CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #2

Rate Expressions: Bromide + Chlorine
case study & lab project
Kumar & Margerum paper

Introduction

Reactions with Chlorine

The Precursors!

HOCl
+ natural organics
(NOM)

Oxidized NOM
and inorganic chloride
• Aldehydes

Chlorinated Organics
• TOX
• THMs
• HAAs

The THMs

Chloroform

Bromochloromethane

Chlorodibromomethane

Bromoform
The Haloacetic Acids

<table>
<thead>
<tr>
<th>Cl</th>
<th>C</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
</tr>
</tbody>
</table>

Trichloroacetic Acid (TCAA)

<table>
<thead>
<tr>
<th>Br</th>
<th>C</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
</tr>
<tr>
<td>Br</td>
<td>Br</td>
<td>Br</td>
</tr>
</tbody>
</table>

Bromodichloroacetic Acid

<table>
<thead>
<tr>
<th>Br</th>
<th>C</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>Br</td>
<td>Br</td>
</tr>
</tbody>
</table>

Chlorodibromoacetic Acid

<table>
<thead>
<tr>
<th>Br</th>
<th>C</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>Br</td>
<td>Br</td>
</tr>
</tbody>
</table>

Tribromoacetic Acid

<table>
<thead>
<tr>
<th>H</th>
<th>C</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>Cl</td>
</tr>
</tbody>
</table>

Dichloroacetic Acid (DCAA)

<table>
<thead>
<tr>
<th>Br</th>
<th>H</th>
<th>C</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>H</td>
<td>C</td>
<td>COOH</td>
</tr>
</tbody>
</table>

Bromochloroacetic Acid

<table>
<thead>
<tr>
<th>Br</th>
<th>H</th>
<th>C</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>H</td>
<td>C</td>
<td>COOH</td>
</tr>
</tbody>
</table>

Dibromoacetic Acid

Distribution: Variability within a single system

Example: New Haven Service Area

- DS model
New Haven Distribution System

- Sept 11, 1997
  - 22:00
  - Chlorine

- Lake Gaillard WTP
- West River WTP
- Lake Saltonstall WTP
- Millrock Basins
- Maltby Tank

- 3,400 pipes
- 2,500 junctions
- 3 MG
- 8.7 MG

- 2.0 mg/L DOC (Treated)
- pH 7
- 1.8 mg/L chlorine dose

TTHM

CEE 697K Lecture #2
Genotoxicity

- Work of Michael Plewa
- Univ. of Illinois

DBP Chemical Class

- Other DBPs
- Haloacarboxylic acids
- Haloacetonitriles
- Haloacetonitriles
- Haloacetic acids

Single Cell Gel Electrophoresis Genotoxicity Potency
Log Molar Concentration (4 h Exposure)

Not Genotoxic: DCAA, TCAA, BDCAA, Dichloroacetamide, 3,3-Dibromo-4-oxopentanoic Acid, 2,3,3-Tribromopropenoic Acid

David A. Reckhow
Bromide: THM Formation

Data from: Minear & Bird, 1980
96 hours, pH 7.0
5 mg/L Chlorine Dose
1 mg/L Humic Acid

Impact of Bromide on DHAA Formation

From Pourmoghaddas, 1990
Formation of Brominated THMs

\[ \text{HOCl} + Br^- \xrightarrow{k} \text{HOBr} + Cl^- \]

Bromo speciation

Full-scale data (small symbols) from Weinberg et al., 2002
Lab data (large symbols) from Hua & Reckhow, 2004
Lines are geometric model

Full-scale data (small symbols) from Weinberg et al., 2002
Lab data (large symbols) from Hua & Reckhow, 2004
Lines are geometric model
Case study: chlorine + bromide

- Observed reaction: \( \text{HOCl} + \text{Br}^- \xrightarrow{k_2} \text{HOBr} + \text{Cl}^- \)
  - Nucleophilic attack of bromide on oxygen in hypochlorous acid
    - \( k_2 = 2.95 \times 10^3 \text{ M}^{-1}\text{s}^{-1} \) at 25°C
  - Note that HOCl deprotonates at elevated pHs
    - From Farkas et al., 1949
  - Transfer of Cl\(^+\) to form intermediate (BrCl)
    - From Kumar & Margerum, 1987

