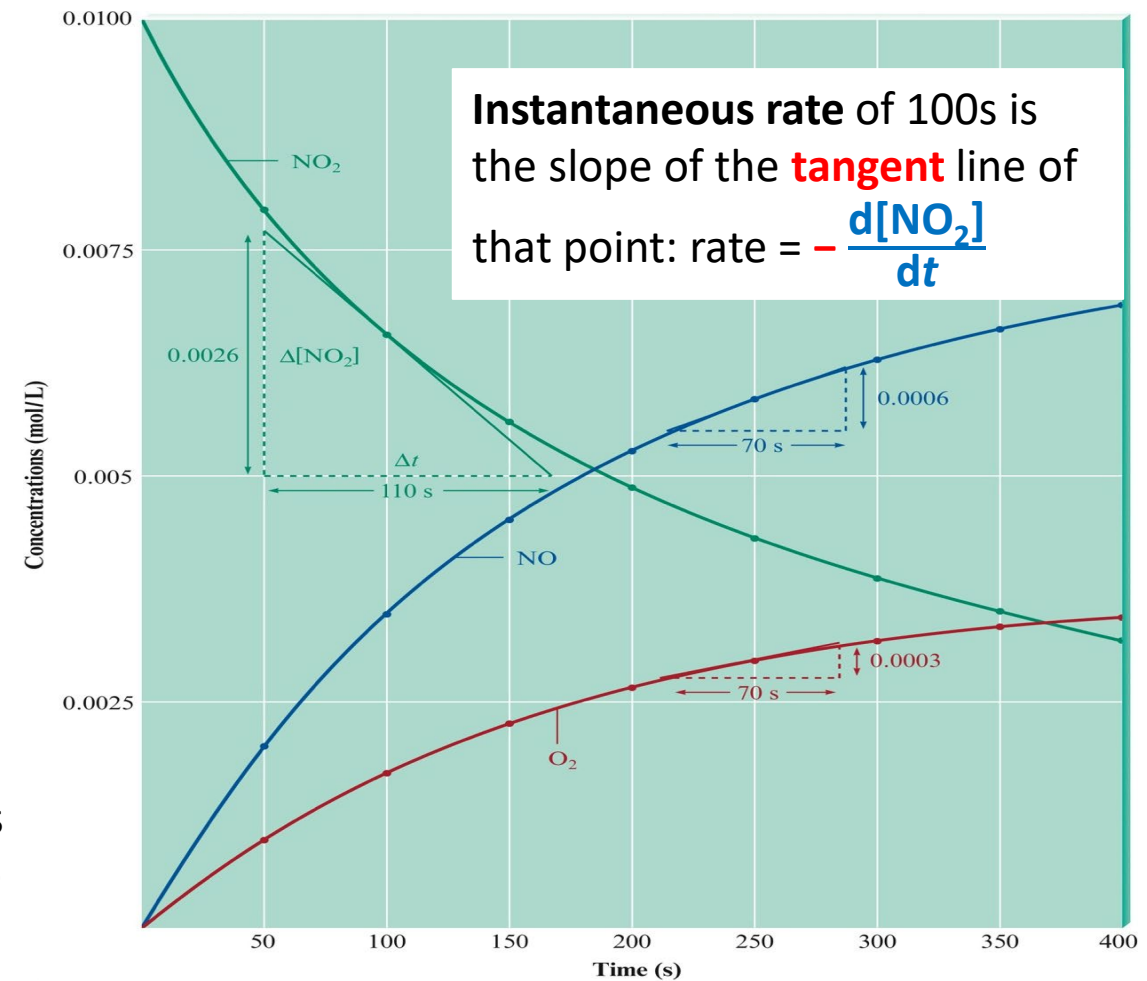
$$\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{[\text{NO}_2]_f - [\text{NO}_2]_i}{t_f - t_i}$$

Table 11-1 | Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)$ (at 300°C)

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

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Average rate from 0 to 50 s is the **slope** of the line connecting the two points



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General case



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

EX: For a reaction: $4\text{NO}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{N}_2\text{O}_5(g)$.

