

Chemical Kinetics

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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).



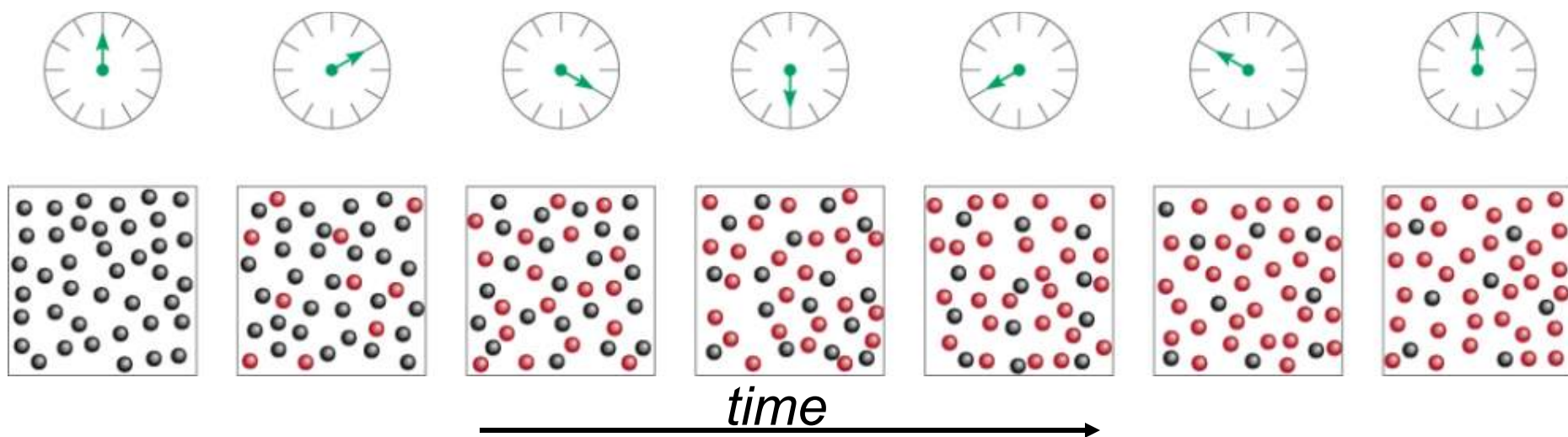
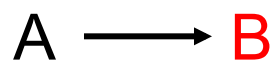
$$\text{rate} = - \frac{D[A]}{Dt}$$

$D[A]$ = change in concentration of A over time period Dt

$$\text{rate} = \frac{D[B]}{Dt}$$

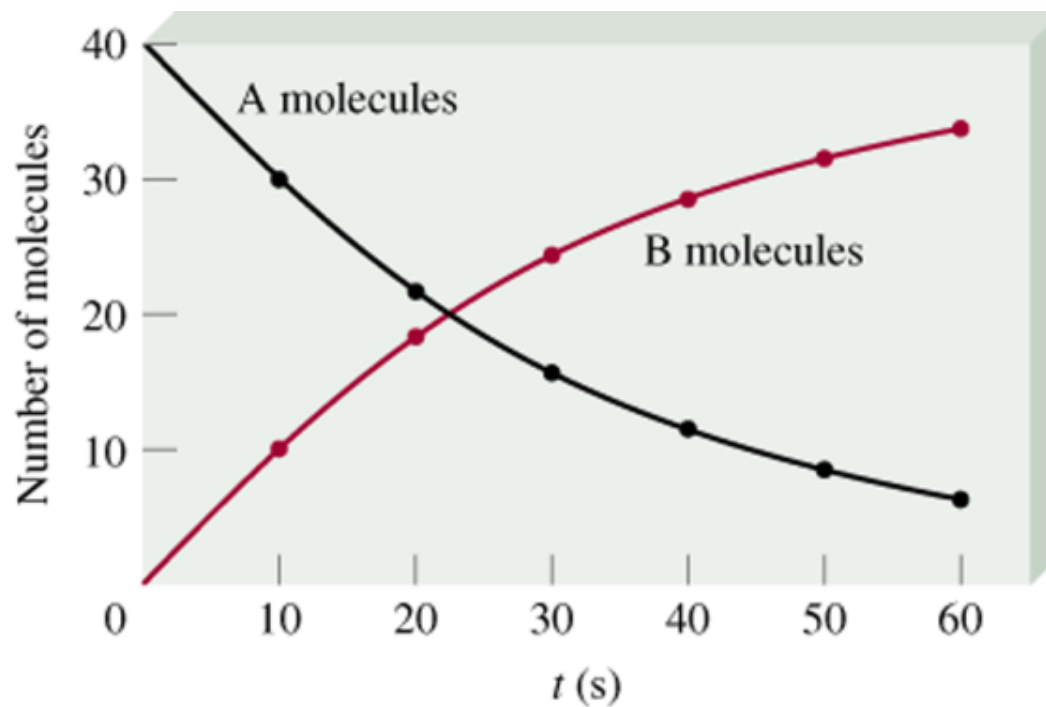
$D[B]$ = change in concentration of B over time period Dt

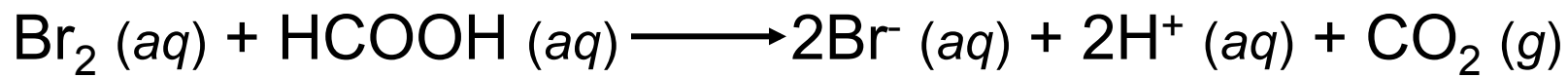
Because $[A]$ decreases with time, $D[A]$ is negative.



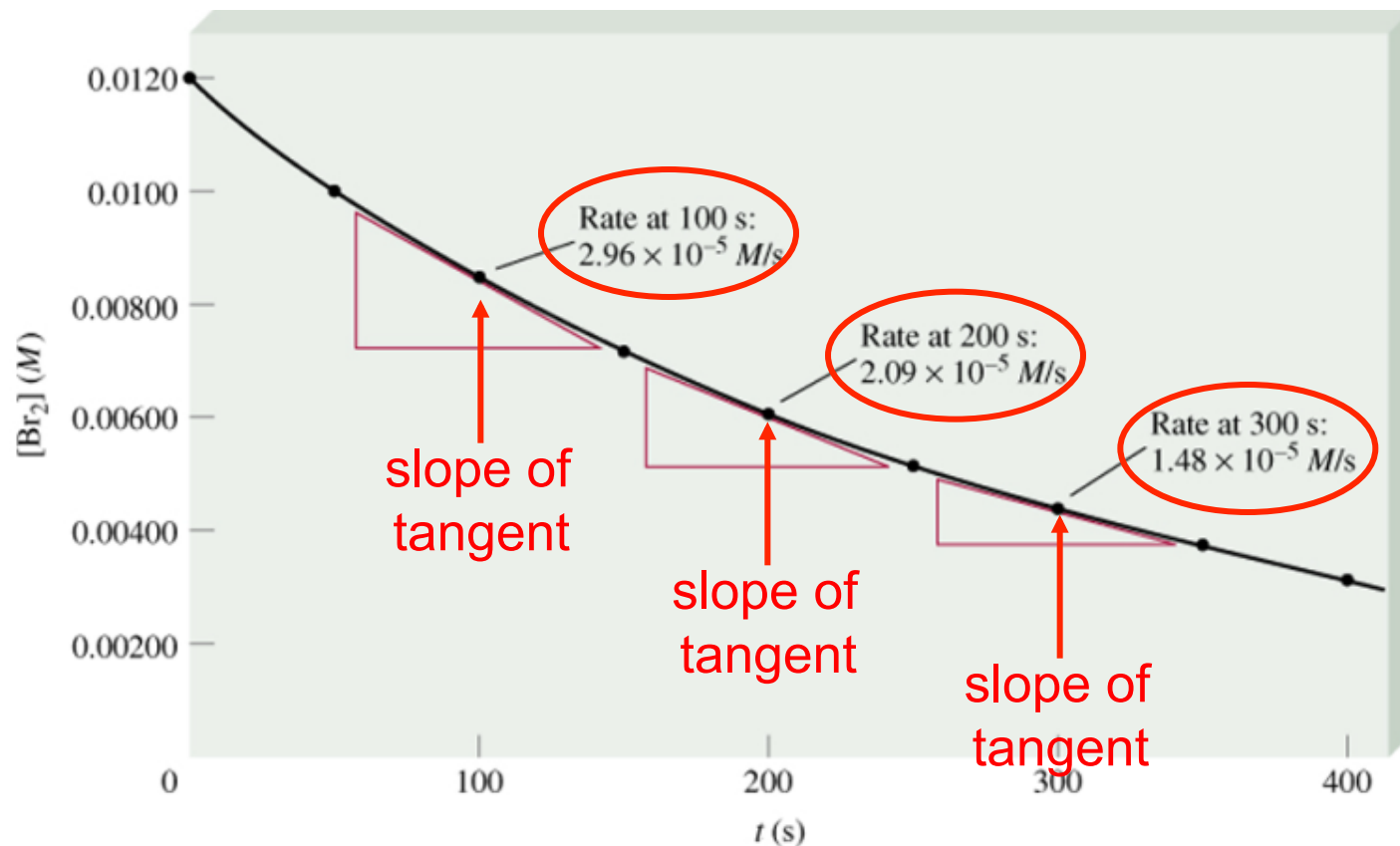
$$\text{rate} = - \frac{D[A]}{Dt}$$

$$\text{rate} = \frac{D[B]}{Dt}$$





Time (s)	[Br ₂] (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296



$$\text{average rate} = - \frac{D[\text{Br}_2]}{Dt} = - \frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}}$$