- Background
  - Absorbance for monitoring reaction
  - Known equilibria

Table I. Absorption Spectral Characteristic of Halogen Species

<table>
<thead>
<tr>
<th>species</th>
<th>( \lambda_{max} ) nm</th>
<th>( e ) M(^{-1}) cm(^{-1} )</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC(^-)</td>
<td>292</td>
<td>350</td>
<td>a</td>
</tr>
<tr>
<td>OB(^-)</td>
<td>329</td>
<td>345</td>
<td>b</td>
</tr>
<tr>
<td>HOCl</td>
<td>230</td>
<td>160</td>
<td>a</td>
</tr>
<tr>
<td>HCl</td>
<td>160</td>
<td>160</td>
<td>a</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>175</td>
<td>175</td>
<td>a</td>
</tr>
<tr>
<td>Br(^2-)</td>
<td>360</td>
<td>360</td>
<td>a</td>
</tr>
</tbody>
</table>


Table II. Precipitation, Hydrolysis, and Formation Constants

<table>
<thead>
<tr>
<th>equilibrium</th>
<th>( K )</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC(^-) + H(^+) \rightleftharpoons HOCl</td>
<td>2.75 \times 10^3</td>
<td>13</td>
</tr>
<tr>
<td>OB(^-) + H(^+) \rightleftharpoons HOBr</td>
<td>5 \times 10^3</td>
<td>5</td>
</tr>
<tr>
<td>Cl(^-) + H(^2+) \rightleftharpoons HCl + H(^+)</td>
<td>1.6 \times 10^{10}</td>
<td>13</td>
</tr>
<tr>
<td>Br(^-) + H(^2+) \rightleftharpoons HBr + H(^+)</td>
<td>4.6 \times 10^{14}</td>
<td>5</td>
</tr>
<tr>
<td>Br(^2-) + H(^2+) \rightleftharpoons Br(^+)</td>
<td>1.7 \times 10^{15}</td>
<td>5</td>
</tr>
<tr>
<td>BrCl + H(^2+) \rightleftharpoons Br(^+) + Cl(^-)</td>
<td>5.2 \times 10^{15}</td>
<td>13</td>
</tr>
<tr>
<td>H(^2+) + HOCl \rightleftharpoons HOBr + H(^+)</td>
<td>1.3 \times 10^{-6}</td>
<td>5</td>
</tr>
</tbody>
</table>

Alkaline Experiments

- Pseudo-1\textsuperscript{st} order
  - Bromide in great excess
- Slow reactions
  - Could be monitored directly by conventional UV spectrophotometer
    - 292 nm peak for hypochlorite (OCl\textsuperscript{-})
  - Followed for 4 half-lives
    - Complete from 1.1 sec – 4 hr
  - Plot ln(A\textsubscript{t} - A\textsubscript{∞}) vs time
    - Slope is k\textsubscript{obs}

<table>
<thead>
<tr>
<th>Br\textsuperscript{-}, M</th>
<th>[OCl\textsuperscript{-}], M</th>
<th>k\textsubscript{obs} \times 10\textsuperscript{n}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.430</td>
<td>(2.19 ± 0.01) \times 10\textsuperscript{8}</td>
</tr>
<tr>
<td>0.100</td>
<td>0.350</td>
<td>(2.89 ± 0.01) \times 10\textsuperscript{8}</td>
</tr>
<tr>
<td>0.100</td>
<td>0.230</td>
<td>(2.80 ± 0.01) \times 10\textsuperscript{8}</td>
</tr>
<tr>
<td>0.100</td>
<td>0.120</td>
<td>(2.80 ± 0.01) \times 10\textsuperscript{8}</td>
</tr>
<tr>
<td>0.100</td>
<td>0.080</td>
<td>(2.80 ± 0.01) \times 10\textsuperscript{8}</td>
</tr>
</tbody>
</table>