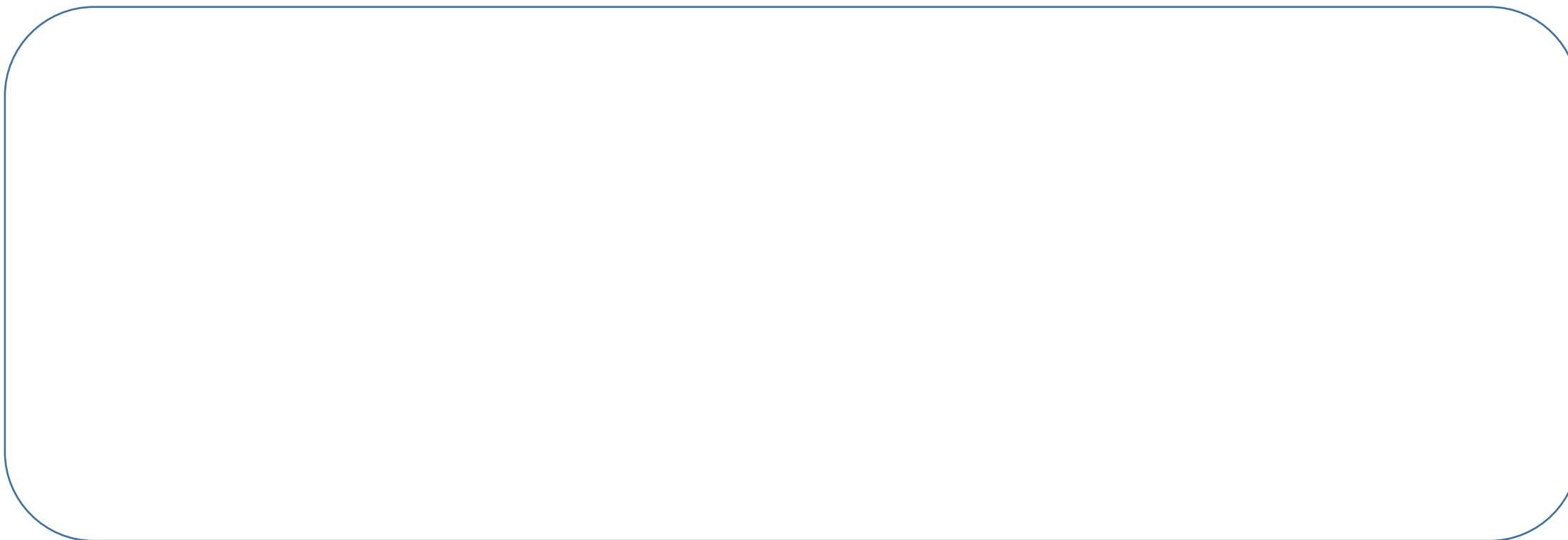
If known N_2O_5 formation rate of 0.048 M/sec ,

Write the rate expression in terms of the disappearance of NO_2 and O_2 and the formation of N_2O_5 .

