Introduction to Chemical Kinetics

CHEM 107
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Reading, etc.

- Kinetics, Chapter 11
  Read and understand section 11.1, but the material is mainly for your edification.
- Read 11.2 - 11.6. Sections 11.7 – 11.8 are descriptive, read for general ideas.

Chemical Kinetics

- Reaction rates
  - “How fast?”
- Reaction mechanisms
  - “How?”
- Answers to these questions depend on the path taken from reactants to products.

Reaction Rates

\[ \alpha A + \beta B \rightarrow \gamma C + \delta D \]

- Follow progress by measuring any one concentration:
  \[ \frac{1}{\alpha} \frac{\Delta [A]}{\Delta t}, \ rac{1}{\beta} \frac{\Delta [B]}{\Delta t}, \ \frac{1}{\gamma} \frac{\Delta [C]}{\Delta t}, \ \frac{1}{\delta} \frac{\Delta [D]}{\Delta t} \]
- Rates of change related by coefficients from balanced equation.

Factors Which Influence Rates

- Identity & form of reactants, products
  - \( H_2 + I_2 \) vs. \( H_2 + Br_2 \)
  - solution vs. gas phase, etc.
- Concentrations of various species
  - usually reactants
  - sometimes products, other species
- Temperature
  - usually, faster at higher T
  - strong dependence
- Catalysts
**Concentration Effects: Rate Laws**

\[ \alpha A + \beta B \rightarrow \text{Products} \]

- Empirically, usually find that
  \[ \text{Rate} = k[A]^n[B]^m \]
  - \(n\) = “order of reaction with respect to A”
  - \(m\) = “order of reaction with respect to B”
  - \(n + m\) = “overall order of reaction”
  - \(k\) = rate constant = \(k(T)\)

**Reaction Orders**

- Order of a reaction can NOT be found by looking at a balanced equation!
  \[ \alpha A + \beta B \rightarrow \text{Products} \]
  \[ \text{Rate} = k[A]^n[B]^m \]
  - In general:
    - \(\alpha\) & \(n\), \(\beta\) & \(m\) are not necessarily equal
    - because this isn’t an elementary step
  - Reaction order can only be found by experiments

**Examples**

\[ 2 \text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2 \]
  - rate = \(k[\text{N}_2\text{O}_5]\)
  - BUT
    \[ 2 \text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2 \]
    - rate = \(k[\text{NO}_2]^2\)
  - CAN’T predict these from equations!

**More Examples**

\[ \text{H}_2 + \text{I}_2 \rightarrow 2\text{HI} \]
  - rate = \(k[\text{H}_2][\text{I}_2]\)
  - BUT
    \[ \text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr} \]
    - rate = \(\frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'[\text{HBr}][\text{Br}_2]^{1/4}}\)

**Finding rate laws, rate constants**

- “Method of Initial Rates”
  - combine known amounts of reactants
  - determine rate by measuring change in some concentration over a “short” time
  - repeat with different initial concentrations
  - find experimental rate law

**Problem**

\[ A + 2B \rightarrow \text{products} \]

<table>
<thead>
<tr>
<th>Expt.</th>
<th>([A]_0)</th>
<th>([B]_0)</th>
<th>Initial Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>0.0032</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.20</td>
<td>0.0032</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.30</td>
<td>0.0128</td>
</tr>
</tbody>
</table>

- find rate law & rate constant, \(k\)
- (concentrations in M, rates in M/min)
Answer to problem

rate = \frac{-1}{2} \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t} = \hat{k}[A]^2

= (0.32)[A]^2 \text{ mol L}^{-1} \text{ min}^{-1}

Integrated Rate Laws

● From initial concentrations & rate law, we can predict all concentrations at any time \( t \).
● Mathematically, this is an initial value problem often involving a simple differential equation.

Simplest Case: First Order

A \rightarrow 2P \quad \text{rate} = -\frac{d[A]}{dt} = \hat{k}[A]

By doing some calculus (pp. 358-9), we can turn this into an equation relating concentration and time:

\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -\hat{k} \int_0^t d't

\ln \frac{[A]}{[A]_0} = -\hat{k} t

First Order Reactions

\ln \frac{[A]_t}{[A]_0} = -\hat{k} t

\frac{[A]_t}{[A]_0} = e^{-\hat{k} t} \text{ so } [A]_t = [A]_0 e^{-\hat{k} t}

● From this, see that a plot of \ln[A] vs. \( t \) will be a line with a slope of -\( \hat{k} \).

Second Order, one reactant

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

= \hat{k} \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = \hat{k} \int_0^t d't

Which has the solution:

\frac{1}{[A]_t} = \frac{1}{[A]_0} = \hat{k} t \text{ or } \frac{1}{[A]_t} = \hat{k} t + \frac{1}{[A]_0}

● If second order kinetics apply, a plot of \frac{1}{[A]} vs. \( t \) will be a line with slope \( \hat{k} \).

1st vs. 2nd Order Kinetics

Both cases shown with \( \hat{k} = 0.693 \)
1st Order Test Plot: ln[A] vs. t

2nd Order Test Plot: 1/[A] vs. t

2nd Order Test Plot: 1/[A] vs. t

A Real Example ...

2 N_2O_5(g) → 4 NO_2(g) + O_2(g)

Experiment at T = 338 K gives:

<table>
<thead>
<tr>
<th>time (s)</th>
<th>[N_2O_5] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.100</td>
</tr>
<tr>
<td>100.</td>
<td>0.0620</td>
</tr>
<tr>
<td>300.</td>
<td>0.0221</td>
</tr>
<tr>
<td>600.</td>
<td>0.0053</td>
</tr>
<tr>
<td>900.</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

Find rate law?

Zero Order?

First Order?

y = -0.00001x + 0.0765
R^2 = 0.7865

y = -0.0048x - 2.3187
R^2 = 0.9997
Second Order?

\[ y = 0.7839x - 92.022 \]
\[ R^2 = 0.8059 \]

Example...

- Graphs show us that the reaction is first order, so:
  \[ \text{rate} = k [N_2O_5] \]
- We can also find \( k \) from slope of graph:
  \[ \ln [N_2O_5] = \ln [N_2O_5]_0 - kt \]
- So slope is equal to \(-k\). Fit gives us:
  \( k = 0.0048 \text{ s}^{-1} \)

Example .... (half life)

- At what time will the \([N_2O_5]\) be equal to one-half of its original value?
- Use integrated rate law:
  \[ \ln [N_2O_5] = \ln [N_2O_5]_0 - kt \]
- solve for \( t \):
  \( kt = \ln [N_2O_5]_0 - \ln [N_2O_5] \)
- or
  \[ t = \frac{1}{k} \ln \left( \frac{[N_2O_5]_0}{[N_2O_5]} \right) \]

Example.... (half-life)

\[ t = \frac{1}{k} \ln \left( \frac{[N_2O_5]_0}{[N_2O_5]} \right) = \frac{1}{k} \ln \frac{1}{2} = \frac{0.693}{k} \]

- So with \( k = 0.0048 \text{ s}^{-1} \), we will get \( t = t_{1/2} = 144 \text{ seconds} \)
- This is called the “half-life” of the reaction.
- For a first order reaction, half-life is independent of initial amount.