instantaneous rate = rate for specific instance in time

TABLE 13.1

Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

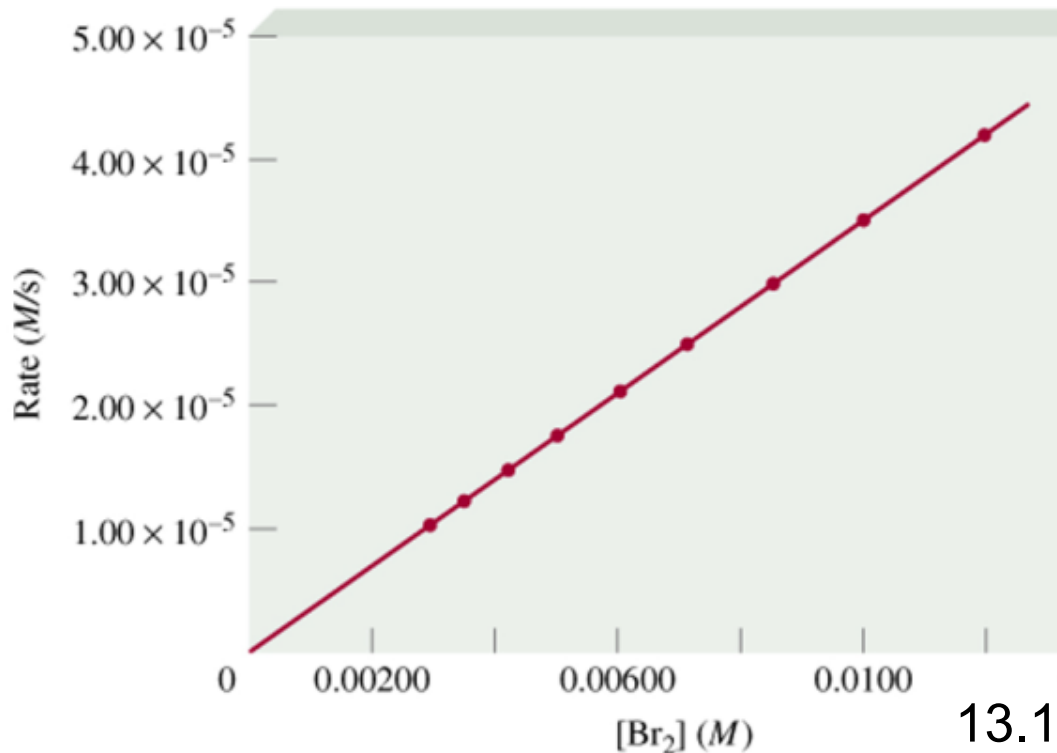
Time (s)	[Br ₂] (M)	Rate (M/s)	$k = \frac{\text{rate}}{[\text{Br}_2]} \text{ (s}^{-1}\text{)}$
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	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}

rate \propto [Br₂]

rate = k [Br₂]

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

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



Factors that Affect Reaction Rate

1. Temperature

- **Collision Theory:** When two chemicals react, their molecules have to collide with each other with sufficient energy for the reaction to take place.
- **Kinetic Theory:** Increasing temperature means the molecules move faster.

2. Concentrations of reactants

- More reactants mean more collisions if enough energy is present

3. Catalysts

- Speed up reactions by lowering activation energy

4. Surface area of a solid reactant

- Bread and Butter theory: more area for reactants to be in contact

5. Pressure of gaseous reactants or products

- Increased number of collisions

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.



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



reaction is **xth order** in A

reaction is **yth order** in B

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

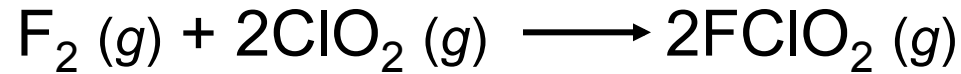


Table 13.2 Rate Data for the Reaction between F_2 and ClO_2

	$[\text{F}_2](M)$	$[\text{ClO}_2](M)$	Initial Rate (M/s)
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}

$$\text{rate} = k [\text{F}_2]^x [\text{ClO}_2]^y$$

Double $[\text{F}_2]$ with $[\text{ClO}_2]$ constant

Rate doubles

$$x = 1$$

Quadruple $[\text{ClO}_2]$ with $[\text{F}_2]$ constant

Rate quadruples

$$y = 1$$

$$\text{rate} = k [\text{F}_2][\text{ClO}_2]$$

Run #	Initial [A] ([A] ₀)	Initial [B] ([B] ₀)	Initial Rate (v ₀)
1	1.00 M	1.00 M	1.25 x 10 ⁻² M/s
2	1.00 M	2.00 M	2.5 x 10 ⁻² M/s
3	2.00 M	2.00 M	2.5 x 10 ⁻² M/s

What is the order with respect to A? 0

What is the order with respect to B? 1

What is the overall order of the reaction? 1

$[\text{NO}_{(g)}]$ (mol dm ⁻³)	$[\text{Cl}_{2(g)}]$ (mol dm ⁻³)	Initial Rate (mol dm ⁻³ s ⁻¹)
0.250	0.250	1.43×10^{-6}
0.250	0.500	2.86×10^{-6}
0.500	0.500	1.14×10^{-5}

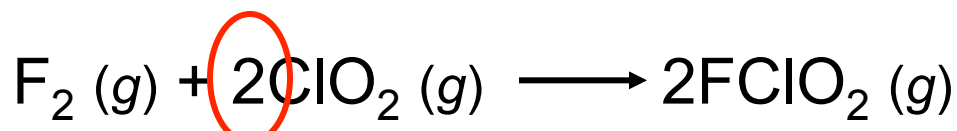
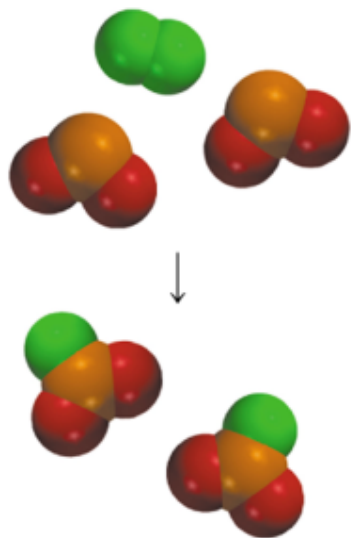
What is the order with respect to Cl_2 ? 1

What is the order with respect to NO ? 2

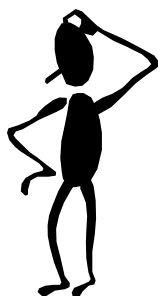
What is the overall order of the reaction? 3

Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



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



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}

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

$$y = 1$$

$$x = 1$$

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

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

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

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

First-Order Reactions

$$\text{rate} = - \frac{D[A]}{Dt}$$

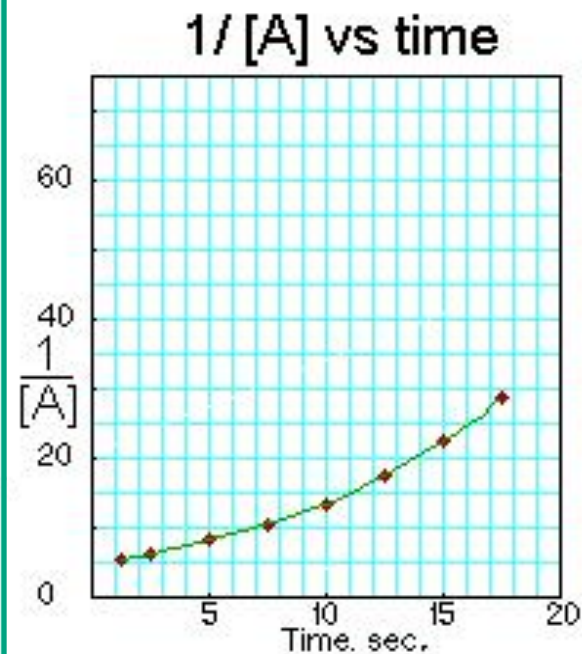
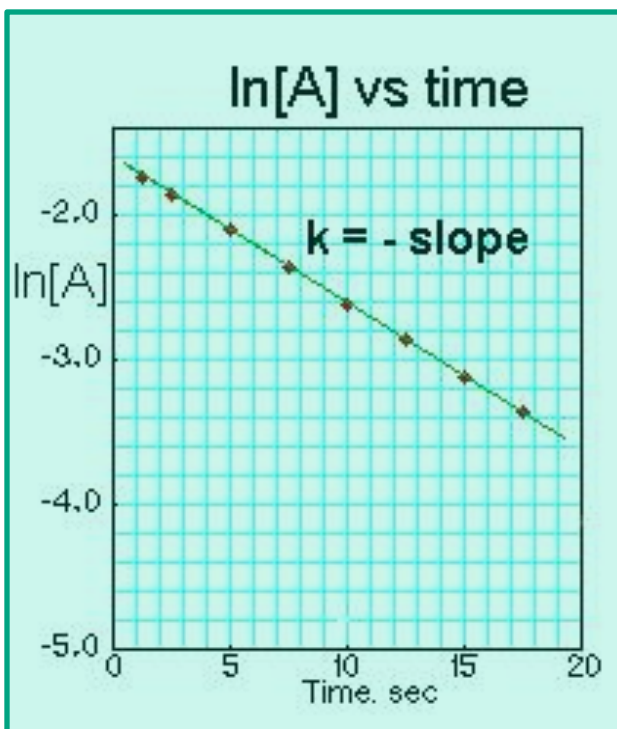
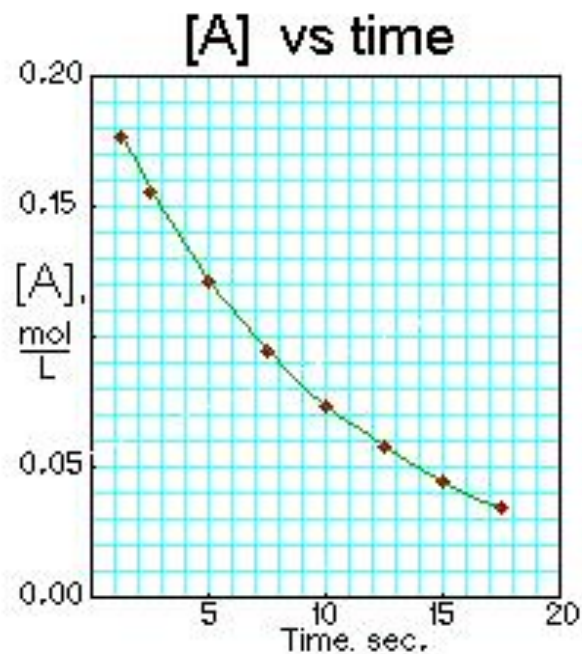
$$\text{rate} = k [A]$$

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

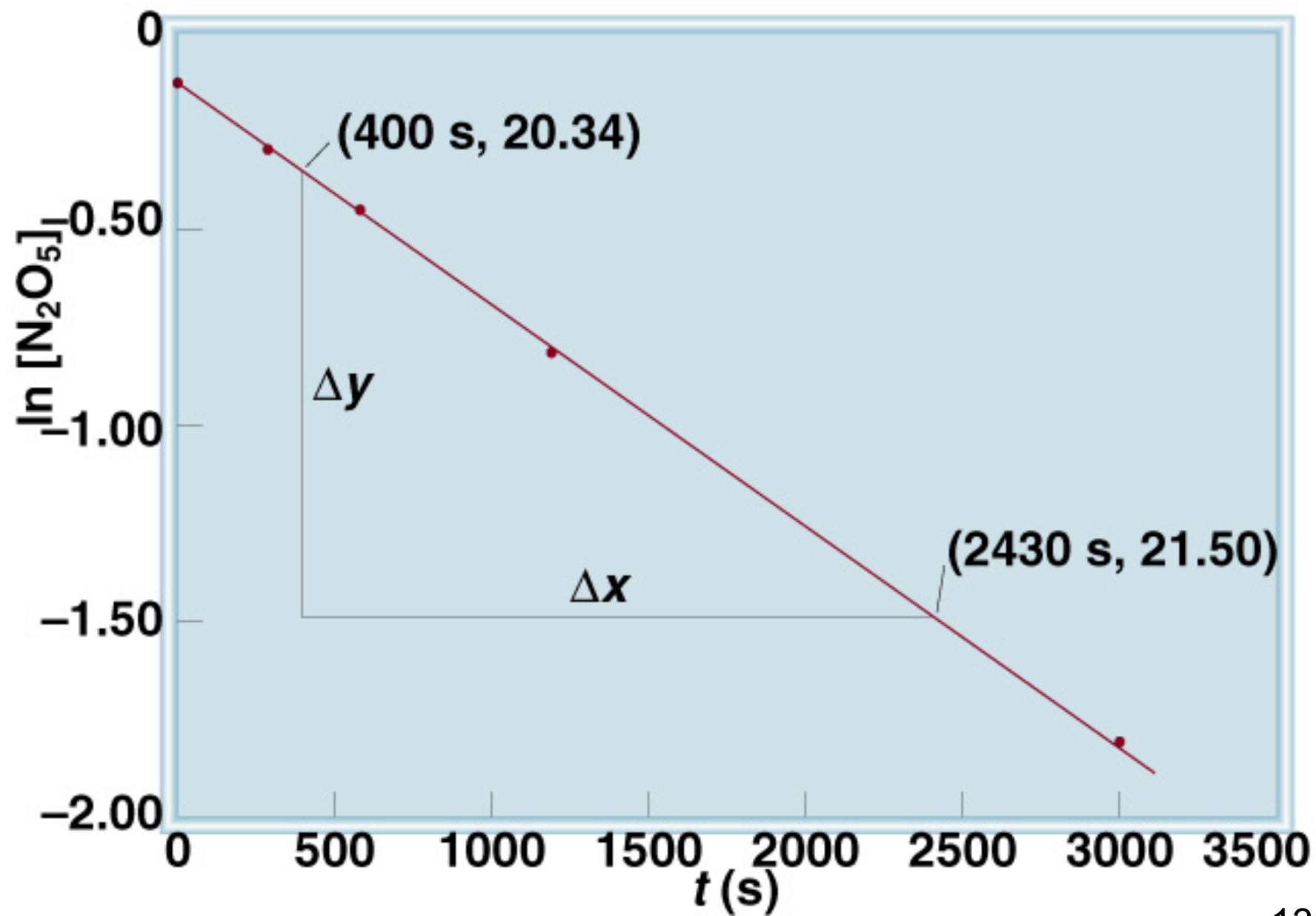
$$\ln[A] - \ln[A]_0 = -kt$$

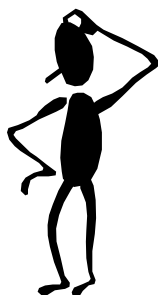
[A] is the concentration of A at any time t

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



Decomposition of N_2O_5





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

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

$$[A]_0 = 0.88 \text{ M}$$

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

$$[A] = 0.14 \text{ M}$$

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

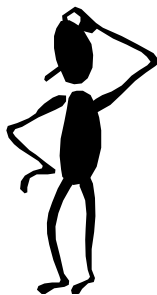
$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \frac{[A]_0}{[A]}}{k} = \frac{\ln \frac{0.88 \cancel{\text{ M}}}{0.14 \cancel{\text{ M}}}}{2.8 \times 10^{-2} \text{ s}^{-1}} = 66 \text{ s}$$

First-Order Reactions

The **half-life**, $t_{1/2}$, is the time required for the concentration of a reactant to decrease to half of its initial concentration.

