Rate Laws (McQuarrie Ch28)

\[ aA + bB \rightleftharpoons gG + hH \]

\[ \sum v_i I = 0 \quad \text{eg} \quad v_A = -a \quad v_G = g \]

Reaction coordinate \( \xi \)

\[ n_A(t) = n_A(0) + v_A \xi(t) = n_A(0) - a \xi(t) \]

\[ n_G(t) = n_G(0) + v_G \xi(t) = n_G(0) + g \xi(t) \]
\[ n_A(t) = n_A(0) + \nu_A \xi(t) = n_A(0) - \alpha \xi(t) \]

\[ \Delta n_A(t) = n_A(t) - n_A(0) = \nu_A \xi(t) \]

\[ \Delta n_i(t) = \nu_i \xi(t) \]

limit where \( t \) is small

\[ \xi = \frac{\phi}{2} \]

\[ \Delta n = d \eta \]

differential

\[ d n_i = \nu_i \, d \xi \]
\[ \frac{dn_i}{dt} = v_i \frac{dP}{dt} \]

"divide" both sides by \( dt \)

\[ \frac{\frac{dn_i}{dt}}{\frac{dt}{dt}} = \frac{v_i \frac{dP}{dt}}{\frac{dt}{dt}} \Rightarrow \frac{dP}{dt} = \frac{1}{v_i} \frac{dn_i}{dt} \]

Divide both sides by volume \( V \)

\[ \frac{1}{V} \frac{\frac{dP}{dt}}{\frac{dt}{dt}} = \frac{1}{V} \frac{1}{v_i} \frac{dn_i}{dt} \]

\[ \frac{1}{V} \frac{dP}{dt} + \frac{1}{v_i} \frac{dn_i}{dt} \]

\[ \text{rate of reaction at time} \ t \]
\[ \frac{1}{V} \frac{d\rho}{dt} = \frac{1}{V_i} \frac{d[p][I]}{dt} \]

E.g., \( 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \)

\[ \nu(t) = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{1}{1} \frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} \]

Want a rate law

tells us rate at time \( t \)

given concentrations
$$2 \text{NO} \ (g) + \text{O}_2 \ (g) \rightarrow 2 \text{NO}_2 \ (g)$$

**Elementary Reaction**  
Direct collision between molecules reacting to form product, no hidden steps

**Rate law for this reaction**

$$V(t) = k \left[ \text{A} \right]^{n_A} \left[ \text{B} \right]^{n_B} \ldots$$

$$V(t) = k \left[ \text{NO}_2 \right]^2 \left[ \text{O}_2 \right]$$
For most reactions, can't guess rate law, have to determine using experiments.

Note: \( v(t) \) always has the same units \( \frac{1}{V} \frac{d\theta}{dt} \).

Units: \( \frac{\text{Mole}}{\text{liter}} \cdot \frac{1}{\text{s}} = \text{M}/\text{s} \)

Units of \( k \) depend on reaction.
Don't know rate law, guess:

\[ v(t) = k [A]^{m_A} [B]^{m_B} \]

Order is \( m_A + m_B + \ldots \)

\( m_A \) order in \( A \), \( m_B \) order in \( B \)

For example

\[ 2 \text{NO} + \text{O}_2 \]

\[ k [\text{NO}]^2 [\text{O}_2] \]

3rd order

2nd order in \( \text{NO} \)

1st order in \( \text{O}_2 \)
\[ v(t) = K [A]^{m_A} [B]^{m_B} \]

Units of \( M/\text{s} \)

0th order reaction

\[ v(t) = k \]

Units of \( k \)

1st order reaction

\[ v(t) = k [A] \]

Units of \( 1/\text{s} \)

2nd order reaction

\[ v(t) = k [A]^2 = k [A][B] \]

Units of \( 1/\text{M} \cdot \text{sec} \)
Can also have rate laws aren't in this form

$$H_2 + Br_2 \rightarrow 2HBr$$

$$\nu(t) = \frac{k'[H_2][Br_2]^{\frac{1}{2}}}{1+k''[HBr][Br_2]}$$

next chapter: reaction mechanisms
How do we determine rate laws using experiments

1. Method of isolation

\[ aA + bB \rightarrow \]

\[ v = k \left[ A \right]^m \left[ B \right]^n \]

Make A in excess (a lot)

\[ K \left[ A \right]^m = k' \]

\[ K' \left[ B \right]^n = k'' \]
\[ V(t) = k'[B]^mB \]

\[-\frac{1}{b} \frac{d[B]}{dt} = V(t) \quad \text{measure} \]

\[ \ln(V(t)) = m_B \ln[B] + \ln(k') \]