$k_{obs}$ is a linear function of Bromide
pH dependency

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.150</td>
<td>0.150×10⁻¹</td>
<td>(1.91 ± 0.01)×10⁻⁷</td>
</tr>
<tr>
<td>0.150</td>
<td>0.250</td>
<td>0.250×10⁻¹</td>
<td>(2.61 ± 0.01)×10⁻⁷</td>
</tr>
<tr>
<td>0.300</td>
<td>0.750</td>
<td>0.750×10⁻¹</td>
<td>(3.73 ± 0.01)×10⁻⁷</td>
</tr>
<tr>
<td>1.000</td>
<td>2.000</td>
<td>2.000×10⁻¹</td>
<td>(5.12 ± 0.01)×10⁻⁷</td>
</tr>
</tbody>
</table>

Overall pH dependence

- How to explain pH effect on 2nd order rate constant?
  - See also, Brezonik, pg 230; figure 4-20

Figure 7. Dependence of the second-order rate constant (in terms of [OCI⁻]r and [Br⁻]) on the acidity (without buffer catalysis effects).
Buffer Tests

- Low pH
- High pH

Buffer Effect

- Proposed dependence on HA

\[ k_{obs} = (k_0 + k_H[H^+] + k_{HA}[HA])(Br^-) \]

\[ [HA] = a_c C_r = \frac{1}{[Br^-]^2 + 1} \frac{[H^+]C_r}{K_a + [H^+]} \]

\[ \frac{k_{obs}}{[Br^-]} - k_0 = k_H + k_{HA} \frac{[buffer]_r}{K_a + [H^+]} \]
High pH only

\[ k_{\text{obs}} = \left( k_0 + k_H[H^+] + k_{HA}[HA] \right) Br^- \]

\[ -\frac{d[OCl^-]}{dt} = \left( k_0 + k_H[H^+] + k_{HA}[HA] \right) OCl^- [Br^-] \]

More generally

\[ -\frac{d[Cl(OCl)]}{dt} = \left( k_0[OCl^-] + k_{HOCl}[HOCl] + k_{HA}[HA][OCl^-] \right) Br^- \]

Acidic Experiments

- Pseudo-1\textsuperscript{st} order
  - Bromide in great excess
- Fast reactions
  - Required high-speed setup
    - Stopped-flow spectrophotometer
  - Could monitor 2\textdegree product
    - 266 nm peak for tribromide (Br\textsubscript{3}^-)
  - Followed for 4 half-lives
    - Complete from 0.40-0.01 sec
  - Plot ln(A\textsubscript{0} - A\textsubscript{t}) vs time
    - Slope is k\textsubscript{obs}