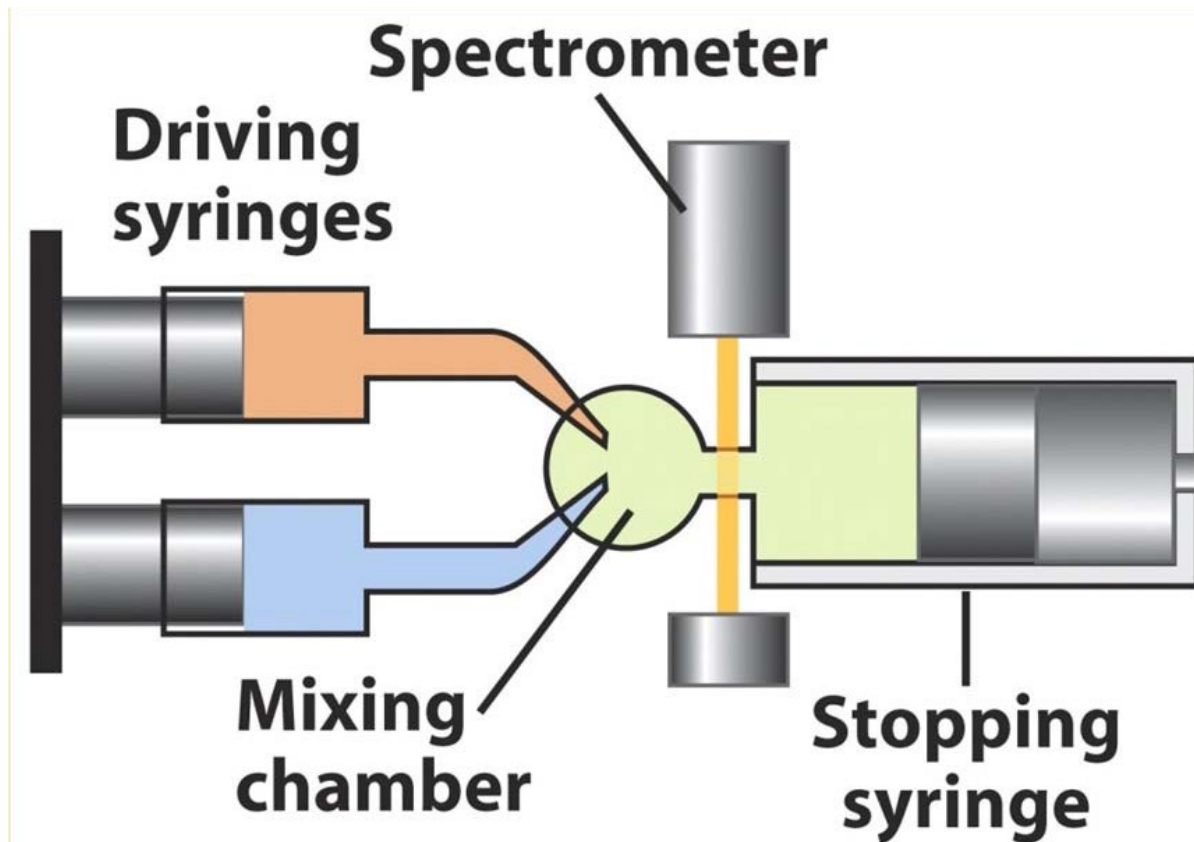
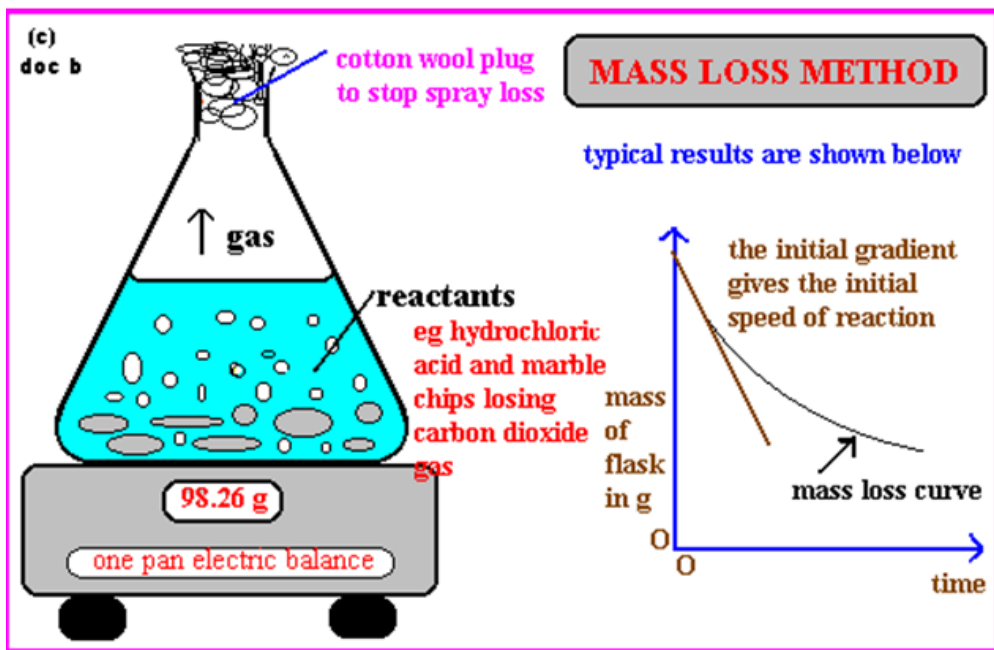
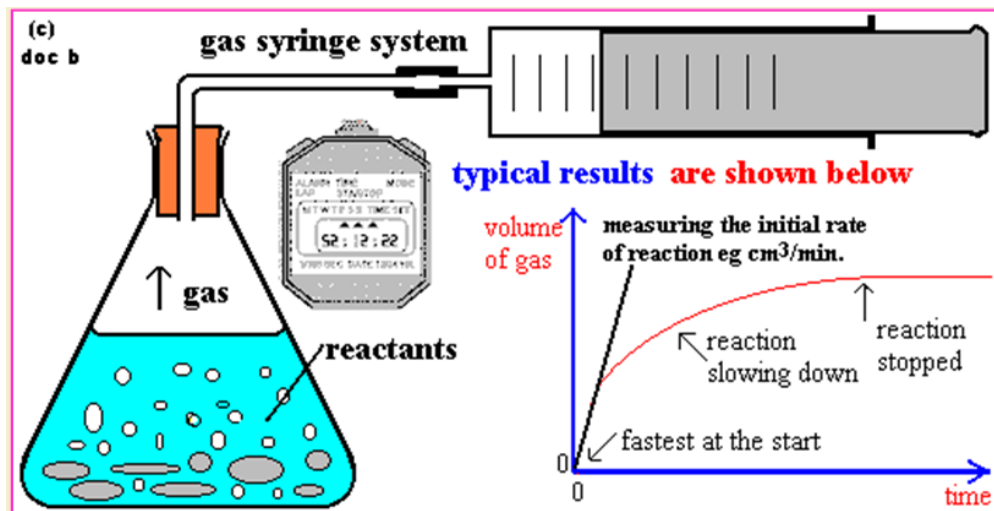
What is O_2 disappearance rate?

What is NO_2 disappearance rate?

What is the overall reaction rate?



How to measure reaction progression ??



