# Lecture 31/36

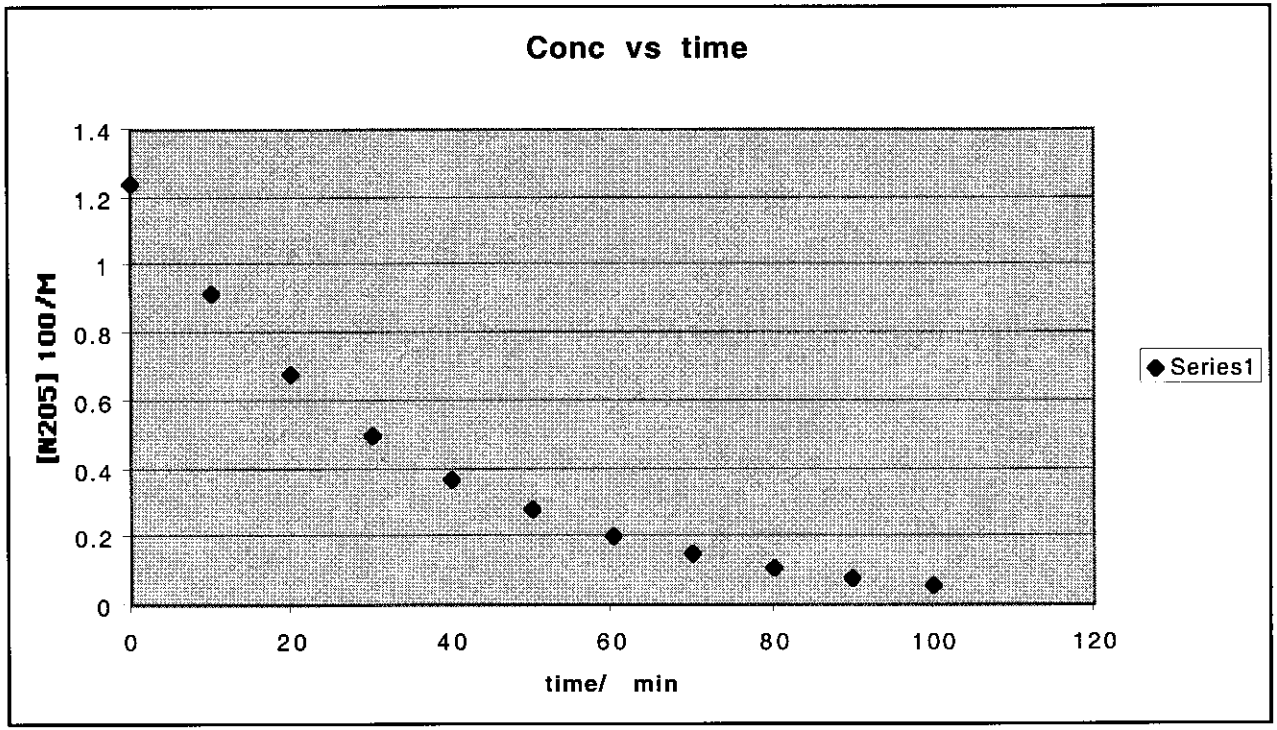
Integrated rate laws

$$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

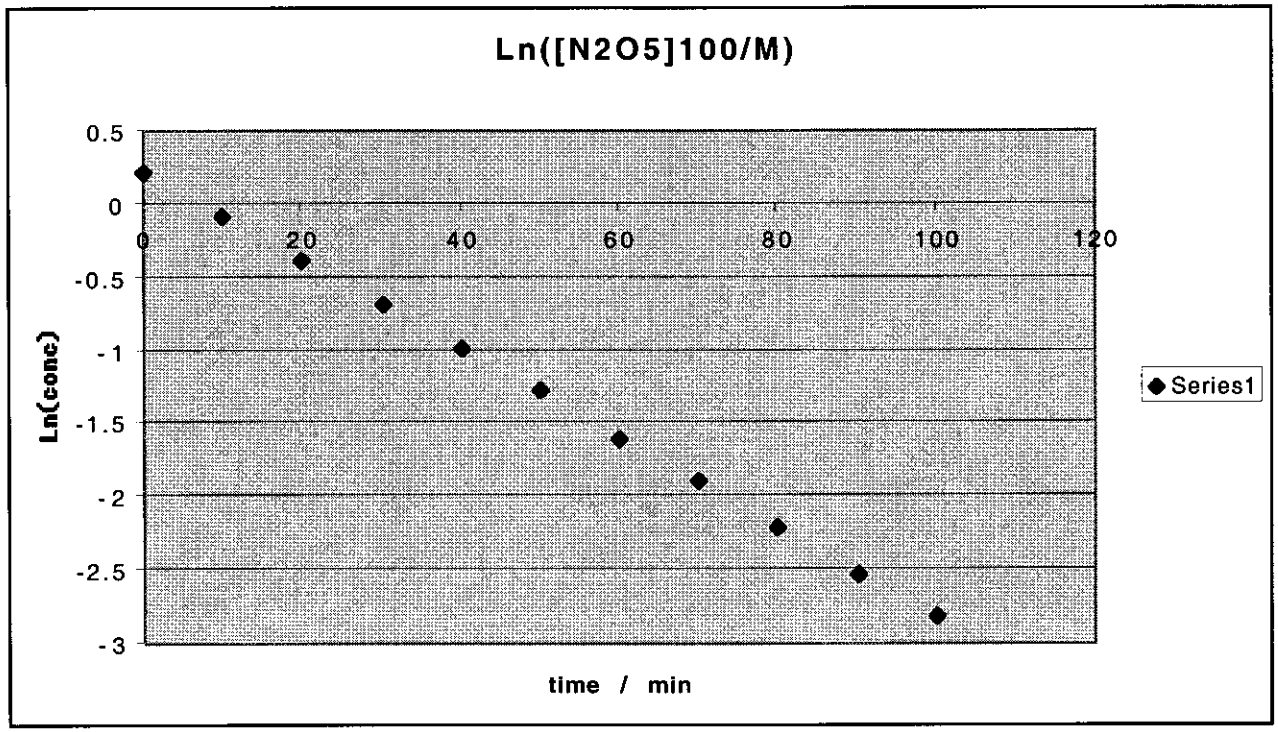
Rate laws

Mechanisms

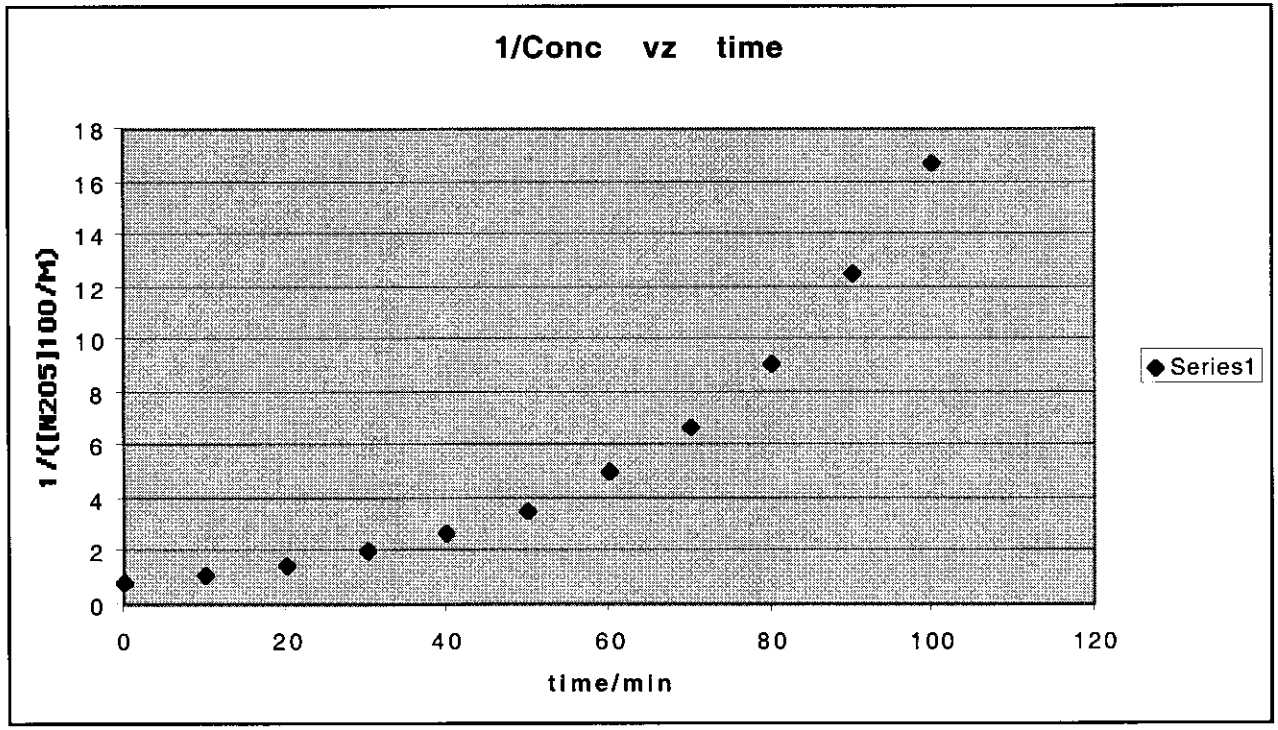
# Zeroth Order



# First Order


Ln([N2O5]100/M)
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
0
20
40
60
80
100
120
Ln(conc)
time / min
Series1

# Second Order



# From data

- The reaction is first order

$$r = k\,[N_2O_5]$$

# Second Order

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

$$r = k[NO_2]^2$$

# Zeroth Order Rate Law

$$2\ NH_3(g) \xrightarrow{W} 3\ N_2(g) + 3\ H_2(g)$$

$$rate = k$$

- Typical of catalytic processes

# First Order Rate Law

$$N_2O_5(g) \rightarrow 2\,N_2O(g) + \frac{1}{2}O_2(g)$$

