Lecture Notes BB: Chemical Kinetics I

1. Definition of the rate

reaction rate = (change in concentration)/ (change in time)

\[ \text{A+B} \rightarrow \text{C+D} \]

\[
\begin{align*}
\text{rate} &= -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} \\
\text{units for the rate are} &\quad \text{(concentration)/time} = \text{(moles/liter)/sec} = \text{M/s}
\end{align*}
\]

Consider the reaction:

\[ 2 \text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2 \text{NO}_2\text{F} (\text{g}) \]

Which of the following is correct?

\[
\begin{align*}
a) \text{rate} &= -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = -\frac{d[F_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2\text{F}]}{dt} & b) \text{rate} &= -\frac{d[\text{NO}_2]}{dt} = -\frac{1}{2} \frac{d[F_2]}{dt} = \frac{d[\text{NO}_2\text{F}]}{dt}
\end{align*}
\]

In general:
2. Initial rate

Consider the reaction: \[2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)\]

The following table shows the concentration of the above species for an experiment that starts with 0.01M \(\text{NO}_2\).

<table>
<thead>
<tr>
<th>time (s)</th>
<th>([\text{NO}_2])</th>
<th>([\text{NO}])</th>
<th>([\text{O}_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0.0065</td>
<td>0.0035</td>
<td>0.0018</td>
</tr>
<tr>
<td>200</td>
<td>0.0048</td>
<td>0.0052</td>
<td>0.0026</td>
</tr>
<tr>
<td>300</td>
<td>0.0038</td>
<td>0.0062</td>
<td>0.0031</td>
</tr>
<tr>
<td>400</td>
<td>0.0031</td>
<td>0.0069</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

What is the initial rate of the reaction?
3. Definition of the order of a reaction

\[ A + B \rightarrow C + D \]

When you change the concentration of a reactant, you change the rate of the reaction according to:

\[
\text{rate} = k [A]^m [B]^n
\]

The reaction is \( m \)^{th} order in \([A]\) and \( n \)^{th} order in \([B]\). The reaction has a total order of \((m+n)\)

Another experiment is performed on the reaction from page 2:

\[ 2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \]

The data is shown below. What is the order of the reaction in \([\text{NO}_2]\)?

<table>
<thead>
<tr>
<th>time (s)</th>
<th>[NO(_2)]</th>
<th>[NO]</th>
<th>[O(_2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0050</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0.0041</td>
<td>0.00087</td>
<td>0.0017</td>
</tr>
</tbody>
</table>
Concept test: If changing the concentration of a reactant, \([A]\), has no effect on the rate of a reaction, what is the order of the reaction in \([A]\).

a) -1    b) 0    c) 1/2    d) 1
Consider the following reaction: \( \text{CO}(g) + \text{NO}_2(g) \rightarrow \text{CO}_2(g) + \text{NO}(g) \)

You do five experiments, measuring the initial rate for a variety of initial concentrations.

<table>
<thead>
<tr>
<th>initial concentrations</th>
<th><a href="M">CO</a></th>
<th><a href="M">NO_2</a></th>
<th>Initial rate (M/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.1x10^{-4}</td>
<td>3.5x10^{-5}</td>
<td>3.4x10^{-8}</td>
</tr>
<tr>
<td>b</td>
<td>5.1x10^{-4}</td>
<td>7.0x10^{-5}</td>
<td>6.8x10^{-8}</td>
</tr>
<tr>
<td>c</td>
<td>5.1x10^{-4}</td>
<td>1.8x10^{-5}</td>
<td>1.7x10^{-8}</td>
</tr>
<tr>
<td>d</td>
<td>10.2x10^{-4}</td>
<td>3.5x10^{-5}</td>
<td>6.8x10^{-8}</td>
</tr>
<tr>
<td>e</td>
<td>15.3x10^{-4}</td>
<td>3.5x10^{-5}</td>
<td>10.2x10^{-8}</td>
</tr>
</tbody>
</table>

a) Derive the rate expression.

b) What is the order of the reaction?

c) Calculate the rate constant
d) Calculate the rate for the following conditions

<table>
<thead>
<tr>
<th>initial concentrations</th>
<th><a href="M">CO</a></th>
<th><a href="M">NO₂</a></th>
<th>Initial rate (M/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.4x10⁻⁴</td>
<td>2.1x10⁻⁵</td>
<td></td>
</tr>
</tbody>
</table>

Concept:
For the reaction \( A(g) + B(g) \rightarrow AB(g) \), the rate is 0.20 M/s when \([A] = [B] = 1.0 \text{ M}\). The reaction is first order in \( B \) and second order in \( A \). What is the rate when \([A] = 2.0 \text{M} \) and \([B] = 3.0 \text{M}\).

a) 1.2 M/s  
b) 2.4 M/s  
c) 3.6 M/s

4. Integrated rate laws:

First order reaction: \( \text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2 \)
Concept test: The half life for the radioactive decay of $^{32}$P is 14 days. You start with 1.000g of $^{32}$P. How many grams are left after $3\times14 = 42$ days.

a) 0.100g   b) 0.125g   c) 0.25g   d) 0.333g

Second order reaction: $2\text{ NO}_2 \rightarrow 2\text{ NO} + \text{ O}_2$
For the simple decomposition reaction: $AB(g) \rightarrow A(g) + B(g)$, the rate $= k[AB]^2$. If it takes 5 minutes for $[AB]$ to reach one-third of its initial concentration of 1.5M, what is $k$ (assume you can ignore the reverse reaction)?