Stopped-Flow experiment

General case



$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C_2]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Rate Law of a reaction

- All rate laws are obtained from experiments

Differential Rate Law

The reaction rate is related to the concentrations of the reacting species

$$\text{Rate} = k [A]^n [B]^m \text{ not } k [A]^a [B]^b$$

k : rate constant (T dependent)

n : order with respect to A

m : order with respect to B

$n + m$: overall reaction order

Integrated Rate Law

The concentration is related to the reaction time

$$-\frac{d[A]}{dt} = k$$

$$[A]_t = kt + c$$

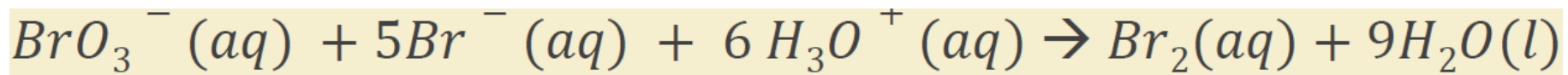
Reaction order

- Rate = $k [R_1]^a [R_2]^b \dots$
- k : reaction constant
- $a+b+\dots$: reaction order
- 1st order reaction
- 2nd order reaction

Unit of k

Order in A	Rate law
0	Rate = k
1	Rate = $k[A]$
2	Rate = $k[A]^2$

Reaction	Rate law*
Gas phase	
$H_2 + I_2 \longrightarrow 2 HI$	$k[H_2][I_2]$
$2 HI \longrightarrow H_2 + I_2$	$k[HI]^2$
$2 N_2O_5 \longrightarrow 4 NO_2 + O_2$	$k[N_2O_5]$
$2 N_2O \longrightarrow 2 N_2 + O_2$	$k[N_2O]$
$2 NO_2 \longrightarrow 2 NO + O_2$	$k[NO_2]^2$
$C_2H_6 \longrightarrow 2 CH_3$	$k[C_2H_6]$
cyclopropane \longrightarrow propene	$k[\text{cyclopropane}]$
Aqueous solution	
$H_3O^+ + OH^- \longrightarrow 2 H_2O$	$k[H^+][OH^-]$
$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$	$k[CH_3Br][OH^-]$
$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2 C_6H_{12}O_6$	$k[C_{12}H_{22}O_{11}][H^+]$



$$\text{Rate} = k [\text{BrO}_3^-]^x [\text{Br}^-]^y [\text{H}_3\text{O}^+]^z$$

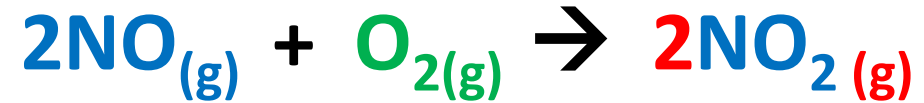
Initial concentration (M)				
Exp.	BrO_3^-	Br^-	H_3O^+	Initial Rate M/sec of BrO_3^-
1	0.1	0.1	0.1	0.0012
2	0.2	0.1	0.1	0.0024
3	0.1	0.3	0.1	0.0035
4	0.2	0.1	0.15	0.0055

EX: For a reaction: $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_2(g)$.

When the $[\text{NO}]$ is doubled, the reaction rate increase by a factor of 4,

When both the $[\text{NO}]$ and $[\text{O}_2]$ are doubled, the reaction rate increase by a factor of 8,

What are the reactant orders, the overall order of the reaction, and the units of k



integrated Rate Law

The concentration is related to the reaction time

0th order

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

1st order

$$\ln([A]_t) = -kt + \ln([A]_0)$$

$$[A]_t = A_0 \exp(-kt)$$

2nd order

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

Table 11-6 | Summary of the Kinetics for Reactions of the Type $aA \rightarrow \text{Products}$ That Are Zero, First, or Second Order in $[A]$

	Order		
	Zero	First	Second
Rate law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Consider the reaction $aA \rightarrow \text{Products}$.

$[A]_0 = 5.0 \text{ M}$ and $k = 1.0 \times 10^{-2}$ (assume the units are appropriate for each case). Calculate $[A]$ after 30.0 seconds have passed, assuming the reaction is:

- a) Zero order 4.7 M
- b) First order 3.7 M
- c) Second order 2.0 M

Using integrated Rate Law to determine reactant concentration and reaction time

Ex: for the reaction $2 \text{N}_2\text{O}_5 \longrightarrow 4 \text{NO}_2 + \text{O}_2$

Its rate law $R = -\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$, where the $k = 5.2 \times 10^{-3} \text{ s}^{-1}$ at 65°C

(1) Assume the initial concentration of N_2O_5 is 0.04 M , what is the concentration of N_2O_5 after 600 s ?

(2) Assume the initial concentration of N_2O_5 is 20 M , how long does it take to reach a concentration of 2 M ?

