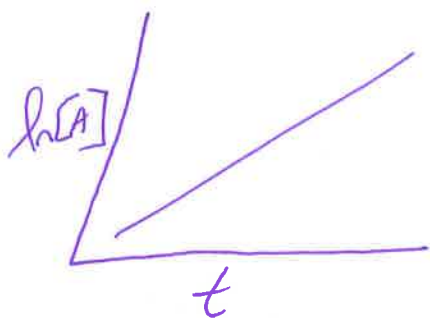


AP Chemistry
KINETICS REVIEW

First Order

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

Integrated Rate Law: $\ln[A]_t = -kt + \ln[A]_0$



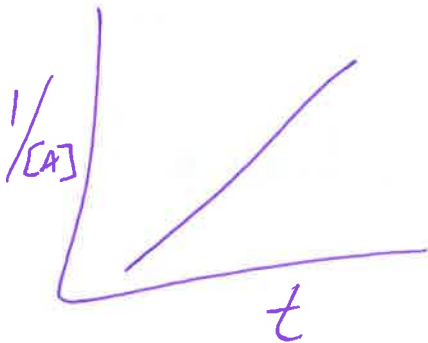
slope = $-k$
y-int = $\ln[A]_0$

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

Second Order

Rate Law: $\text{Rate} = k[A]^2$

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



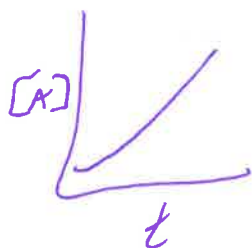
slope = k
y-int = $\frac{1}{[A]_0}$

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

Zero Order

RL: $\text{Rate} = k[A]^0 = k$

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



slope = $-k$
y-int = $[A]_0$

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

Example:

The reaction of butyl-bromide $(\text{CH}_3)_3\text{CBr}$ with water is represented by the equation:



The following data were obtained from three experiments using the method of initial rates:

	Initial $[(\text{CH}_3)_3\text{CBr}]$ mol L^{-1}	Initial $[\text{H}_2\text{O}]$ mol L^{-1}	Initial rate $\text{mol L}^{-1}\text{min}^{-1}$
Experiment 1	5.0×10^{-2}	2.0×10^{-2}	2.0×10^{-6}
Experiment 2	5.0×10^{-2}	4.0×10^{-2}	2.0×10^{-6}
Experiment 3	1.0×10^{-1}	4.0×10^{-2}	4.0×10^{-6}

- What is the order with respect to $(\text{CH}_3)_3\text{CBr}$?
- What is the order with respect to H_2O ?
- What is the overall order of the reaction?
- Write the rate equation.
- Calculate the rate constant k for the reaction, including units.
- What is the half life of this reaction?

Rate = $k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n$

$$\frac{E_{x2}}{E_{x1}} = \frac{2 \times 10^{-6}}{2 \times 10^{-6}} = \frac{k(5 \times 10^{-2})^m(4 \times 10^{-2})^n}{k(5 \times 10^{-2})^m(2 \times 10^{-2})^n}$$

$$1 = \frac{2^n}{2^n} \Rightarrow n = 0$$

$$\frac{E_{x3}}{E_{x2}} = \frac{4 \times 10^{-6}}{2 \times 10^{-6}} = \frac{k(1 \times 10^{-1})^m(4 \times 10^{-2})^n}{k(5 \times 10^{-2})^m(4 \times 10^{-2})^n}$$

$$2 = \frac{2^m}{2^m} \Rightarrow m = 1$$

a) 1st

b) \emptyset

c) 1st

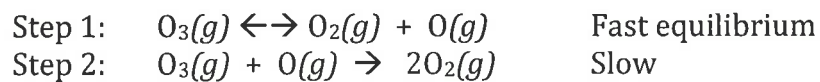
d) Rate = $k[(\text{CH}_3)_3\text{CBr}]$

e) $4 \times 10^{-6} \text{ mol/L}_{\text{min}} = k(1 \times 10^{-1} \frac{\text{mol}}{\text{L}})$ $k = 4 \times 10^{-5} \text{ min}^{-1}$

f) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4 \times 10^{-5}} = 17325 \text{ min}$

Example:

The decomposition of ozone in the upper atmosphere to dioxygen occurs by a two-step mechanism. The first step is a fast reversible step and the second is a slow reaction between an oxygen atom and an ozone molecule:



- Which is the rate determining step?
- Write the rate equation for the overall reaction.

a) Step 2 (slowest step)

b) $\text{Rate} = k[\text{O}_3][\text{O}]$ ←

$$K = \frac{[\text{O}][\text{O}_2]}{[\text{O}_3]} \quad [\text{O}] = \frac{K[\text{O}_3]}{[\text{O}_2]}$$

$$\boxed{\text{Rate} = k'[\text{O}_3]^2[\text{O}_2]^{-1}}$$