### Table IV. Pseudo-First-Order Rate Constants for the Oxidation of Bromide by Hypobromous Acid\textsuperscript{a}

<table>
<thead>
<tr>
<th>Buffer Solutions</th>
<th>( [\text{Br}^-] ), M</th>
<th>(-\log [\text{H}^+])</th>
<th>([\text{buffer}]_0), M</th>
<th>( k_{\text{obs}}, s^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>3.23</td>
<td>0.05 (A)</td>
<td>24.7 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.020</td>
<td>3.23</td>
<td>0.05 (A)</td>
<td>46.1 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>0.030</td>
<td>3.23</td>
<td>0.05 (A)</td>
<td>115 ± 4\textsuperscript{b}</td>
<td></td>
</tr>
<tr>
<td>0.040</td>
<td>3.23</td>
<td>0.05 (A)</td>
<td>265 ± 4\textsuperscript{b}</td>
<td></td>
</tr>
<tr>
<td>0.050</td>
<td>4.78</td>
<td>0.01 (A)</td>
<td>10.83 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>0.060</td>
<td>4.78</td>
<td>0.02 (A)</td>
<td>11.17 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>0.070</td>
<td>4.78</td>
<td>0.05 (A)</td>
<td>12.58 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>0.080</td>
<td>4.78</td>
<td>0.10 (A)</td>
<td>14.63 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>0.090</td>
<td>4.78</td>
<td>0.20 (A)</td>
<td>18.8 ± 0.8</td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>2.90</td>
<td>0.01 (C)</td>
<td>16.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>0.120</td>
<td>2.87</td>
<td>0.032 (C)</td>
<td>19.46 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>0.150</td>
<td>2.85</td>
<td>0.050 (C)</td>
<td>22.2 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>0.200</td>
<td>2.84</td>
<td>0.100 (C)</td>
<td>27.8 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.300</td>
<td>2.83</td>
<td>0.153 (C)</td>
<td>30.0 ± 0.4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peroxidic Acid Solutions</th>
<th>( [\text{Br}^-] ), M</th>
<th>(10^4[\text{H}^+]), M</th>
<th>( k_{\text{obs}}, s^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0020</td>
<td>1.063</td>
<td>6.33 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>0.0030</td>
<td>1.063</td>
<td>9.75 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>0.0040</td>
<td>1.063</td>
<td>12.7 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>0.0050</td>
<td>1.063</td>
<td>16.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>0.0100</td>
<td>1.063</td>
<td>31.7 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.0200</td>
<td>1.063</td>
<td>63.2 ± 0.7</td>
<td></td>
</tr>
<tr>
<td>0.0300</td>
<td>1.59</td>
<td>19.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>0.0400</td>
<td>2.66</td>
<td>26.4 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>0.0500</td>
<td>5.24</td>
<td>45.1 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>0.0500</td>
<td>11.16</td>
<td>81.2 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>0.0500</td>
<td>21.79</td>
<td>156 ± 4\textsuperscript{e}</td>
<td></td>
</tr>
</tbody>
</table>

\( [\text{HOCI}] = (0.5-6.00) \times 10^4 M, \mu = 0.5 M (\text{NaClO}), 25.0 \degree C, \lambda = 266 \text{ or } 393 \text{ nm.} \)  \( ^{e} \)Buffers used are A = acetic acid and C = chloroacetic acid.  \( ^{f} \)Rate constants are corrected for mixing.  \( ^{g} \)
Stopped-flow

**Principle**

**Commercial instruments**

**Limitations**
- Correct for slow mixing speed ($k_m$)
  - For Durrum instrument: $k_m = 1700 \text{ s}^{-1}$

$$k_{obs} = \frac{k'_{obs}}{1 - \left(\frac{k_m}{k_{obs}}\right)}$$

$K_{obs}$ is still linear with Br-

**No difference in mechanism?**

Figure 4. Pseudo-first-order rate constants (25.0 °C, $pH = 0.50$) for the reaction of HOCl and Br⁻: (A) $[H^+] = 1.063 \times 10^3 \text{ M}$; (B) $-\log [H^+] = 5.22 (0.02 \text{ M sodium buffer})$. 

$K_{obs}$ is still linear with Br⁻.
Acidic data: impact of acids

- General and specific acid
  - Figure 5. Dependence of the second-order rate constant (HOCl + Br⁻) on HOCO₃⁻ concentration.
  - Figure 6. Dependence of the second-order rate constant (HOCl + Br⁻) on the concentration of general acids.

Overall pH dependence

- Three effective zones
  - See also, Brezonik, pg 230; figure 4-20
  - Figure 7. Dependence of the second-order rate constant (in terms of [OCl⁻] and [Br⁻]) on the acidity (without buffer catalysis effects).
Catalysis: comparison with pKa

- Bronsted catalysis
  \[ k_{HA} = G_A (K_a)^\alpha \]