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

$$t_{1/2} = \frac{\ln \frac{[A]_0}{[A]_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

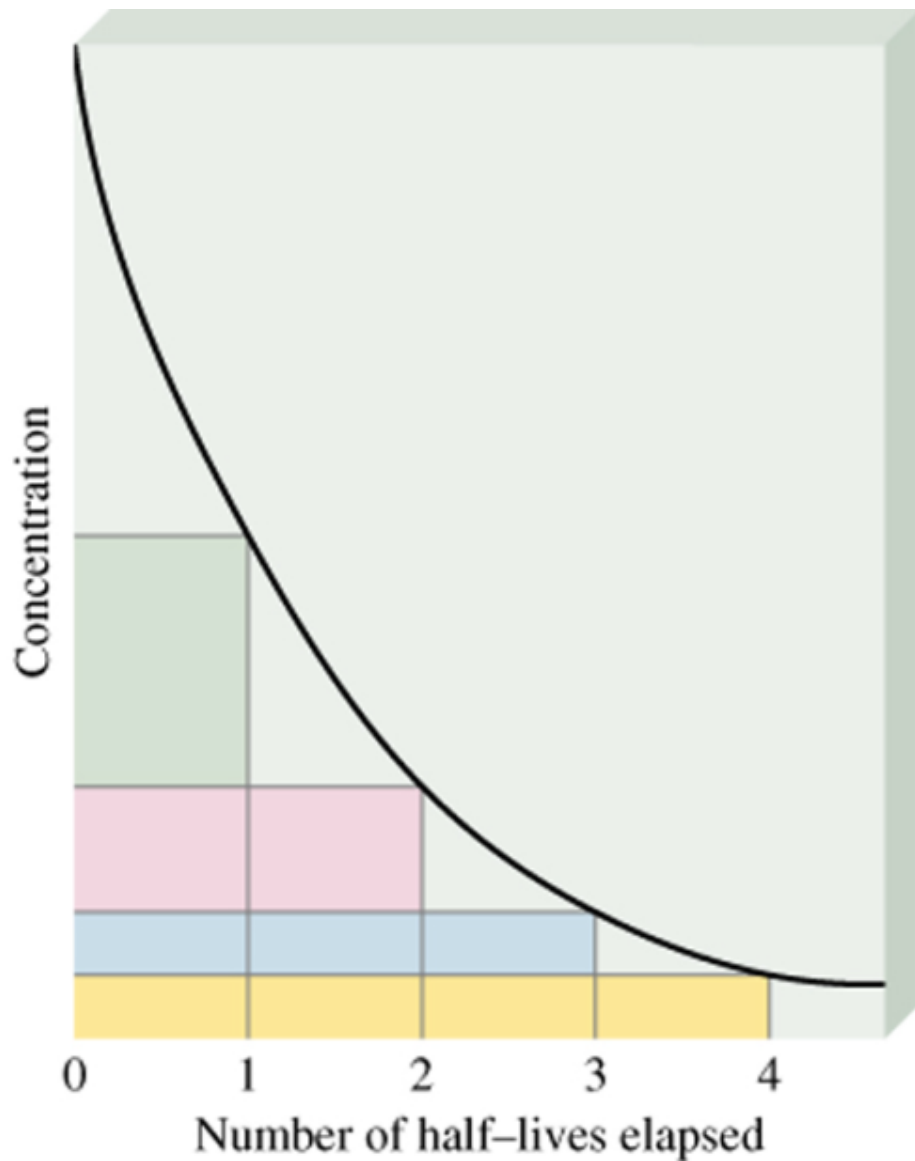


What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4} \text{ s}^{-1}$?

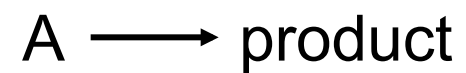
$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4} \text{ s}^{-1}} = 1200 \text{ s} = 20 \text{ minutes}$$

How do you know decomposition is first order?

