Problem Set 3

Problems

1. The bleaching of Bromphenol Blue (BPB) by OH\(^{-}\) can be followed by measuring the Absorbance at a particular Wavelength via Beer's Law:

\[
A = \varepsilon bc
\]

The reaction is:

\[
\text{BPB} + \text{OH}^{-} \rightarrow \text{BPBOH}^{-}
\]

The product does not absorb at the wavelength used.

a) Express the Rate of Reaction \(\frac{d[A]}{dt}\), in terms of the change of Absorbance with Time, \(\frac{dA}{dt}\).

b) If \(A_0\) is absorbance of the solution at \(t=0\), derive the relation between \(A\) and \(t\). What quantity should be plotted against time to determine the Rate Constant? Assume that the reaction is First Order with respect to each of the reactants and that they are mixed in the stoichiometric ratio.

2. The Rate of the Reaction:

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

has been studied at 826°C. Some of the data are:

<table>
<thead>
<tr>
<th>Run</th>
<th>Initial P of H(_2) (Pa)</th>
<th>Initial P of NO (kPa)</th>
<th>Initial Rate (kPa/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53.3</td>
<td>40.0</td>
<td>0.137</td>
</tr>
<tr>
<td>2</td>
<td>53.3</td>
<td>20.3</td>
<td>0.033</td>
</tr>
<tr>
<td>3</td>
<td>38.5</td>
<td>53.3</td>
<td>0.213</td>
</tr>
<tr>
<td>4</td>
<td>19.6</td>
<td>53.3</td>
<td>0.105</td>
</tr>
</tbody>
</table>

What are the Orders of the Reaction with respect to NO and with respect to H\(_2\)?

3. Derive the integrated rate law for a chemical reaction whose rate law is:

\[
\text{Rxn Rate} = k [A]^{3/2}
\]
Derive an expression for the Half-Life.

4. The rate of decomposition NH₃ on the surface of a heated Tungsten Wire has been measured. The results are given below.

<table>
<thead>
<tr>
<th>time (sec)</th>
<th>P of NH₃ (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>100</td>
<td>86.5</td>
</tr>
<tr>
<td>200</td>
<td>76.5</td>
</tr>
<tr>
<td>300</td>
<td>66.5</td>
</tr>
<tr>
<td>400</td>
<td>57.5</td>
</tr>
<tr>
<td>500</td>
<td>49</td>
</tr>
<tr>
<td>800</td>
<td>25</td>
</tr>
<tr>
<td>900</td>
<td>13</td>
</tr>
</tbody>
</table>

Determine the Order of the Reaction and the Rate Constant graphically.

5. At 24.8°C, the reaction:

\[
\text{C}_6\text{H}_5(\text{CH}_3)_2 + \text{CH}_3\text{I} \rightarrow \text{C}_6\text{H}_5(\text{CH}_3)_3^+ + \Gamma
\]

has a Rate constant \( k = 8.39 \times 10^{-5}\text{ M}^{-1}\text{sec}^{-1} \). The reaction is First Order with respect to each of the reactants.

If equal volumes of solutions that are 0.12M in Dimethylaniline and Methyl Iodide are mixed, how much time is required for 70% of the reactants to disappear?

6. Why is it unlikely the following reaction occurs in a single bimolecular step:

\[
\text{NH}_3 + \text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2
\]

7. A mechanism for the reaction:

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

is proposed to be:

\[
2\text{A} \thicksim \text{D} \quad k_1 \text{ and } k_{-1} \quad \text{Approx. Equil.}
\]

\[
\text{B} + \text{D} \rightarrow \text{A} + \text{C} \quad k_2
\]
Determine the Rate Law for \( d[C]/dt \) based on this mechanism.

8. Using the Lindemmann Mechanism for unimolecular reactions, we could write:

\[
k' = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2}
\]

a) Show that a plot of \( 1/k' \) vs. \( 1/P_0 \), where \( P_0 \) is the initial pressure of the system, should result in a straight line.

b) For the reaction:

\[
\text{Cyclopropane} \rightarrow \text{Propylene}
\]

The following data has been obtained.

<table>
<thead>
<tr>
<th>( P_0 ) [Torr]</th>
<th>( k' ) [sec(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>0.0000958</td>
</tr>
<tr>
<td>211</td>
<td>0.000104</td>
</tr>
<tr>
<td>388</td>
<td>0.000108</td>
</tr>
<tr>
<td>760</td>
<td>0.000111</td>
</tr>
</tbody>
</table>

Use this data to determine \( k' \) at \( P = \infty \), as well as \( k_1 \) and \( k_1/k_2 \) for this reaction.

Additional Problems for 527 Students

9. A free-radical chain mechanism for the decomposition of Acetaldehyde has been provided by Rice and Herzfeld; JACS 56 (1934) 284. Assume only reactions (1), (4), (5) and (6) are important in the forward direction. Apply the Steady-State Approximation to \([\text{CH}_3]\) and \([\text{CH}_2\text{CHO}]\). Determine the rate of formation of \( \text{CH}_4 \):

\[
\frac{d[\text{CH}_4]}{dt} = ?
\]

Calculate the Activation Energy for this reaction based on your results. Compare this with the experimentally determined value.