

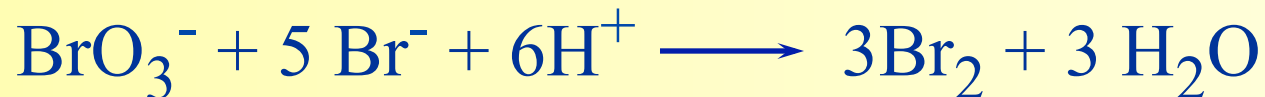
Using Initial Rates to Determine Rate Laws

- A reaction is zero order in a reactant if the change in concentration of that reactant produces no effect.
- A reaction is first order if doubling the concentration causes the rate to double.
- A reaction is n th order if doubling the concentration causes an 2^n increase in rate.
- Note that the rate constant does not depend on concentration.

- This method requires that a reaction be run several times.
- The initial concentrations of the reactants are varied.
 - The goal is to vary only one concentration at a time
- The reaction rate is measured just after the reactants are mixed.

Example

- For the reaction




- The general form of the Rate Law is

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

- We use experimental data to determine the values of m, n, and p

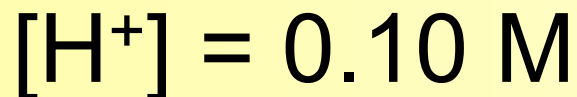
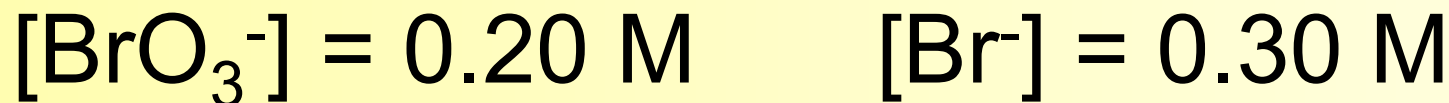
Initial concentrations (M)



$[\text{BrO}_3^-]$	$[\text{Br}^-]$	$[\text{H}^+]$	Rate (M/s)
0.10	0.10	0.10	8.0×10^{-4}
0.20	0.10	0.10	1.6×10^{-3}
0.20	0.20	0.10	3.2×10^{-3}
0.10	0.10	0.20	3.2×10^{-3}

Now we have to see how the rate changes with concentration

1. Determine the Rate Law.
2. Calculate the value of k , and determine its units.
3. Calculate the initial rate of the reaction if the initial concentrations are:



1. $\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$

2. $k = 8.0 \text{ M}^{-3} \text{ s}^{-1}$

3. $\text{Rate} = 4.8 \times 10^{-3} \text{ M s}^{-1}$



<u>Exp</u>	<u>[NH₄⁺]</u>	<u>[NO₂⁻]</u>	<u>Initial Rate</u>
1	0.100 M	0.0050 M	1.35 x 10 ⁻⁷
2	0.100 M	0.010 M	2.70 x 10 ⁻⁷
3	0.200 M	0.010 M	5.40 x 10 ⁻⁷

1. Determine the rate law.
2. Calculate k, and determine its units.



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1. Determine the rate law.

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

2. Calculate k, and determine its units.

$$k = 2.70 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

First Order Reactions

- Goal: convert rate law into a convenient equation to give concentrations as a function of time.
- For a first order reaction, the rate doubles as the concentration of a reactant doubles.