<table>
<thead>
<tr>
<th>HA</th>
<th>pK_a</th>
<th>( k_{apo} )</th>
<th>( k_{apo} )</th>
<th>( k_{apo} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2O</td>
<td>15.5</td>
<td>1.8 ± 0.3 × 10^{-3}</td>
<td>27.9 ± 5.5</td>
<td>0.27</td>
</tr>
<tr>
<td>CH_2ClCOOH</td>
<td>11.9</td>
<td>8.5 ± 0.2</td>
<td>(1.25 ± 0.15) × 10^{-2}</td>
<td>0.75</td>
</tr>
<tr>
<td>HPO_4^-</td>
<td>12.8</td>
<td>(1.25 ± 0.15) × 10^{-2}</td>
<td>(3.8 ± 0.5) × 10^{-2}</td>
<td>0.75</td>
</tr>
<tr>
<td>CH_3COOH</td>
<td>4.8</td>
<td>4.9 ± 0.4</td>
<td>1.2 ± 0.1</td>
<td>0.75</td>
</tr>
<tr>
<td>HClO_2</td>
<td>7.5</td>
<td>3.2 ± 0.2</td>
<td>1.0 ± 0.1</td>
<td>0.75</td>
</tr>
<tr>
<td>HOCl</td>
<td>7.4</td>
<td>3.2 ± 0.2</td>
<td>1.0 ± 0.1</td>
<td>0.75</td>
</tr>
</tbody>
</table>

- Indicates that HA engages in greater donation of proton to OCI^- than to HOCl

Mechanisms

- Proposed mechanism
- Alternative
  - Less likely
Temperature: Arrhenius Equation

- Arrhenius Equation
  \[ k = A e^{-E_a / RT} \]
  - Where \( R \) is the universal gas constant
    \[ R = 8.3145 \frac{J}{M^\circ K} \]
  - Transforms to:
    \[ \ln(k_T) = \ln(A) - \left( \frac{E_a}{R} \right) \frac{1}{T} \]
    \[ k_{Tb} = k_{Ta} e^{\frac{E_a}{R} \left( \frac{1}{T_b} - \frac{1}{T_a} \right)} \]

Pizza Kinetics

- Leenson, 1999
  - What are the kinetics of pizza spoilage?
  - Do they conform to Arrhenius?

*J. Chem Ed.*, 76:4:504-505
Pizza II

- Arrhenius plot
  - $t \sim k$

![Arrhenius plot](image)

Figure 1. Arrhenius plot of the storage time data provided on the frozen pizza package.

Lab Project Example Data #1

- 0.1 M NaOH

![Absorbance vs Time](image)

What is the $A_{Abs}$?
Lab Project Example Data #II

\[ 0.1 \text{ M NaOH} \]

\[ \begin{align*}
\text{Time (min)} & \\
0 & 2 \quad 4 \quad 6 \quad 8 \\
\text{Ln} (A_{292} - A_{292\inf}) & \\
-6 & -5 \quad -4 \quad -3 \\
\end{align*} \]

\[ \begin{align*}
b[0] & = -1.5509712892 \\
b[1] & = -0.0400283854 \\
\end{align*} \]

Set \( A_{\text{inf}} = 0.085 \)

Lab Project Example Data #III

\[ 0.05 \text{ M NaOH} \]

Set \( A_{\text{inf}} = ? \)
Lab Project Example Data #IV

- 0.05 M NaOH

Set $Abs_{inf} = 0.094$

Maybe too high?
Downward curvature

Lab Project Example Data #V

- 0.05 M NaOH

Set $Abs_{inf} = 0.092$

Looks better, except for final data where relative error is high, Use only earlier data?
Lab Project Example Data #VI

- **0.05 M NaOH**

![Graph](image1)

*Set Abs$_{ref} = 0.092$*

Using only earlier data where relative error is low, better linearity and estimate of $k_{obs}$?

