### Differential Method – Graphical Equal Area – Last Lecture Prob

<table>
<thead>
<tr>
<th>time</th>
<th>$C_A$</th>
<th>$(-\Delta C_A/\Delta t)$</th>
<th>$(-dC_A/dt)$</th>
<th>$\ln(-dC_A/dt)$</th>
<th>$\ln(C_A)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
<td>0.3700</td>
<td>0.3900</td>
<td>-0.9416</td>
<td>1.3863</td>
</tr>
<tr>
<td>3</td>
<td>2.89</td>
<td>0.3200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.25</td>
<td>0.2667</td>
<td>0.3000</td>
<td>-1.2040</td>
<td>0.8109</td>
</tr>
<tr>
<td>8</td>
<td>1.45</td>
<td>0.2250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>0.1750</td>
<td>0.2100</td>
<td>-1.5606</td>
<td>0.0000</td>
</tr>
<tr>
<td>12</td>
<td>0.65</td>
<td>0.1333</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.25</td>
<td>0.0720</td>
<td>0.1000</td>
<td>-2.3026</td>
<td>-1.3863</td>
</tr>
<tr>
<td>17.5</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\alpha = \frac{Rise}{Run}
\]

\[
k = \left( \frac{-dC_A}{dt} \right)_P
\]

Best to pick from a point in the middle of the data
Polynomial Fit method

\[ C_A = 0.01t^2 - 0.3992t + 3.999 \]

\[ R^2 = 1 \]
\[ \ln(-d\text{CA}/dt) = 0.5146 \ln(\text{CA}) - 1.6218 \]

\[ R^2 = 0.9996 \]

Polynomial Fit method

\[ \alpha \exp(-1.6218) = k_A \]

\[ \ln(-d\text{CA}/dt) = 0.5146 \ln(\text{CA}) - 1.6218 \]

\[ R^2 = 0.9996 \]
2. Integral Method

For the integral method we guess the reaction order and then integrate the differential equation used to model the batch system.

If the assumed order is correct, the appropriate plot (determined from integration) of the concentration –time data should be LINEAR.

Trial and error procedure

Looking for the appropriate function of concentration corresponding to a particular rate law that is linear with time.

You should be familiar (write down within seconds) the functions for zero, first and second order reactions.
A $\rightarrow$ P
carried out in a constant volume batch reactor

**Zero order:** $-r_A = kC_A^0 = k$

Integrate the function.

Limits $C_A = C_{A0}$ at $t=0$

**Postulated (guessed rate law)**

Combined w/ mole balance

$-\frac{dC_A}{dt} = k$

$C_A = C_{A0} - kt$

**IF the reaction order is zero then a plot of $C_A$ vs $t$ will be linear.**

Zero Order, $\alpha = 0$

$slope = -k$
First Order:

\[-r_A = kC_A^{1} = kC_A\]

\[-\frac{dC_A}{dt} = kC_A\]

Integrate the function.

Limits \(C_A = C_{A_0}\) at \(t = 0\)

\[\ln\left(\frac{C_{A_0}}{C_A}\right) = kt\]

IF the reaction is first order then a plot of \(\ln(C_{A_0}/C_A)\) vs \(t\) will be linear.
Second Order:

\[-r_A = kC_A^2\]

\[-\frac{dC_A}{dt} = kC_A^2\]

Integrate the function.

Limits $C_A = C_{A0}$ at $t = 0$

IF the reaction is second order then a plot of $1/C_{A0}$ vs $t$ will be linear.
Classroom Exercise:

In order to study the photochemical decay of aqueous bromine in bright sunlight, a small quantity of liquid bromine was dissolved in water contained in a glass battery jar and placed in direct sunlight. The following data were obtained at 25 °C.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm Br₂</td>
<td>2.45</td>
<td>1.74</td>
<td>1.23</td>
<td>0.88</td>
<td>0.62</td>
<td>0.44</td>
</tr>
</tbody>
</table>

a) Determine whether the reaction rate is zero, first, or second order in bromine, and calculate the reaction rate constant in units of your choice.

Note: ppm= parts of bromine per million parts of brominated water by weight. In dilute aqueous solutions, 1 ppm = 1 mg/L
Homework Assignment: Due date Monday 3/19/07

5.5

5-7