Rate Law

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

Integrated
Rate Law

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

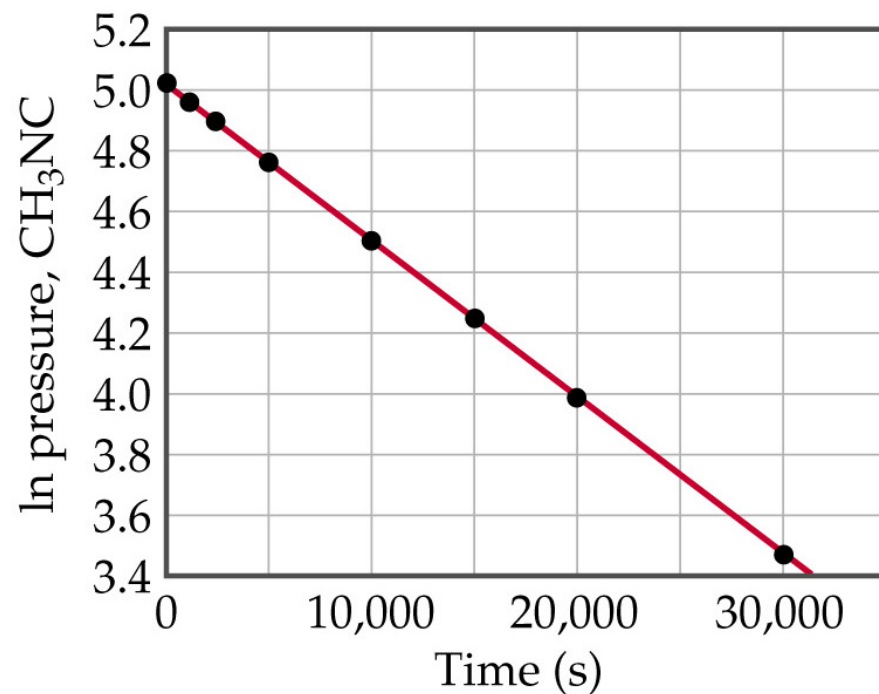
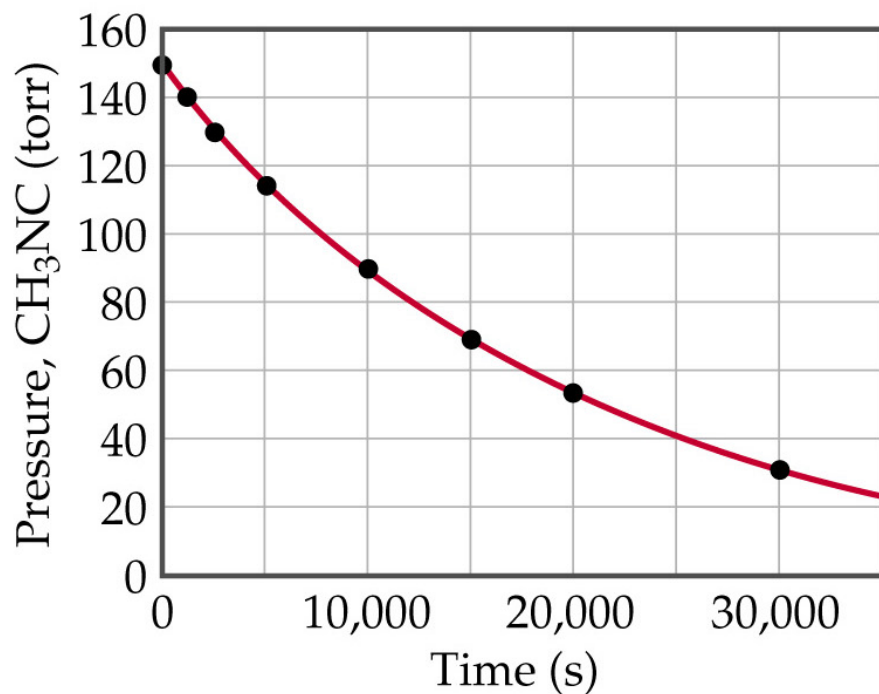
$$\ln \frac{[A]_t}{[A]_0} = -kt$$

The Change of Concentration with Time

- A plot of $\ln[A]_t$ versus t is a straight line with slope $-k$ and intercept $\ln[A]_0$ (for first order)
- In the above we use the natural logarithm, \ln , which is log to the base e .