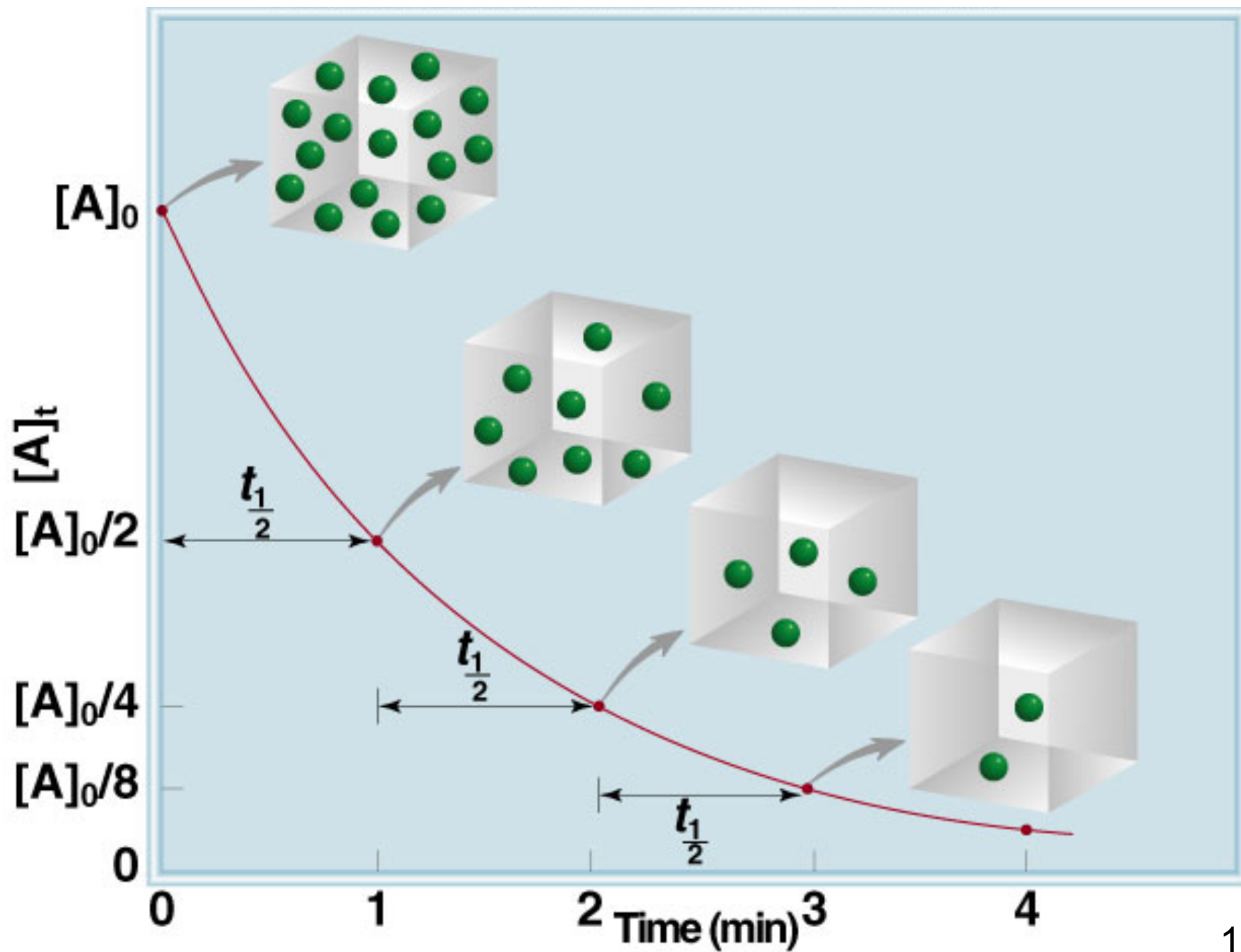
units of k (s^{-1}) 13.3



First-order reaction



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



Second-Order Reactions

$$\text{rate} = -\frac{D[A]}{Dt}$$

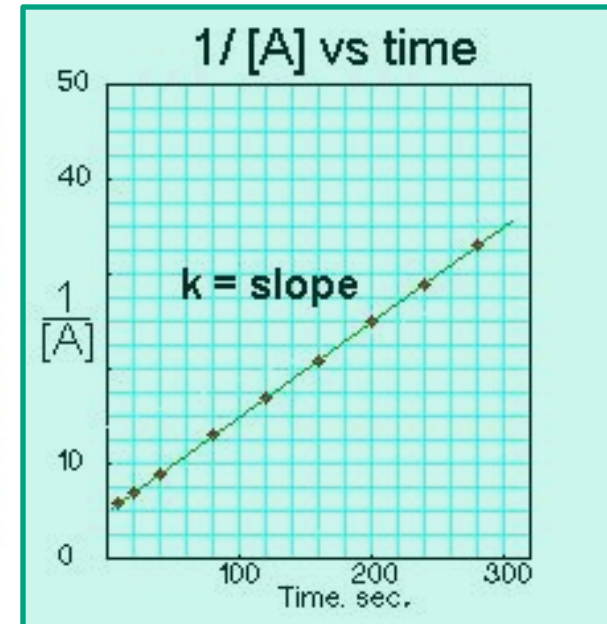
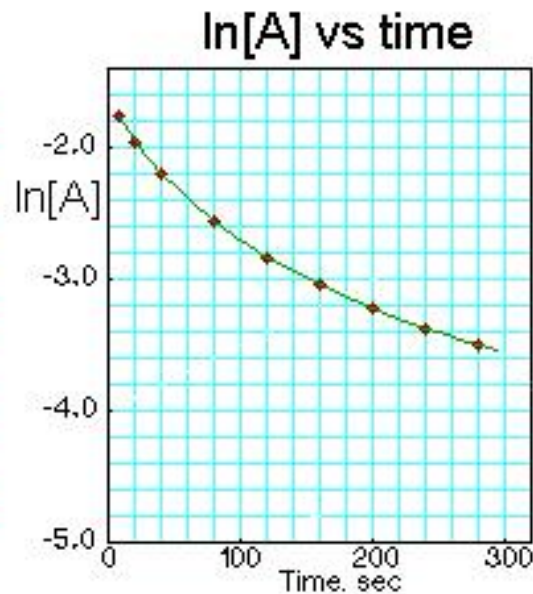
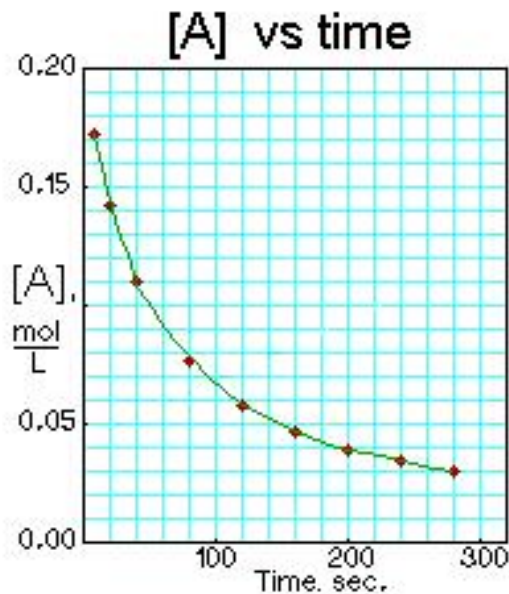
rate = $k[A]^2$ [A] is the concentration of A at any time t
[A]₀ is the concentration of A at time $t=0$

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

Half life for second order

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

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



Zero-Order Reactions

$$\text{rate} = - \frac{D[A]}{Dt}$$

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

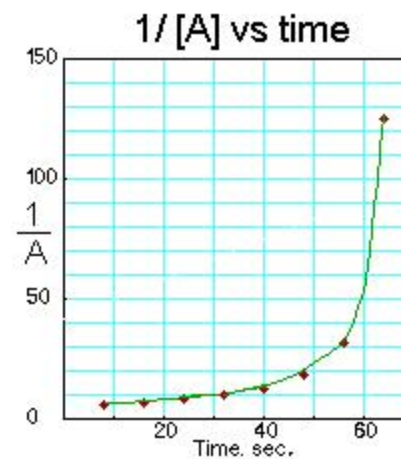
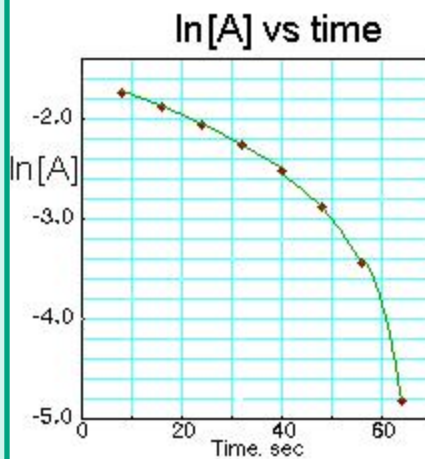
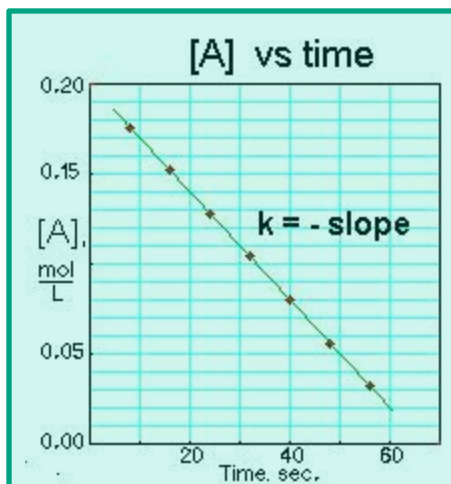
$$[A] - [A]_0 = kt$$

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

Half life for zero order

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

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

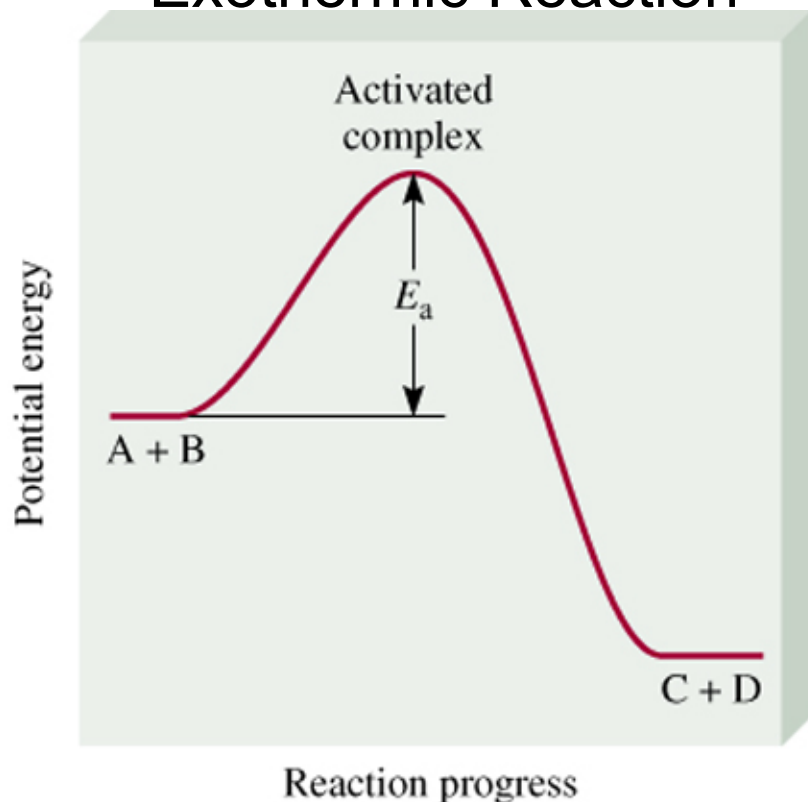


Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

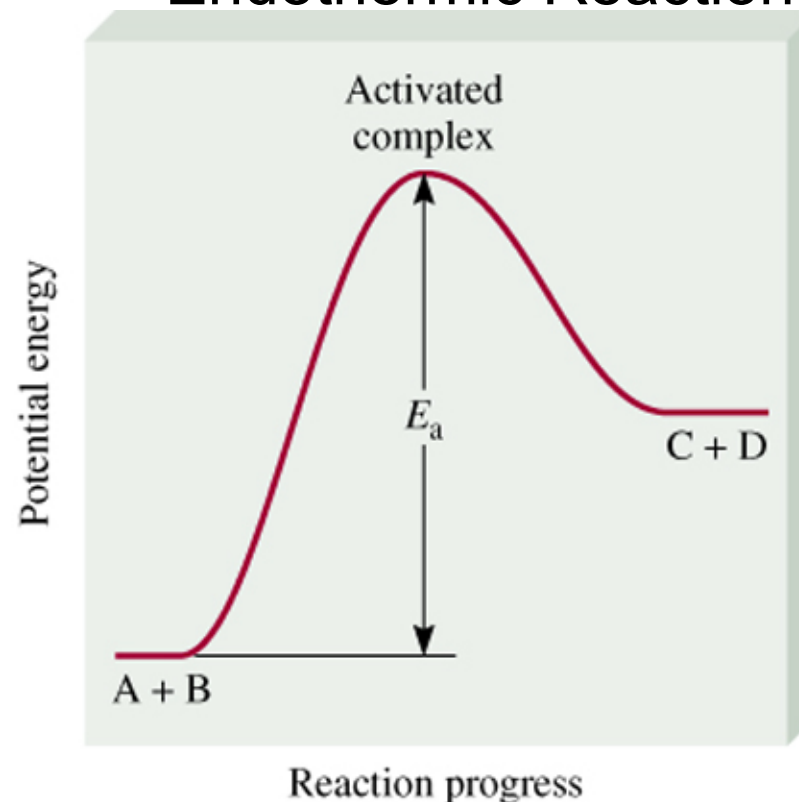
Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] - [A]_0 = -kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k [A]$	$\ln[A] - \ln[A]_0 = -kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k [A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$t_{1/2} = \frac{1}{k[A]_0}$