Make \( B \) in excess \( V(t) = k''[A]^nA \)

\[ \ln(V(t)) = m_A \ln[A] + \ln(k'') \]
But can't always have a big excess

(2) Method of initial rates

\[ [A]_0, [B]_0 \]

\[ \nu(t) \approx -\frac{1}{a} \frac{\Delta [A]}{\Delta t} = k \ [A]_0^{m_A} \ [B]_0^{m_B} \]

Do multiple measurements

\[ \nu_1 = k \ [A]_0^{m_A} \ [B]_1^{m_B} \]

\[ \nu_2 = k \ [A]_0^{m_A} \ [B]_2^{m_B} \]
a) $V_1 = k [AT_0]_{mA} [B]_{mB} > \frac{1}{2}$ experiments
$V_2 = k [AT_0]_{mA} [B]_{mB}$

$\frac{V_1}{V_2} = \left( \frac{[B]_1}{[B]_2} \right)^{mB} < \text{unknown}$

Measure \( \uparrow \text{determine} \)

$m_B = \ln \left( \frac{V_1}{V_2} \right) / \ln \left( \frac{[B]_1}{[B]_2} \right)$

b) Do same to get $m_A$
c) \( V(t) = k[CA]_x^m [BJ]_y^m \)

\[ \begin{array}{cccc}
\text{exp. 1} & \text{V(t)} & [CA] & [BJ] & [CA]_x^m [BJ]_y^m \\
\text{exp. 2} & - & - & - & - \\
\text{exp. 3} & - & - & - & - \\
\end{array} \]

\( k = \text{test 1, test 2, test 3} \)

**Limitation here:** for slowish reactions
First order reactions

\[ A \rightarrow aB + cD + \ldots \]

\[ \nu(t) = k[A] \]
\[ = -\frac{d[A]}{dt} = k[A] \Rightarrow \frac{1}{[A]} \frac{d[A]}{dt} = -k \]

\[ [A](t) = [A]_0 e^{-kt} \]

Plot \( \ln\left(\frac{[A](t)}{[A]_0}\right) \) vs. \( t \) is linear
Slow reaction

\[ \text{slow reaction slope is } -k \]

Fast reaction

\[ \ln \left( \frac{A}{A_0} \right) = -kt \]

Special property

\[ [A] \left( t_{1/2} \right) = \frac{1}{2} [A_0] \]

\[ \ln \left( \frac{1}{2} \right) = -kt_{1/2} \Rightarrow t_{1/2} = \frac{\ln(2)}{k} \approx 0.693 \]

time is independent of initial concentration
Example 28-3

\[ A \rightarrow aB \]

\[-\frac{dA}{dt} = k[A] = \frac{1}{b} \frac{d[B]}{dt} \]

\[ d[B] \]

\[ \frac{d[B]}{dt} = bk[A] = bk[A]_0 e^{-kt} \]

\[ B(\tau) - B(0) = \int_0^\tau b k[A]_0 e^{-kt} \]

\[ \int e^{-kt} = -\frac{1}{k} e^{-kt} \]
\[ B(t) - B(0) = \int_0^t bk [A]_0 e^{-kt} \]

\[ \int e^{-kt} = -\frac{1}{k} e^{-kt} \]

\[ = b[A]_0 (1 - e^{-kt}) \]

\[ [B](t) = [B]_0 + b[A]_0 (1 - e^{-kt}) \]

Sketch: 
- \( [B]_0 \) and \( B_0 + b[A]_0 \) at the y-axis
- \( \frac{[B]}{[B]_0} \) as a sigmoidal function of \( t \)
2nd order

\[ -p[A] = k[A]^2 \]

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

\[ \Rightarrow [A] = [A]_0 \]

Plot \( \frac{1}{[A]} \) vs time, slope = rate constant

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

depends on how much you start with
Reversible reactions

\[ A \stackrel{k}{\rightleftharpoons} B \text{ as example} \]

\[-\frac{d[A]}{dt} = \frac{d[B]}{dt} \implies \frac{d[A]}{dt} + \frac{d[B]}{dt} = 0\]

\[-\frac{d[A]}{dt} = k[A] - k_{-1}[B]\]

\[[A] + [B] = \text{constant}\]
\[ [A] + [B] = \text{const} \]

Start experiment with \([B]_0 = 0\)

\[ [B] = [A]_0 - [A] \]

\[ \frac{d[A]}{dt} = -k[A] + k_{-1} ([A]_0 - [A]) \]

\[ = -(k + k_{-1})[A] + k_{-1} [A]_0 \]

Check

\[ [A] - [A]_{\text{eq}} = ([A]_0 - [A]_{\text{eq}}) e^{-(k + k_{-1})t} \]
\[ \frac{[A] - [A]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{([A]_0 - [A]_{\text{eq}})}{[A]_{\text{eq}}} e^{-(k + k_{-1})t} \]