First Order Reactions

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



Second Order Reactions

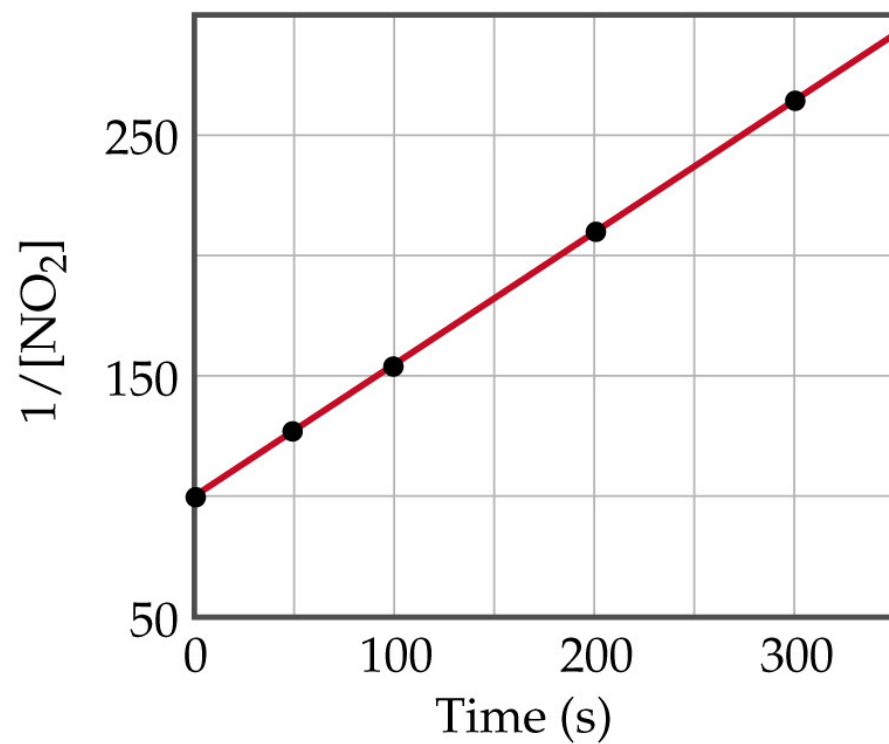
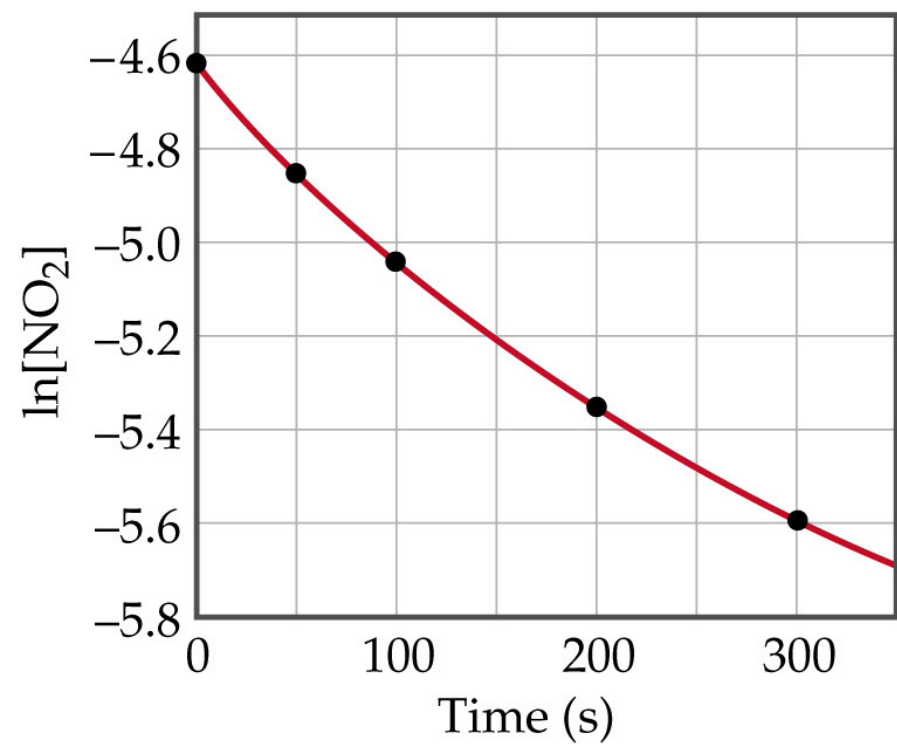
- For a second order reaction with just one reactant

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

- A plot of $1/[A]_t$ versus t is a straight line with slope k and intercept $1/[A]_0$
- For a second order reaction, a plot of $\ln[A]_t$ vs. t is not linear.

Second Order Reactions

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



Zero Order Rate Law

- Rate = $k[A]^0 = k$
- Rate does not change with concentration.
- Integrated $[A] = -kt + [A]_0$
- When $[A] = [A]_0 / 2$ $t = t_{1/2}$
- $t_{1/2} = [A]_0 / 2k$