**Related systems**

*Table VI. Third-order Rate Constants for the Oxidation of Halides by Hypochlorite and by Hypohalous Acids*

<table>
<thead>
<tr>
<th>reactants</th>
<th>$k$, M$^{-2}$ s$^{-1}$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+ + OCl^- + Br^-$</td>
<td>$3.65 \times 10^{12}$</td>
<td>a</td>
</tr>
<tr>
<td>$H^+ + OCl^- + I^-$</td>
<td>$4.4 \times 10^{15}$</td>
<td>b</td>
</tr>
<tr>
<td>$H^+ + HOCl + Cl^-$</td>
<td>$2.8 \times 10^{8}$</td>
<td>c</td>
</tr>
<tr>
<td>$H^+ + HOCl + Br^-$</td>
<td>$1.3 \times 10^{6}$</td>
<td>a</td>
</tr>
<tr>
<td>$H^+ + HOBr + Br^-$</td>
<td>$1.6 \times 10^{10}$</td>
<td>d</td>
</tr>
<tr>
<td>$H^+ + HOI + I^-$</td>
<td>$4.4 \times 10^{12}$</td>
<td>d</td>
</tr>
</tbody>
</table>

*This work. aReference 2. bReference 13. cReference 5.

\[
H_2O_2 + Br^- \overset{2.3 \times 10^{9} M^4 s^{-1}}{\rightarrow} OH^- + HOBr \quad (22)
\]

\[
H^+ + H_2O_2 + Br^- \overset{1.4 \times 10^2 M^2 s^{-1}}{\rightarrow} H_2O + HOBr \quad (23)
\]
Introduction: Simple Rate Laws
Breznik, pp. 31-39

Variable Kinetic Order

- Any reaction order, except $n=1$

$$\frac{dc}{dt} = -k_c^n$$

$$\frac{1}{c^{n-1}} = \frac{1}{c_o^{n-1}} + (n-1)k_nt$$

$$C = C_o \frac{1}{\left[1 + (n-1)k_nC_o^{n-1}t\right]^{(n-1)}}$$
Half-lives

- Time required for initial concentration to drop to half, i.e., \( c = 0.5c_o \)
  - For a zero order reaction:
    \[
    c = c_o - kt \quad \text{and} \quad 0.5c_o = c_o - kt_{\frac{1}{2}}
    \]
  - For a first order reaction:
    \[
    c = c_o e^{-kt} \quad \text{and} \quad 0.5c_o = c_o e^{-kt_{\frac{1}{2}}}
    \]
    \[t_{\frac{1}{2}} = \frac{0.5c_o}{k}\]
    \[t_{\frac{1}{2}} = \frac{\ln(2)}{k} = 0.693\frac{k}{k}\]

**Example: Benzyl Chloride**

- Use:
  - Manufacture of benzyl compounds, perfumes, pharmaceuticals, dyes, resins, floor tiles
- Toxicity
  - Intensely irritating to skin, eyes, large doses can cause CNS depression
- Emission
  - 45,000 lb/yr
- Fate
  - Benzyl chloride undergoes slow degradation in water to benzyl alcohol
Benzyl chloride II

- Benzyl chloride to benzyl alcohol

\[ \text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{OH} \]

- Nucleophilic substitution
  - \( S_N1 \) or \( S_N2 \)?
  - How to distinguish?
  - Salt effects

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0.1°C</th>
<th>25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.042x10^{-5} s^{-1}</td>
<td>1.38x10^{-5} s^{-1}</td>
</tr>
<tr>
<td>( T_{1/2} )</td>
<td>19.1 d</td>
<td>0.58 d</td>
</tr>
</tbody>
</table>

Mixed Second Order

- Two different reactants
  - Rate: \( \frac{dx}{dt} = \frac{d[A]}{dt} = \frac{1}{V} \frac{dV}{dx} = \frac{k_c [A] [B]}{V_0} \)
  - Initial Concentrations are different; \( [A]_0 \neq [B]_0 \)
  - The integrated form is:
    \[ \ln \left( \frac{[A]_0 - [A]}{[B]_0 - [B]} \right) = k_c t \]
  - Which can be expressed as:
    \[ \log \frac{[A]}{[B]} = 0.43k_c ([A]_0 - [B]) - \log \frac{[B]}{[A]_0} \]
Mixed Second Order

$A + B \xrightarrow{k_2} \text{products}$

- Initial Concentrations are the same; $[A]_0 = [B]_0$

\[
\frac{dx}{dt} = k_2[A][B] = k_2([A]_0 - x)([B]_0 - x)
\]