Exothermic Reaction

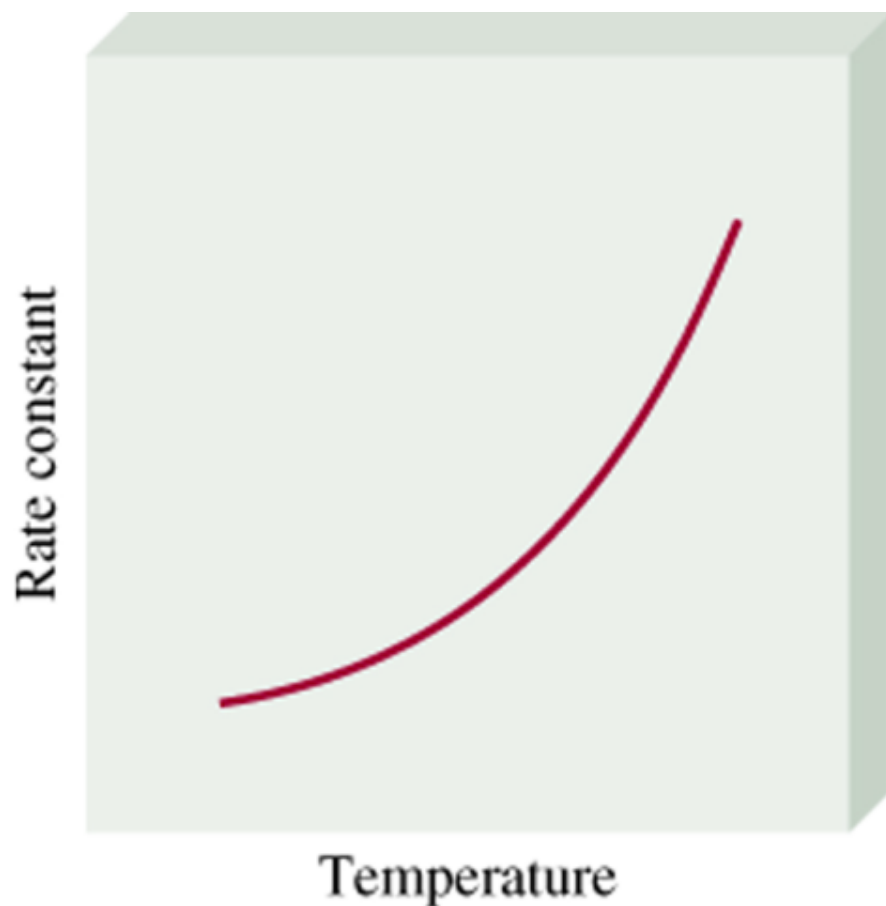


Endothermic Reaction



The **activation energy** (E_a) is the minimum amount of energy required to initiate a chemical reaction.

Temperature Dependence of the Rate Constant



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

(Arrhenius equation)

E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

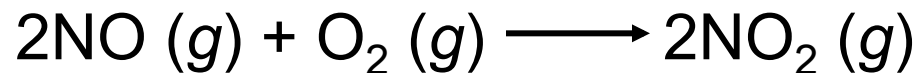
A is the frequency factor

$$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A$$

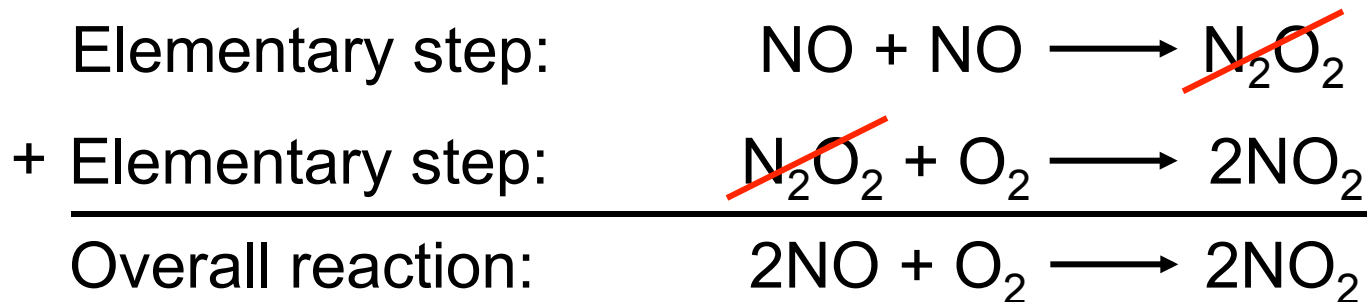
Reaction Mechanisms

The overall progress of a chemical reaction can be represented at the molecular level by a series of simple ***elementary steps*** or ***elementary reactions***.

The sequence of ***elementary steps*** that leads to product formation is the ***reaction mechanism***.



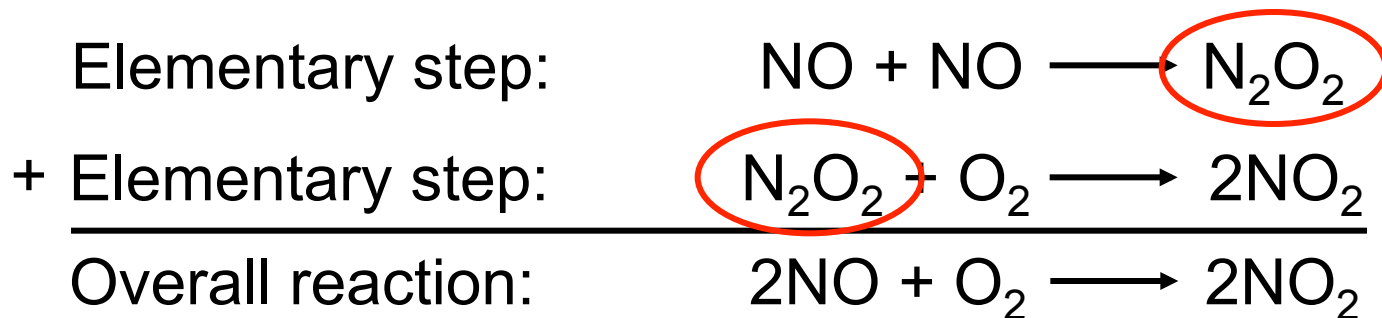
N_2O_2 is detected during the reaction!



Reaction Intermediates

Intermediates are species that appear in a reaction mechanism **but not** in the overall balanced equation.

An **intermediate** is always formed in an early elementary step and consumed in a later elementary step.



Rate Laws and Rate Determining Steps

Writing plausible reaction mechanisms:

- The sum of the elementary steps **must** give the overall balanced equation for the reaction.
- The rate-determining step should predict the same rate law that is determined experimentally.