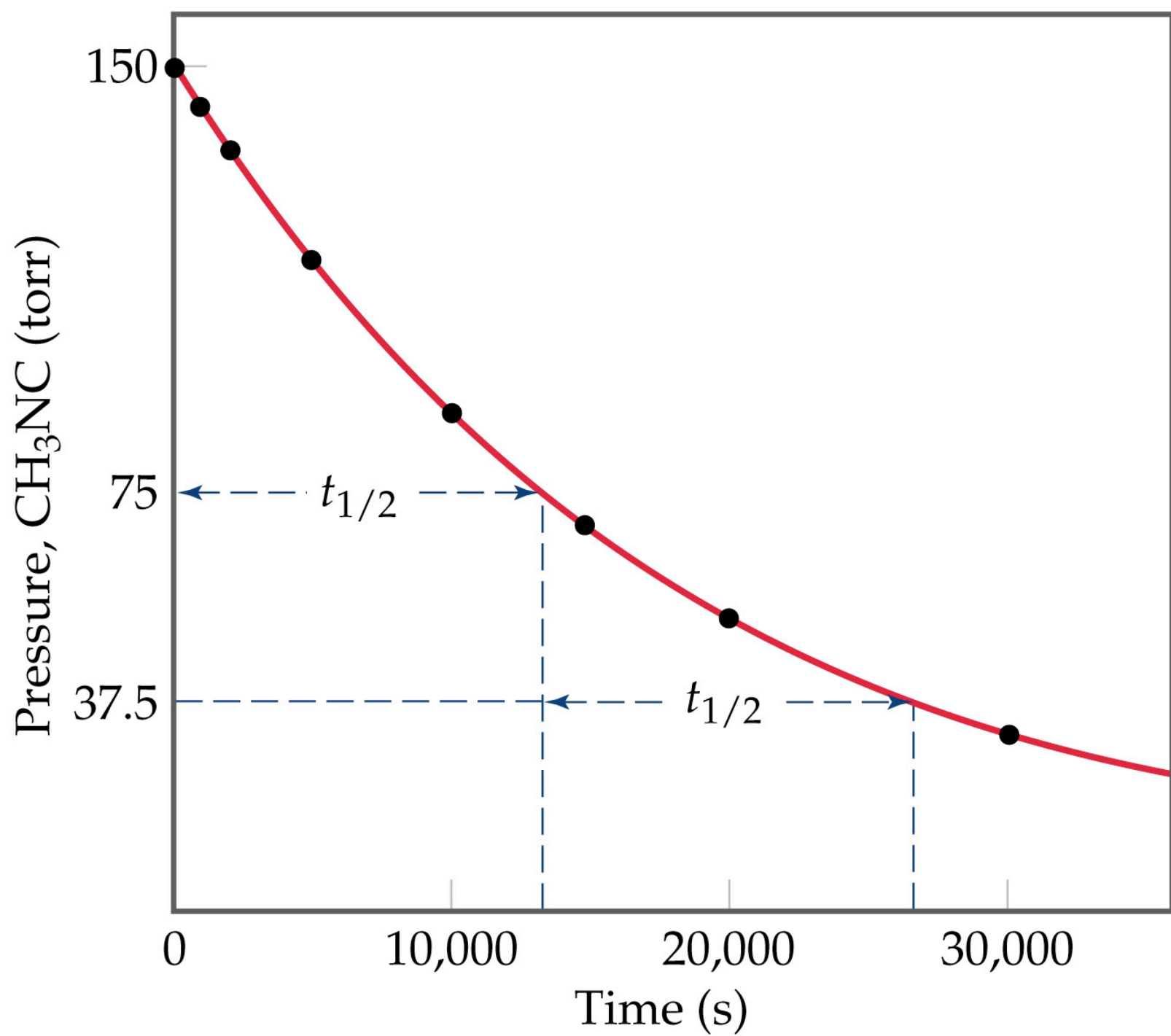
Zero Order Rate Law

- Most often when reaction happens on a surface because the surface area stays constant.
- Also applies to enzyme chemistry.

Half-Life

- Half-life is the time taken for the concentration of a reactant to drop to half its original value.
- For a first order process, half life, $t_{1/2}$ is the time taken for $[A]_0$ to reach $\frac{1}{2}[A]_0$.
- Mathematically,

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



For a second order reaction, half-life depends on the initial concentration:

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

Summary of Rate Laws

	Zero Order	1 st Order	2 nd Order
Diff. Rate Law	K	$k[A]$	$K[A]^2$
Int. Rate Law	$[A] = -kt + [A]_0$	$\ln [A] = -kt + \ln [A]_0$	$1/[A] = kt + 1/[A]_0$
Straight Line Plot	$[A]$ vs. t $m = -k$	$\ln [A]$ vs. t $m = -k$	$1/[A]$ vs. t $m = k$
Half-Life	$[A]_0/2k$	$(\ln 2)/k$	$1/k[A]_0$