- The integrated form is:

\[
\int \frac{d[A]}{[A]} = \int v_{k_2}dt \quad \Rightarrow \quad \frac{1}{[A]} - \frac{1}{[A]_0} = 2k_2t
\]

- Which can be integrated:

\[
\frac{1}{[A]} = 2k_2t + \frac{1}{[A]_0}
\]

Pseudo first order

$A + B \xrightarrow{k_2} \text{products}$

- For most reactions, $n=1$ for each of two different reactants, thus a second-order overall reaction

- Many of these will have one reactant in great excess (e.g., $B$)

- These become "pseudo-1st order in the limiting reactant, as the reactant in excess really doesn't change in concentration"

\[
k = 3.9 \times 10^{-5} \text{ Lmg}^{-1} \text{ min}^{-1}
\]

\[
\frac{dc}{dt} = -k_2c_A^1c_B^1
\]
Pseudo-1\textsuperscript{st} order (cont.)

\[ \frac{dc}{dt} = -k_2 C_A C_B \]

\[ C_A = C_{A0} e^{-k_{obs}t} \]

- Since \( C_2 \) changes little from its initial 820 mg/L, it is more interesting to focus on \( C_A \)
- \( C_A \) exhibits simple 1\textsuperscript{st} order decay, called pseudo-1\textsuperscript{st} order
  - The pseudo-1\textsuperscript{st} order rate constant is just the "observed rate" or \( k_{obs} \)

Example: \( \text{O}_3 \) & Naphthalene

- How long will it take for ozone (4.8 mg/L dose) to reduce the concentration of naphthalene by 99%?
  - Used in moth balls and as a chemical intermediate
  - 2\textsuperscript{nd} order reaction; \( k_2 = 3000 \text{ M}^{-1}\text{s}^{-1} \)
    - Table 1 in Holmme & Bader, 1983 [Wat. Res. 17:2:173]
  - Industrial WW with 0.1 mM naphthalene
    - Both reactants are at same (0.1 mM) concentration
    - Therefore, this reduces to a simple 2\textsuperscript{nd} order reaction

\[ \frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t \]

\[ \frac{1}{10^{-6}} = \frac{1}{10^{-4}} + 3000 t \]

\[ 3000 t = 990,000 \]
\[ t = 330 \text{ sec} \]
\[ = 5.5 \text{ min} \]
O₃ & Naphthalene (cont.)

- Contaminated river water (0.001 mM)
  - Now ozone is in great molar excess, so this is a pseudo-1ˢᵗ order reaction
    \[ [A] = [A]₀ e^{-k₂[B]₀t} \]
    \[
    \ln\left(\frac{[A]}{[A]₀}\right) = -k₂[B]₀t \\
    \ln(10^{-8} / 10^{-6}) = -3000(10^{-2}) \\
    -4.605 = -0.3t \\
    t = 15.4 \text{ sec} \]

Molecularity of three: 3ʳᵈ order kinetics

- Quite improbably, but sometimes happens
  - Three different reactants \[ A + B + C \rightarrow \text{products} \]
    \[ \frac{dx}{dt} = k₃[A][B][C] = k₃([A]₀ - x)([B]₀ - x)([C]₀ - x) \]
    - Complicated integrated form exists
  - Two different reactants \[ 2A + B \rightarrow \text{products} \]
    \[ \frac{dx}{dt} = k₃[A]²[B] = k₃([A]₀ - 2x)([B]₀ - x) \]
    - Integrated form:
3\textsuperscript{rd} Order (cont.)

- Only one reactant or Initial Concentrations are the same

\[
\frac{dx}{dt} = k_x[A][A][A] \\
= k_x([A]_0 - x)([A]_0 - x)([A]_0 - x)
\]

- The integrated form is:

\[
\int \frac{d[A]}{[A]} = \int v_0 k_x dt \\
\frac{1}{[A]} - \frac{1}{[A]_0} = -2v_0 k_x t = 6k_1 t
\]

3\textsuperscript{rd} Order (cont.)