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



Rate Laws and Elementary Steps

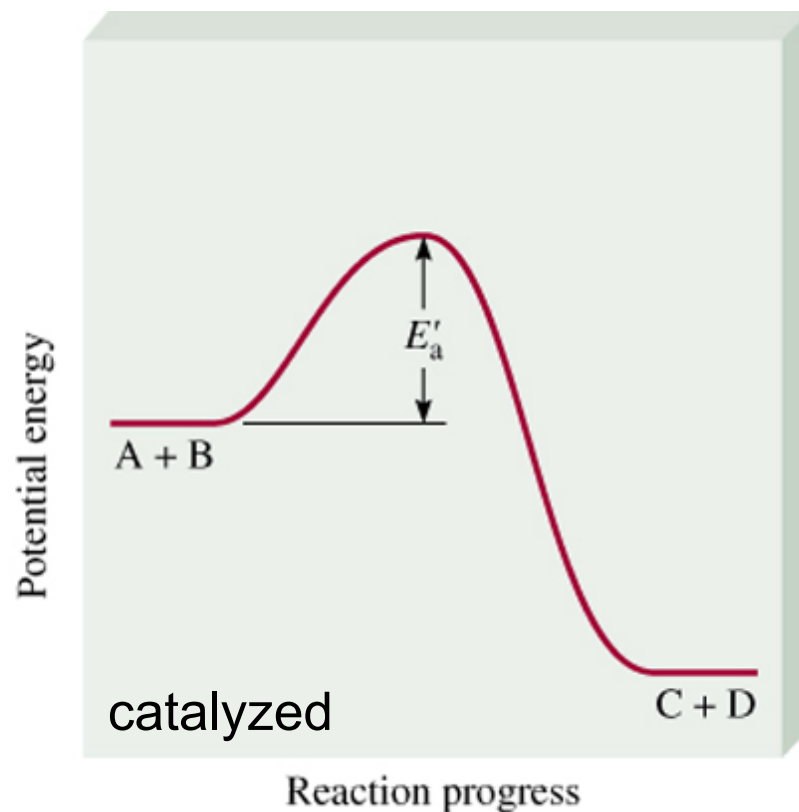
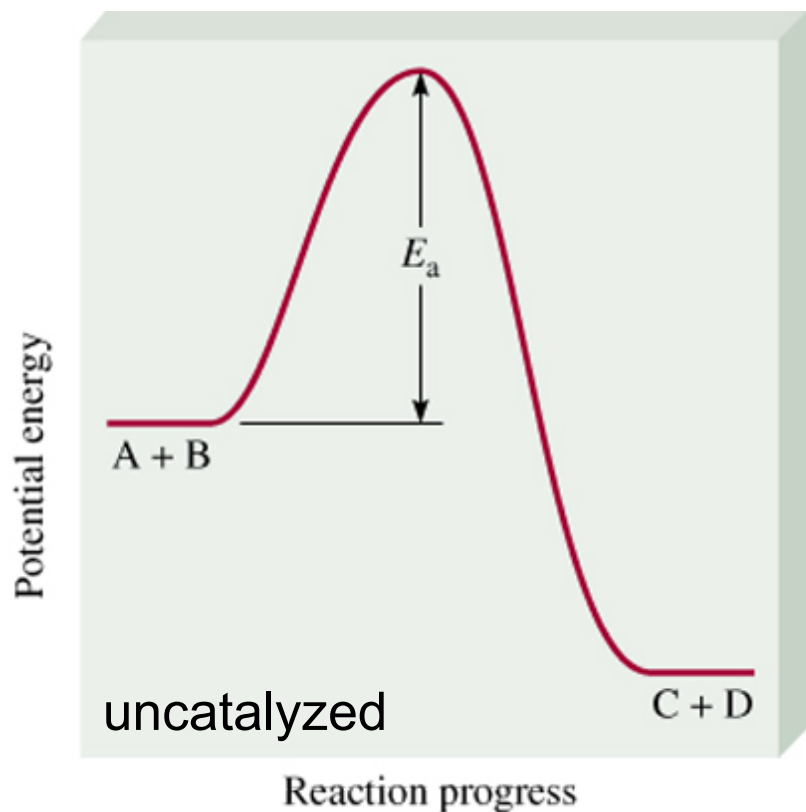
Unimolecular reaction $A \longrightarrow \text{products}$ rate = $k [A]$

Bimolecular reaction $A + B \longrightarrow \text{products}$ rate = $k [A][B]$

Bimolecular reaction $A + A \longrightarrow \text{products}$ rate = $k [A]^2$

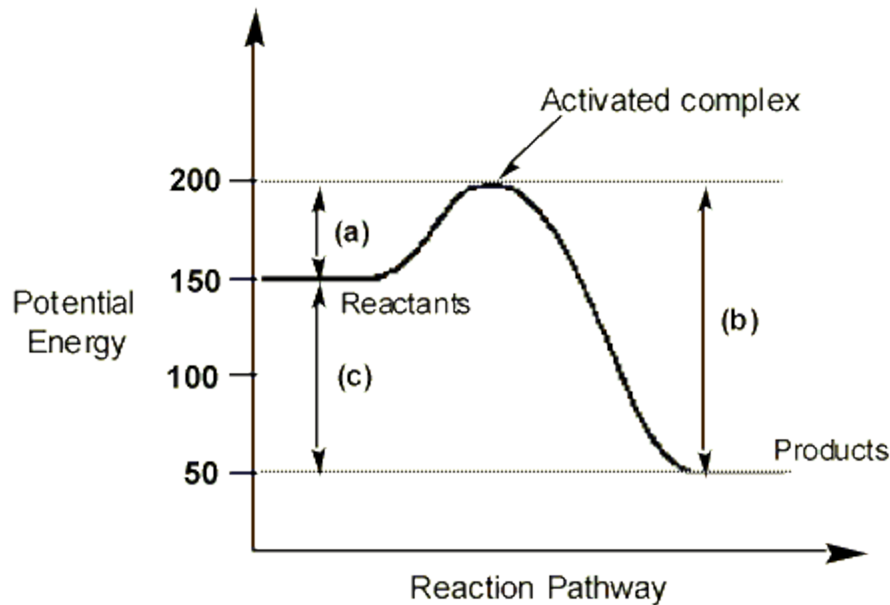
A ***catalyst*** is a substance that increases the rate of a chemical reaction without itself being consumed.

$$E_a \downarrow \quad k \uparrow$$

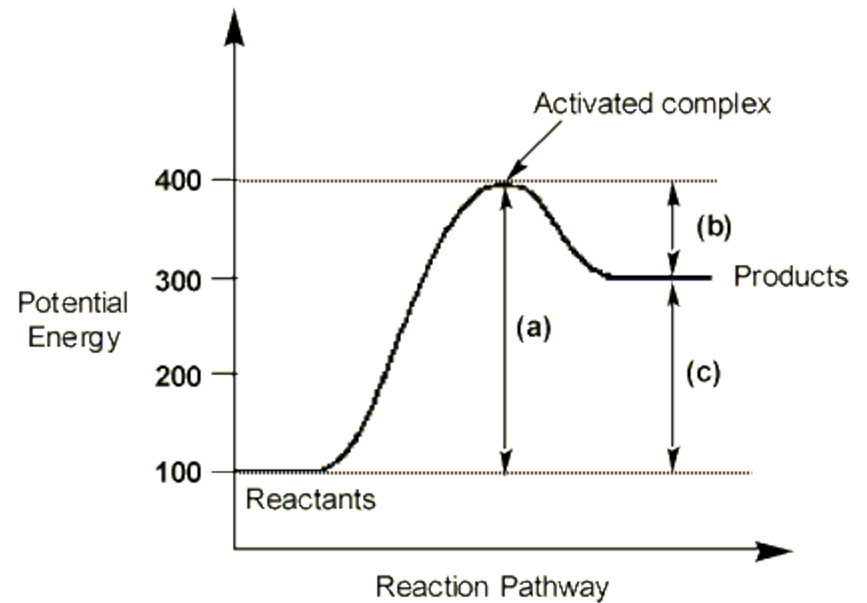


$$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$$

Energy Diagrams



Exothermic



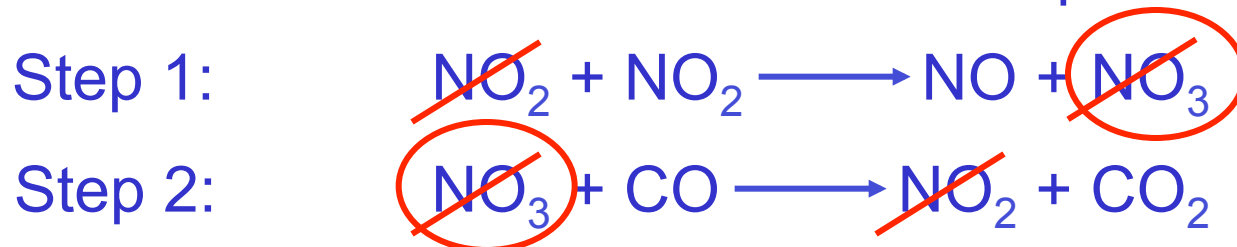
Endothermic

- (a) Activation energy (E_a) for the forward reaction
- (b) Activation energy (E_a) for the reverse reaction
- (c) ΔH

50 kJ/mol	300 kJ/mol
150 kJ/mol	100 kJ/mol
-100 kJ/mol	+200 kJ/mol



The experimental rate law for the reaction between NO_2 and CO to produce NO and CO_2 is $\text{rate} = k[\text{NO}_2]^2$. The reaction is believed to occur via two steps:



What is the equation for the overall reaction?