Using integrated Rate Law to determine Half live

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

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

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

$$k \cdot t_{1/2} = \ln 2 = 0.693$$

If the rate constant of decomposition of N_2O_5 at 25°C is $3.7 \times 10^{-5} \text{ 1/sec}$, please calculate the time need for the concentration of N_2O_5 to fall to

- One-half
- 15 % of its original value
- One-nineth $t_{1/9} = 59384.45 \text{ sec}$

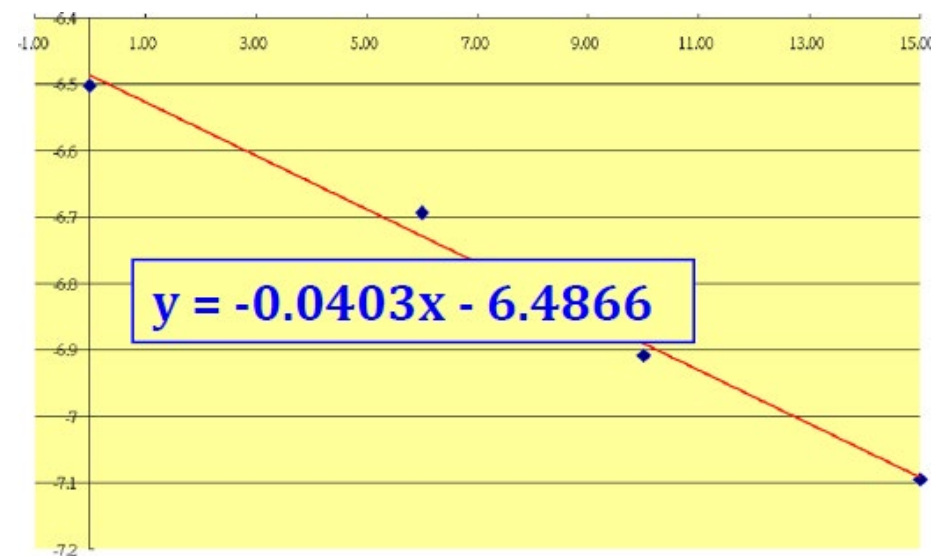
Using integrated Rate Law to determine the reaction order

When cyclopropane, C_3H_6 , is heated to $500^\circ C$, it changes into an isomer, propene, C_3H_6 . The data in the accompanying table show the concentration of cyclopropane at a series of times after the start of the reaction. Please confirm that the reaction is first order in C_3H_6 and calculate the rate constant.

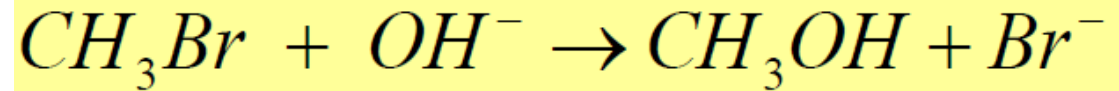
t (min)	$[C_3H_6]$ (M)	$\ln[C_3H_6]$
0	0.0015	-6.50229
6	0.00124	-6.69264
10	0.00100	-6.90776
15	0.00083	-7.09408

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

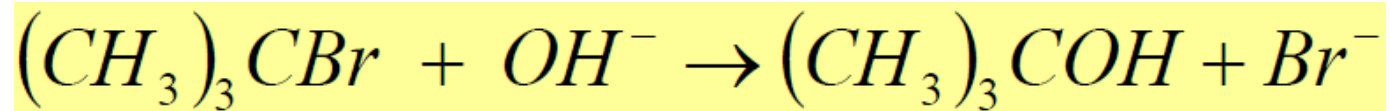
$$[A]_t = [A]_0 e^{-kt}$$



Reaction Mechanisms



$$k[CH_3Br][OH^-]$$



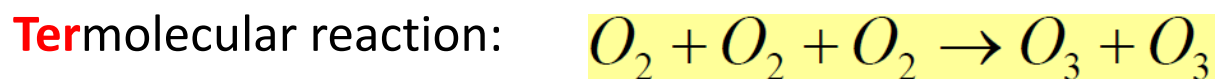
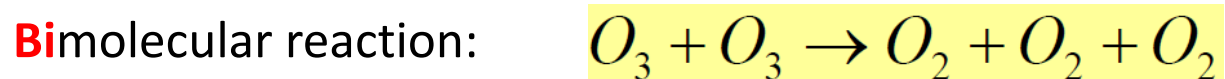
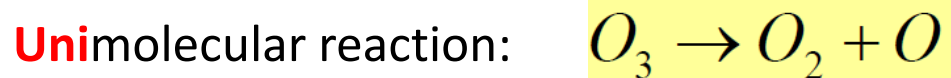
$$k[(CH_3)_3CBr]$$

Why?

How to propose a reasonable mechanism?