- Pseudo-2\textsuperscript{nd} order reactions

- When one of the reactants has a fixed concentration
  - E.g., present in excess or buffered, or acts catalytically
- Like a regular 2\textsuperscript{nd} order reaction with two reactants but observed constant is fundamental rate constant times concentration of the 3\textsuperscript{rd} reactant.

- The integrated form:

\[
\frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]} = k_3[C]t \to k_{obs}
\]
Example: chlorate formation

- Formation of chlorate in concentrated hypochlorite solutions
  - Concern: chlorate is toxic
    - MCLG=0.2 mg/L
  - Stoichiometry
    \[ 3\text{OCI}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^- \]
  - Is this 3rd order? Be skeptical!
- Observed kinetics
  \[ \frac{d[\text{ClO}_3^-]}{dt} = k_{obs} [\text{OCI}^-]^3 \]
  - So, why is it 2nd order?

Chlorate example (cont.)

- Answer: this is a reaction pathway composed of two elementary reactions
  - Step #1
    \[ 2\text{OCI}^- \xrightarrow{\text{slow}} \text{ClO}_3^- + \text{Cl}^- \]
  - Step #2
    \[ \text{OCI}^- + \text{ClO}_3^- \xrightarrow{\text{fast}} \text{ClO}_3^- + \text{Cl}^- \]
- In multi-step reactions such as these, we say that
  - the overall rate is determined by the slowest step
    - Called the "rate-limiting step" or RLS
  - Rate law is written based on the RLS
    - Subsequent steps are ignored
    - Prior steps are incorporated as they determine the concentrations of the RLS reactants

Homework #2 is based on this reaction
Reversible reaction kinetics

For a general reversible reaction:

\[ aA + bB \leftrightarrow pP + qQ \]

And the rate law must consider both forward and reverse reactions:

\[ \text{rate} = k_f C_A^a C_B^b - k_r C_P^p C_Q^q \]

where,
- \( k_f \) = forward rate constant, [units depend on \( a \) and \( b \)]
- \( k_b \) or \( k_r \) = backward rate constant, [units depend on \( a \) and \( b \)]
- \( C_P \) = concentration of product species P, [moles/liter]
- \( C_Q \) = concentration of product species Q, [moles/liter]
- \( p \) = stoichiometric coefficient of species P
- \( q \) = stoichiometric coefficient of species Q

Reversible 1\textsuperscript{st} order reactions

- **Kinetic law**
  \[ \frac{d[B]}{dt} = k_1[A] - k_2[B] \]
  \[ [B] = \frac{k_1}{k_2} \approx K_{eq} \]

- **Eventually the reaction slows and,**
  **Reactant concentrations approach the equilibrium values**

\[ \frac{d[B]}{dt} = 0 = k_1[A] - k_2[B] \]

**Stumm & Morgan**

**Fig. 2.10**

**Pg. 69**

**Reversible Reaction**

\[ A \xrightleftharpoons[k_2][k_1] B \]

\[ [A]_0 = 4.0 \times 10^{-3} \text{ M} \]

\[ [B]_0 = 0.0 \text{ M} \]

**Case 1**

\[ k_1 = 0.15 \text{ day}^{-1} \]

\[ k_2 = 0.05 \text{ day}^{-1} \]

\[ K = \frac{k_1}{k_2} = 3.0 \]

**Figure 2.10.** Single reversible reaction.
Reversible 1\textsuperscript{st} order (cont.)

- Solution to non-equilibrium reaction period
  - See Brezonik, pg 37-38 for details
  \[
  [A] = \frac{1}{k^*} [A]_0 \left( k_r + k_f e^{-k^*_t} \right)
  \]
  - Where $k^* = k_f + k_r$
  - And:
    \[
    \frac{[A] - [A]_{\text{equ}}}{[A] - [A]_{\text{equ}}} = e^{-k^*_t}
    \]
    \text{Linearized version}
  - Where:
    \[
    \frac{k_f}{k_r} (= K_{\text{equ}}) = \frac{[P]_{\text{equ}}}{[A]_{\text{equ}}}
    \]

To next lecture