$$rate = k[N_2O_5]$$

- Mechanism

# Complex Rate Law

$$CH_3COH \rightarrow CH_4 + CO$$

$$rate = k[CH_3COH]^{3/2}$$

- Order is not necessary an integer

# Second Order Rate Law

$$H_2(g) + I_2(g) \rightarrow 2\,HI(g)$$

$$rate = k[H_2][I_2]$$

- This is not a simple bimolecular process

# Complex Rate Law

$$H_2(g) + Br_2(g) \rightarrow 2\ HBr(g)$$

$$rate = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr][Br_2]^{-1}}$$

- Mechanism

# Complex Rate Law

$$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O$$

$$rate = k[BrO_3^-][Br^-][H^+]^2$$

- From the B-Z reaction

# Elementary Processes

- First Order Process

$$A \xrightarrow{k_1} P$$

$$r = k_1[A]$$

- Second Order Process

$$A + B \xrightarrow{k_2} P$$

$$r = k_2[A][B]$$

- Third Order Process

$$A + B + C \xrightarrow{k_3} P$$

$$r = k_3[A][B][C]$$

# Mechanism

- Overall reaction

$$NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$$

$$r_{exp} = k^{obs}[NO_2]^2$$

- Mechanism

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO(g) + NO_3(g) \quad \text{SLOW}$$

$$r_1 = k_1[NO_2]^2$$

$$NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g) \quad \text{FAST}$$

$$r_2 = k_2[NO_3][CO]$$

# Mechanism

- Overall reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

$$r_{exp} = k^{obs}[H_2][I_2]$$

- Mechanism

$$I_2(g) \overset{K_1}{\longleftrightarrow} 2\,I(g)$$

$$I(g) + H_2(g) \overset{K_2}{\longleftrightarrow} H_2I(g)$$

$$H_2I(g) + I(g) \xrightarrow{k_3} 2\,H\;\;I(g) \quad \text{SLOW}$$