- The sum of **elementary steps** must give the overall balanced equation
- The mechanism must agree with the **experimentally determined rate law**

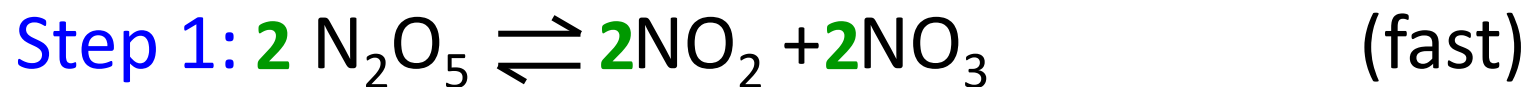
Elementary Steps (**Molecularity**)



Reaction involve single elementary steps



Reaction involve multi-elementary steps: use **Rate Determining Step** to write the rate law

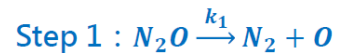


Reactant:

Product:

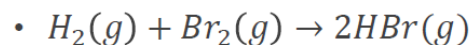
Intermediate:

- The gas-phase decomposition of N_2O is believed to occur via two elementary steps:

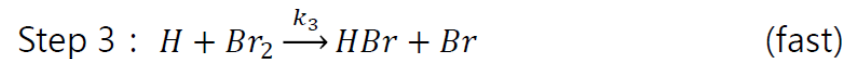
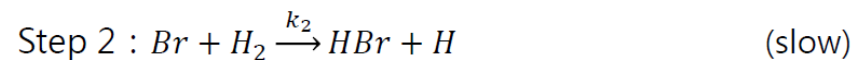


- Experimentally, the rate law is found to be $\text{rate} = k[N_2O]$
 - Write the equation for the overall reaction.
 - Identify the intermediates.
 - What can you say about the relative rates of steps 1 and 2?

- Under certain conditions, the experimental rate law for the gas-phase reaction of molecular hydrogen with molecular bromine



- is given by $\text{rate} = k[H_2][Br_2]^{1/2}$
- Show that the unusual half-reaction order for Br_2 can be explained by the following mechanism:



Other players for chemical kinetics

The Arrhenius Equation

Higher temperature → faster reaction rates
(faster moving molecule)

$$k = Ae^{-E_a/RT}$$

k = rate constant

A = frequency factor

E_a = activation energy (J/mol)

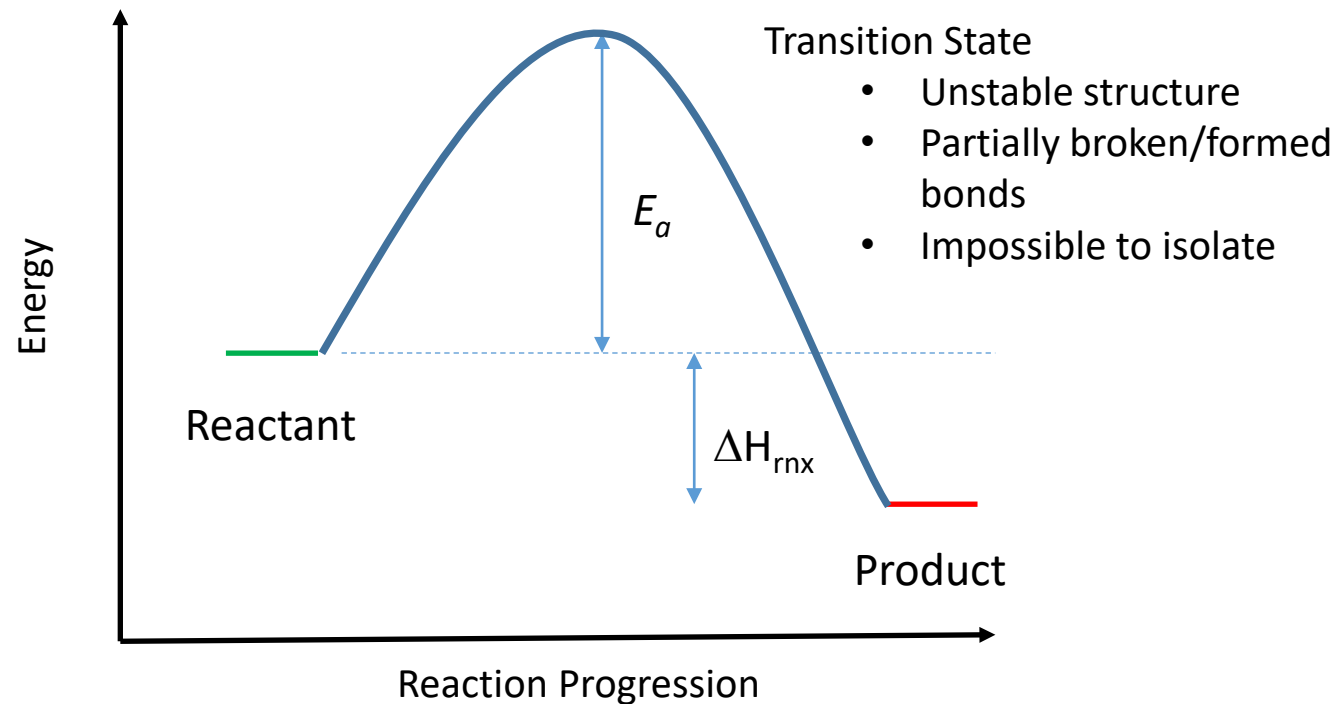
R = gas constant (8.3145 J/K·mol)

