5.60 Thermodynamics & Kinetics
Spring 2008

Kinetics: Reaction Rates, Orders, Half Lives

$$aA + bB \rightarrow cC + dD$$

Rate of Reaction:

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

Experimentally $\Rightarrow$ $\text{Rate} = k\prod_{i=1}^{N} C_i^{\gamma_i}$

Where
- k = rate constant
- C_i = Concentration of Reactant "i"
- γ_i = Order of reaction with respect to reactant "i"

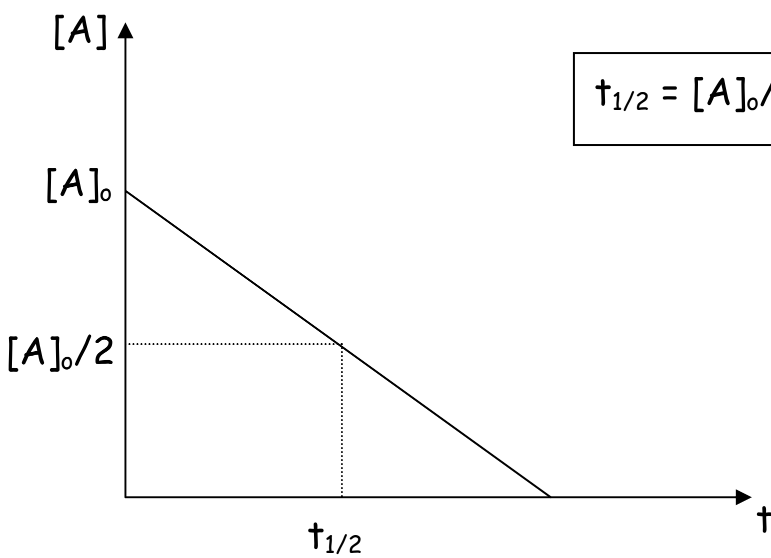
$$\sum_i \gamma_i = \text{Overall rate of reaction}$$

I) Zero Order Reactions (rare)

