Rate Laws (Ch 28 McQuarrie)

\[ aA + bB \rightleftharpoons cC + dD \]

Reaction coordinate $\xi$

\[ n_A(t) = n_A(0) + \nu_A \xi(t) \]

\[ n_D(t) = n_D(0) + \nu_D \xi(t) + \Delta \]

$G$

$U$

$\xi$

$\nu$'s neg for reactants
\[ n_A(t) - n_A(0) = -\nu_A \left[ \frac{\xi(t) - \xi(0)}{\epsilon} \right] \]

\[ \text{Im} \quad t > 0 \]

\[ \frac{dn_A}{dt} = \nu_A \frac{d\xi}{dt} \]
\[ \frac{d n_A}{d t} = n_A \frac{d n_B}{d t} \]

\[ \frac{d n_B}{d t} = \frac{1}{V_A} \frac{d n_A}{d t} = \frac{1}{V_B} \frac{d n_B}{d t} \]

reaction rate \[ r(t) = \frac{1}{V} \frac{d n_B}{d t} \]
\[ 2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g) \]

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

If we can measure any concentration, we can calculate the reaction rate.
Goal: a rate law tells us the rate given just concentrations

Usually looks like

\[ r(t) = k[A]^m[A]^n \]

Special case - elementary reaction

Reactants collide with each other
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Reactants collide with each other

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

so could be

\[ = k [NO]^2 [O_2] \]
Key: Have to determine rate law experimentally.

Example: $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ actually a multistep process.

\[ r(t) = k' [\text{H}_2][\text{Br}_2]^{\frac{1}{2}} \]

\[ 1 + k'' \frac{[\text{HBr}]}{[\text{Br}_2]} \]
Important to consider units

\[ \dot{c}(t) \text{ always has units } \frac{M}{s} = \frac{mol}{L \cdot s} \]

\[ \frac{mol}{L \cdot s} = \frac{mol}{(dm)^3 \cdot s} \]

\[ dm = 10 \text{ cm} \]
\[ ml = cm^3 \]

\[ \dot{c}(t) = K [A]^{m_A} [B]^{m_B} \ldots \]

1st order reaction - \( n = \sum m_i \)

2nd in NO

2nd in NO

2NO + O_2
Units of $k$

0th order reaction

1st order reaction

2nd order reaction

etc

$\frac{k}{M/s}$

$\frac{1}{s}$

$\frac{1}{sM}$

most common
How do we figure out rate laws

1. Method of isolation

\[ aA + bB \rightarrow \]

\[ \Gamma(t) = k[A]^m[B]^n \]

What are \( k, m, n \)?

First make \([A]\) in huge excess

Second make \([B]\) in huge excess
\[ r(t) = k' [B]^m_B \quad A \text{ excess} \]

\[ k' = k[A]^m_A \]

\[ r(t) = k'' [A]^m_A \quad k'' = k[B]^m_B \]

For several values of \( B \)

\[ r(t) \quad \cdots \quad m_B = 1 \]

\[ [A]^m_A = 2 \]
2) Method of initial rates

Get measurements \( \frac{d[AJ]/dt} \) right after mixing for different \( [A]_0, [B]_0 \)

\[
\begin{align*}
\tau(t) &= -\frac{1}{a} \frac{AA}{\Delta t} = k[A]^m [B]^n B \\
\tau_1 &= k[A]_0^m [B]^n_b \\
\tau_a &= k[A]_0^m [B]_2^m_b \\
\end{align*}
\]

Measure

\[
\tau_2 = \left( \frac{[B]_2}{[B]_1} \right)^{m_b}
\]
$$m_B = \ln \left( \frac{r_1}{r_2} \right) / \ln (\text{[B]}_3 \text{[B]}_2)$$

...do again

$$m_A = \ln \left( \frac{r_3}{r_4} \right) / \ln (\text{[A]}_3 \text{[A]}_4)$$

(const B)

only need min 3 reactions

* example
Time to mix could be limiting. Can't use these techniques.

Relaxation methods

How fast something decays to equilibrium.

\[ [A] \rightarrow [A]_{\text{eq}} \]
1st order & second order reactions

1. 1st order reactions

\[ A \rightarrow bB + cC \]  

[eg. nuclear decay]

Exponential relaxation

\[ r(t) = - \frac{1}{t} \frac{d[A]}{dt} = K[A] \]

\[ \frac{1}{[A]} \frac{d[A]}{dt} = -K \]
\[
\int \frac{1}{[A]} \frac{d[A]}{dt} dt = \int_{t_0}^{t'} -k dt
\]

\[
\ln \left( \frac{[A](t_i)}{[A](t_0)} \right) = -k \Delta t
\]

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

\( k \) has units of \( \text{1/time} \).
\[ \text{fast} \quad \text{slow} \]

\[ \text{when is it half used up} \]

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\[ \sum A \vec{J}(t) = \sum A \vec{J}(0) e^{-kt} \]

\[ \frac{1}{2} = e^{-kt} \]

\[ \ln \left( \frac{1}{2} \right) = -kt_v \]

\[ t_v = \frac{\ln(2)}{k} \approx \frac{0.693}{k} \]
1st order reaction for reactant

\[ A \rightarrow bB \quad -\frac{dA}{dt} = \frac{1}{b} \frac{d[B]}{dt} \]

\[ \frac{dB}{dt} = bK[A][S] = bK[A_0]e^{-kt} \]

\[ [B](t) = [B]_0 + b[A]_0(1 - e^{-kt}) \]
\[ [B](t) = [B]_0 + b \cdot \lambda A_0 (1 - e^{-kt}) \]
2nd order
\[- \frac{dA}{dt} = k [CA]^2\]

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

\[t_{y_2} = \frac{1}{k[CA]_0}\]
\[ A \rightleftharpoons B \quad kf \text{ & } kb \]

\[ -\frac{d[A]}{dt} = \frac{d[B]}{dt} \quad \text{at equilibrium} \]

\[ [A] + [B] \text{ is constant} \]

\[ \frac{d[A]}{dt} = -kf[A] + kb[B] \]

\[ \frac{d[B]}{dt} = kf[A] - kb[B] \]
Assume start from all $A$, $\Sigma B = 0$

$$\frac{d[A]}{dt} = -k_f[A]_0 + k_b ( [CA]_0 - [CA] )$$

$$= -(k_f + k_b) [A] + k_b [CA]_0$$

Substitute $u = (k_f + k_b) [CA] - k_b [CA]_0$

Use $k[A]_{eq} = k_b [B]_{eq}$
\[
\frac{[A] - [A]_{eq}}{[A]_{eq}} = ([A]_0 - [A]_{eq}) e^{-k_{rxn} t}
\]

\[k_{rxn} = k_b + K_f\]