T = temperature (in K)



1st order kinetics

- Double $[\text{CH}_3\text{NC}]$, double the rate
- Rate = $k[\text{CH}_3\text{NC}]$



Frequency Factor – a closer look (unimolecular vs bimolecular)

$$k = A e^{-\frac{E_a}{RT}}$$



Exponential Factor:

- Function of reactant molecules with sufficient energy to react

Frequency Factor:

- The number of approaches to the activation barrier per second
- The number of reaction attempts per second

Unimolecular:

One molecule involved,
Frequency Factor depends on the rate of those specific molecular vibrations that are favorable for chemical reaction

Bimolecular:

Two molecule involved,
Frequency Factor depends on the rate at which 'favorable collision' occur.

$$A = pz$$

z = collision frequency

p = orientation factor



(improper orientation)
unfavorable



(proper orientation)
favorable

EX: Given the following kinetic data for the chemical reaction, $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$, find E_a and A

$T(\text{K})$	$k(\text{s}^{-1})$
450	6.8×10^{-6}
475	6.5×10^{-5}
500	5.6×10^{-4}
525	3.1×10^{-3}

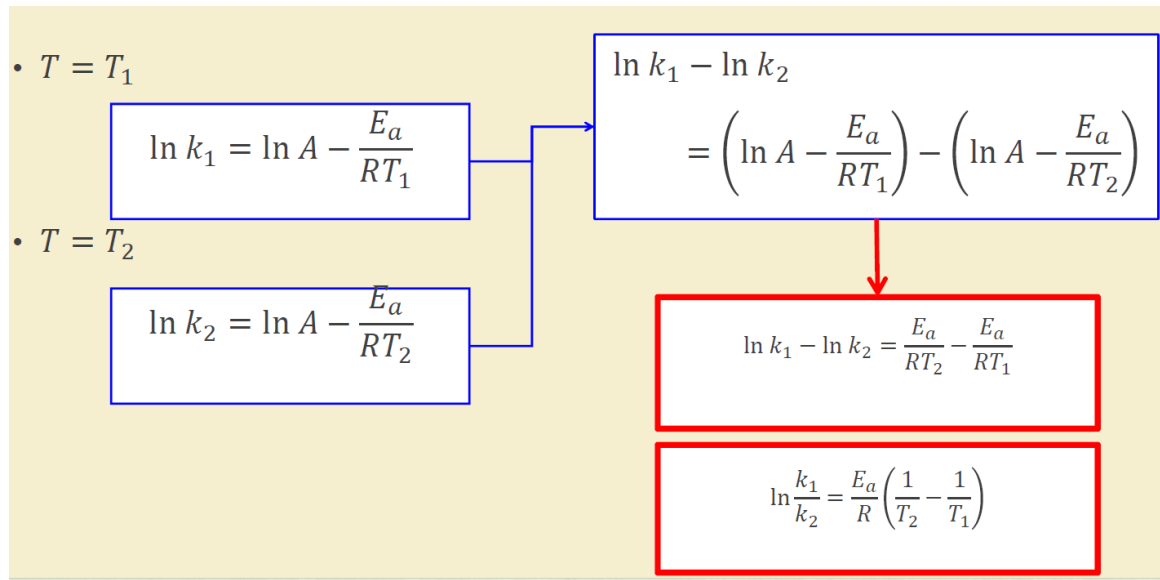
$$k = Ae^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$1/T$	$\ln k$
0.00222	-11.9
0.00211	-9.64
0.00200	-7.49
0.00191	-5.78

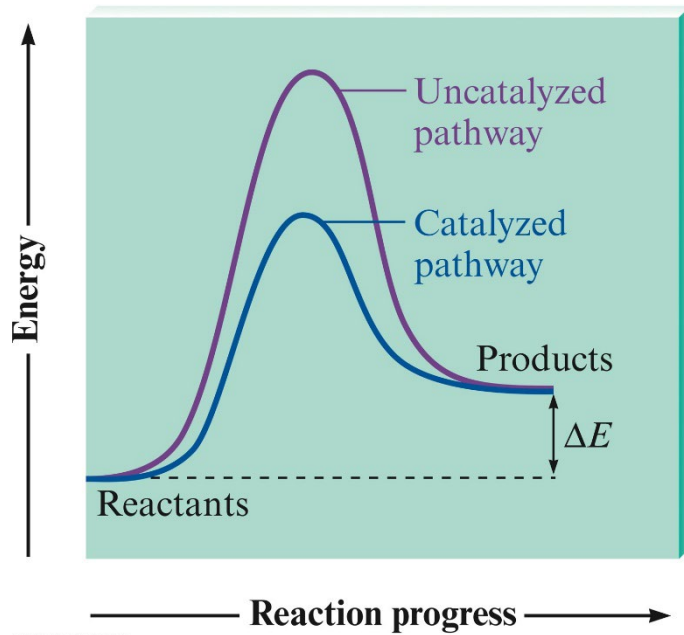
$$k = Ae^{-E_a/RT}$$
$$\ln k = \ln A - \frac{E_a}{RT}$$