$A \rightarrow$ products

$$-\frac{d[A]}{dt} = k$$ {k is in [moles/(liter sec)]}

$$\boxed{[A] = -kt + [A]_o}$$



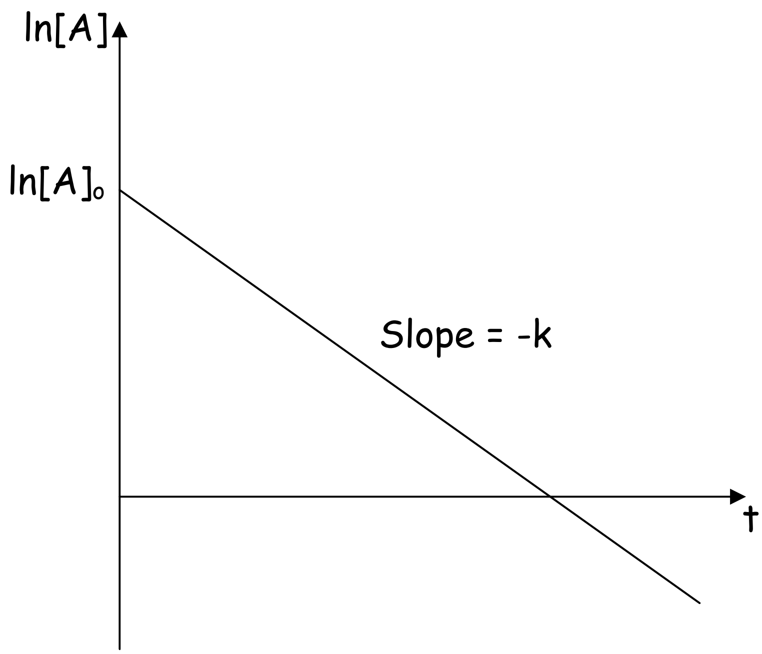
$$t_{1/2} = [A]_o/(2k)$$

II) First Order Reactions

$A \rightarrow$ products

$$-\frac{d[A]}{dt} = k[A]$$ {k is in [1/sec]}

$[A] = [A]_o e^{-kt}$ $\ln[A] = -kt + \ln[A]_o$



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

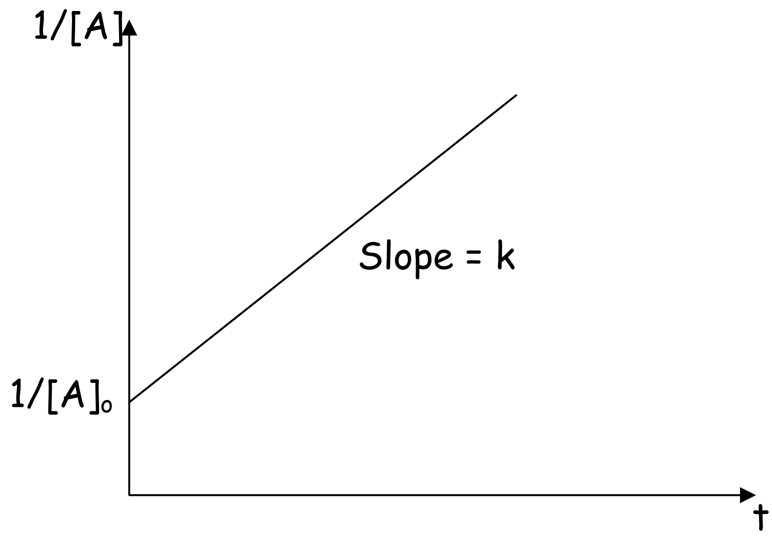
III) Second Order Reactions

a) Second order in one component

$A \rightarrow$ products

$$-\frac{d[A]}{dt} = k[A]^2$$

$$\boxed{\frac{1}{[A]} = \frac{1}{[A]_o} + kt}$$



$$\boxed{t_{1/2} = 1/(k[A]_o)}$$

b) First order in each of two components

A +B $\rightarrow$ products

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

$$\boxed{kt = \frac{1}{[A]_o - [B]_o} \ln \frac{[A][B]_o}{[A]_o[B]} \qquad [A]_o \neq [B]_o}$$

Special cases:

i) $[A]_o = [B]_o \Rightarrow$ $\boxed{\frac{1}{[A]} = \frac{1}{[A]_o} + kt \qquad [A] = [B]}$

This is like 2nd order in one component

ii) $[B]_o << [A]_o \Rightarrow$ $\boxed{[B] = [B]_o e^{-k't}}$

where $\boxed{k' = [A]_o k}$

This is pseudo 1st order

Determining Orders of Reactions

I) Getting the data

a) Quench the reaction, measure concentrations
b) For gas phase, measure pressure vs. time
c) Spectroscopically follow reactants/products

Etc…

II) Analyzing the data

A) Reactions with one reactant:

$$A \rightarrow \text{products}$$

a) Plot or analyze $[A]$ vs. t
$\ln[A]$ vs. t
$1/[A]$ vs. t
…

and find which gives a straight line.

b) Half-life method: measure $t_{1/2}$ vs. $[A]_o$

1st order $\rightarrow$ $t_{1/2} \propto [A]_o^0$

2nd order $\rightarrow$ $t_{1/2} \propto [A]_o^{-1}$

etc….

c) Multiple lifetimes ($t_{3/4}$ and $t_{1/2}$) (at $t_{3/4}$, $[A]=[A]_o/4$)

$$1^{st} \text{ order } \rightarrow t_{3/4} = (2\ln 2)/k \Rightarrow \frac{t_{3/4}}{t_{1/2}} = 2$$

$$2^{nd} \text{ order } \rightarrow t_{3/4} = 3/([A]_o k) \Rightarrow \frac{t_{3/4}}{t_{1/2}} = 3$$

B) Reactions with <u>more than one</u> reactant:

e.g. $A + B + C \rightarrow$ products

a) <u>Initial Rate Method</u>

For $[A]_o$ $$\left.\frac{\Delta[A]}{\Delta t}\right|_{t=0} = R_o \approx k[A]_o^{\alpha}[B]_o^{\beta}[C]_o^{\gamma}$$

For $[A]_o^{/}$ $$\left.\frac{\Delta[A]^{/}}{\Delta t}\right|_{t=0} = R_o^{/} \approx k[A]_o^{/\,\alpha}[B]_o^{\beta}[C]_o^{\gamma}$$

Experimentally determine $$\frac{R_o}{R_o^{/}} = \left(\frac{[A]_o}{[A]_o^{/}}\right)^{\alpha}$$

If $2[A]_o^{/} = [A]_o$ then, if $\frac{R_o}{R_o^{/}} = 1 \Rightarrow \alpha = 1$

if $\frac{R_o}{R_o^{/}} = \sqrt{2} \Rightarrow \alpha = ½$

if $\frac{R_o}{R_o^{/}} = 2 \Rightarrow \alpha = 1$

if $\frac{R_o}{R_o^{/}} = 4 \Rightarrow \alpha = 2$

etc…

b) <u>Flooding or Isolation</u> (goal is to try to make problem look like a one-reactant system)

take $[A]_o \ll [B]_o$, $[C]_o$

e.g. flood system with B and C

Then $[B] \sim [B]_o$ and $[C] \sim [C]_o$

So that $$-\frac{d[A]}{dt} \approx k'[A]^{\alpha}$$

Where $$k' = k[B]_o^{\beta}[C]_o^{\gamma}$$

The reaction then becomes pseudo α-order with one reactant.