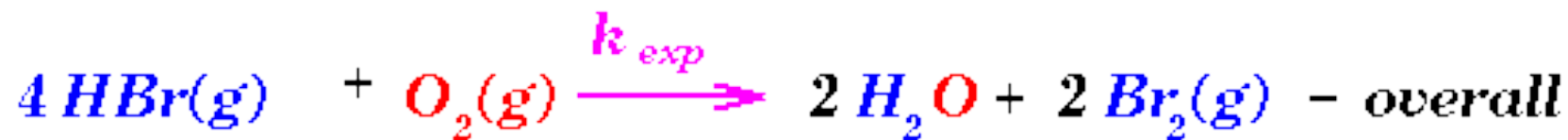
What is the intermediate? Catalyst?



What can you say about the relative rates of steps 1 and 2?

$\text{rate} = k[\text{NO}_2]^2$ is the rate law for step 1 so
step 1 must be slower than step 2

Proposed Mechanism:



Write the rate law for this reaction.

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

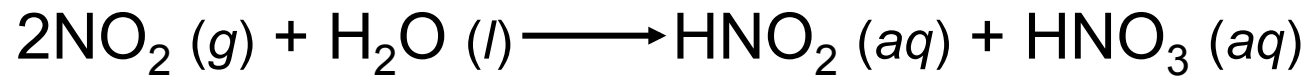
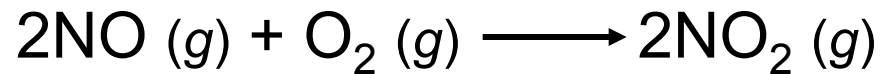
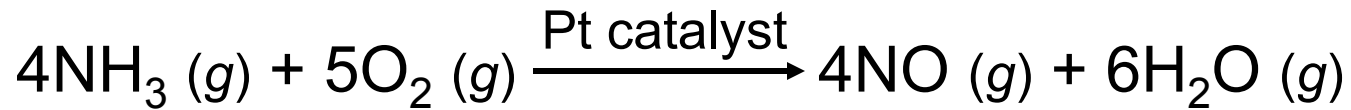
List all intermediates in this reaction.

HOObBr, HOBr

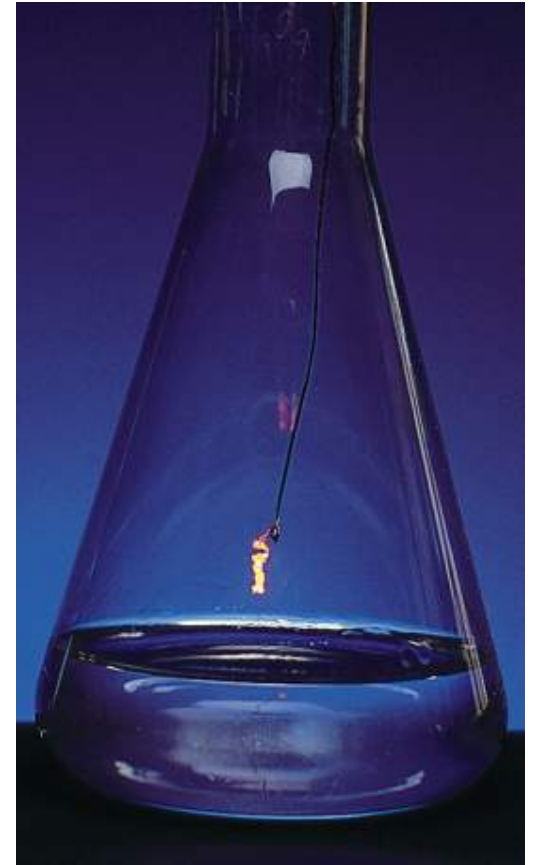
List all catalysts in this reaction.

None

Ostwald Process

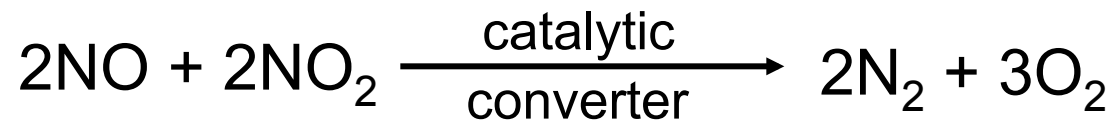
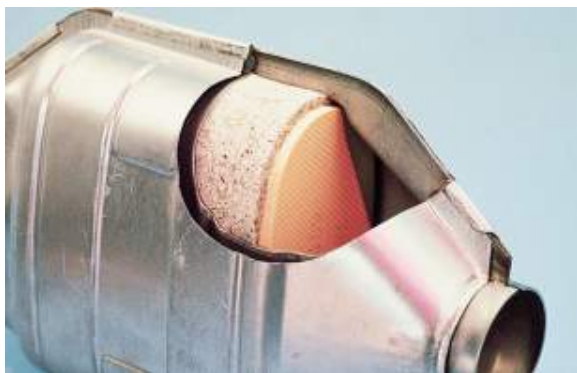
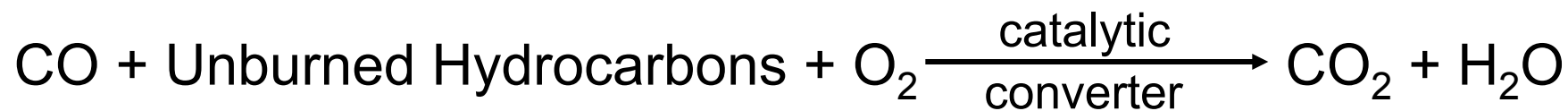
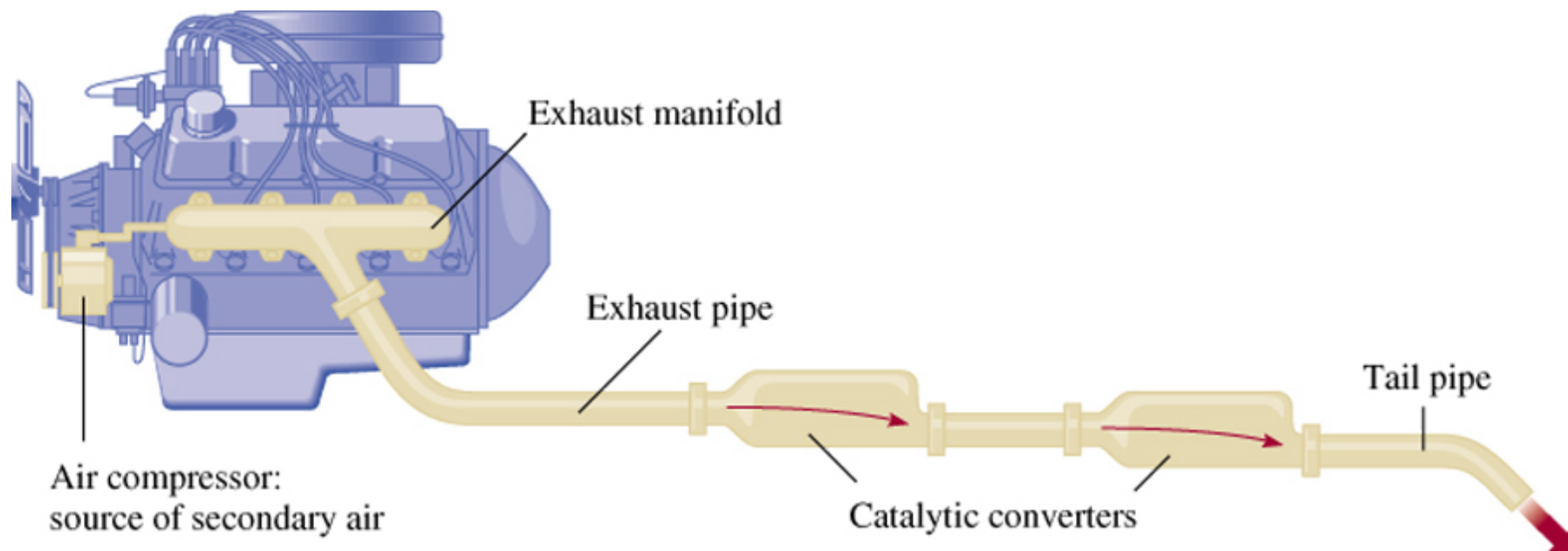


Pt-Rh catalysts used
in Ostwald process



Hot Pt wire
over NH_3 solution

Catalytic Converters



Enzyme Catalysis