The rate constant of a first-order reaction is $3.46 \times 10^{-2} \text{ s}^{-1}$ at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

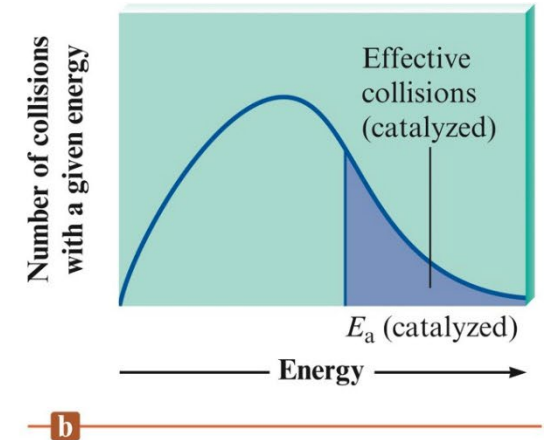
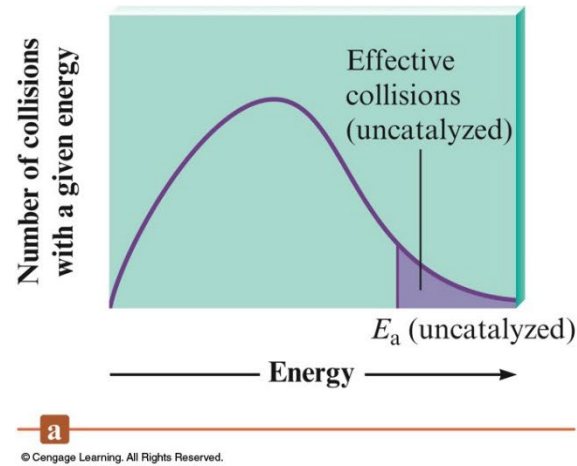


Catalyst

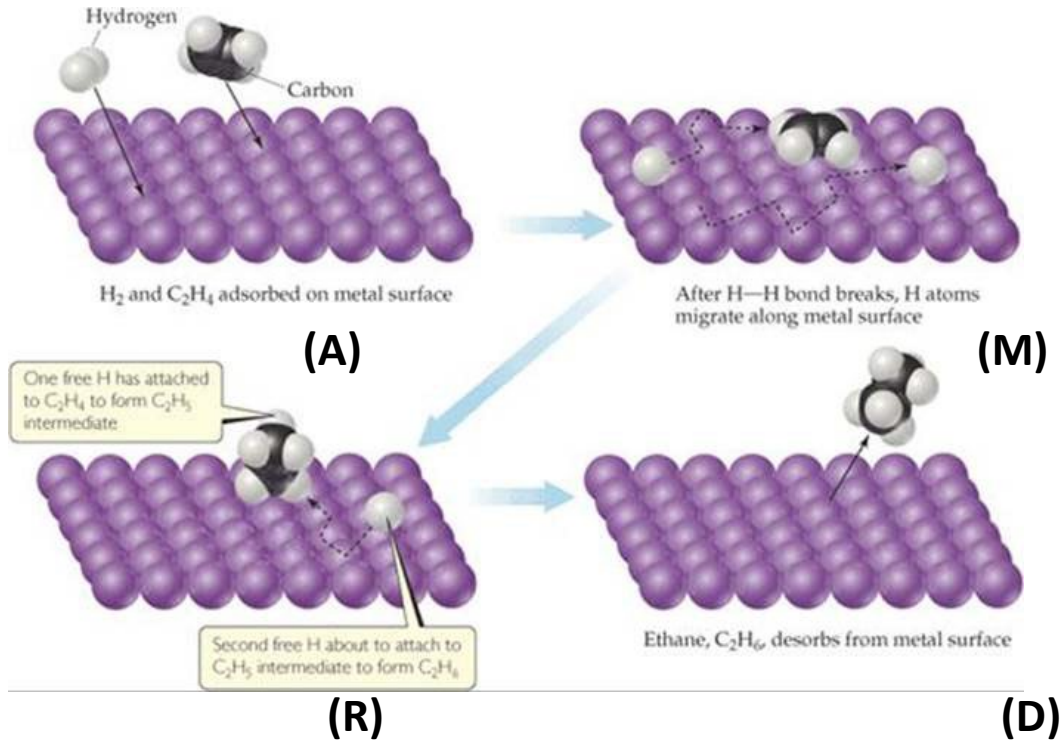
- A substance that speeds up a reaction without **being consumed itself**.
- Provides a new pathway for the reaction with a lower **activation energy**.



Effect of a Catalyst on the Number of Reaction-Producing Collisions



Heterogeneous Catalyst



Homogeneous Catalyst

- Exists in the same phase as the reacting molecules.
- Enzymes are nature's catalysts.