Kinetics I

Silberberg 2nd Ed, Chapter 16
www.chem.usyd.edu.au/hpage3.htm (login “chem”, passwd “chem@usyd”)
Any questions or requests - email to c.kepert@chem.usyd.edu.au
Review on Gases:
Equations to Remember

\[ PV = nRT \]

**Dalton’s Law:** Total pressure of mixture of gases = sum of pressures that each would exert if it were alone.

\[ \text{mole fraction of gas i} = \frac{\text{no. moles}_i}{\text{total no. moles}} = \frac{P_i}{\text{total pressure}} \]

Rate of gas effusion/diffusion \( \propto \frac{1}{\sqrt{\text{molar mass}}} \)
Review on Gases: 
Equations to Understand

\[
\left( P + \frac{n^2a}{V^2} \right) \times (V - nb) = nRT
\]

Energy = 1/2 mv^2 \propto \text{Temperature}
Kinetics: How fast a reaction occurs

Reactions are **not instantaneous** - they take a finite time.

Demonstration: \(2H^+ + 3I^- + H_2O_2 \rightarrow 2H_2O + I_3^-\)

Rate (speed) of reaction = \[
\frac{d(\text{concentration})}{d(\text{time})}
\]
2H⁺ + 3I⁻ + H₂O₂ → 2H₂O + I₃⁻

Rate (speed) of reaction = \frac{d(\text{concentration})}{d(\text{time})}

\[
\text{rate} = \frac{d[I^-_3]}{dt} = \frac{1}{2} \frac{d[H_2O]}{dt} = - \frac{1}{2} \frac{d[H^+]}{dt} = - \frac{1}{3} \frac{d[I^-]}{dt}
\]

etc.
Evaluating Reaction Rates cont’d

\[ 2H^+ + 3I^- + H_2O_2 \rightarrow 2H_2O + I_3^- \]

total mass of iodine = constant in time, whether present as I\(^-\) or I\(_3^-\)

\[ \Rightarrow \text{total mass of iodine} \propto [I^-] + 3[I_3^-] \]

Hence: \[ \frac{d(\text{total mass})}{dt} = 0 = \frac{d[I]}{dt} + 3\frac{d[I_3^-]}{dt} \]

and \[ \frac{d[I_3^-]}{dt} = -\frac{1}{3} \frac{d[I]}{dt} \text{ etc.} \]
Rate Laws:
Dependence on Concentration

Reaction rate = \(-d[A]/dt\)
= - slope of graph
Rate Laws: Dependence on Concentration

“Differential” rate law:
How does the rate vary with concentration of each species?

For our iodine reaction:

\[2H^+ + 3I^- + H_2O_2 \rightarrow 2H_2O + I_3^-\]

found that \(\frac{d[I_3^-]}{dt} = \text{constant} \times [I^-] \times [H_2O_2]\)

⇒ “reaction rate law”
⇒ does not follow stoichiometry
Complex Rate Laws

For \( aA + bB \rightarrow cC \ldots \),

\[
\text{Rate} = k \ [A]^x \ [B]^y \ldots
\]

where \( x, y \) can have any value \((0, 1, -1/2 \ldots)\).

Exponent of \([A]\) (ie value of \(x\))

\( \Rightarrow \) order of reaction with respect to \(A\)

\( = 1, \) first order in \(A\),
\( = 2, \) second order in \(A\), …

\( k = \) rate coefficient (or “rate constant”)

Units of \(k\) depend on order of reaction
Rate Laws

2H^+ + 3I^- + H_2O_2 \rightarrow 2H_2O + I_3^-}

\[
\text{Rate} = \frac{\text{d}[I_3^-]}{\text{dt}} = k \times [I^-] \times [H_2O_2]
\]

Reason for non-stoichiometric dependence on concentration:
the overall reaction is actually many \textit{elementary reactions} occurring simultaneously.
Example: \( \text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl} \)

Four elementary reactions occurring simultaneously:

\[
\begin{align*}
\text{Cl}_2 & \rightarrow 2\text{Cl} \\
\text{Cl} + \text{H}_2 & \rightarrow \text{HCl} + \text{H} \\
\text{H} + \text{Cl}_2 & \rightarrow \text{HCl} + \text{Cl} \\
2\text{Cl} & \rightarrow \text{Cl}_2
\end{align*}
\]

* A \( \text{H}_2 \) molecule and a \( \text{Cl}_2 \) molecule \textit{never} react by colliding together to form two \( \text{HCl} \) molecules!

\textit{Instead:}

- isolated \( \text{Cl}_2 \) molecule falls apart to form two \( \text{Cl} \) atoms
- a \( \text{Cl} \) atom can collide with a \( \text{H}_2 \) molecule to form a \( \text{HCl} \) molecule and a \( \text{H} \) atom.
Elementary Reactions

There are only two types of elementary reactions:

unimolecular, e.g. \( \text{Cl}_2 \rightarrow 2\text{Cl} \)
isolated molecule reacts

bimolecular, e.g. \( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \)

two molecules (atoms) collide and react
Only single Cl + H\(_2\) encounters (not all of which are reactive).
Example: \( \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \)

Suppose we detect HCl in Cl/H\(_2\) beam experiment:
- if [Cl] in beam is doubled, then we find the no. of HCl molecules seen per second is also doubled.
- similarly, doubling [H\(_2\)] doubles no. of HCl molecules
Unimolecular Reactions

Example: \( \text{Cl}_2 \rightarrow 2 \text{Cl} \)

Set up apparatus with single beam of \( \text{Cl}_2 \):
- looking at \([\text{Cl}]\) with detector, it is found that the number \( \text{Cl} \) atoms per second is be proportional to \([\text{Cl}_2]\)
Finding the Rate Law Experimentally

**Simplest: “initial rate” method.**

Problem: concentrations vary with time.

⇒ At early time, concentrations of reactants have hardly changed.

\[
\text{rate} = \frac{\text{d}(\text{concentration})}{\text{d}(\text{time})}
\]

units = concentration × time$^{-1}$

Demonstration: iodine clock reaction

\[
2\text{IO}_3^- + 5\text{SO}_3^- + 2\text{H}^+ \rightarrow \text{I}_2 + 5\text{SO}_4^{2^-} + \text{H}_2\text{O}
\]
For reaction $A \rightarrow \text{product}$, the rate equation is:

$$\text{Rate} = \frac{d[\text{product}]}{dt} = ?$$

**Initial rates:**

<table>
<thead>
<tr>
<th>initial [A] / M</th>
<th>Rate / M s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>5.0</td>
</tr>
<tr>
<td>0.20</td>
<td>10.0</td>
</tr>
</tbody>
</table>