Graded Assignment No. 2 (of 2)

This assignment is due in the professor’s office or mailbox by 4:30 PM Friday, March 3. Submission on Monday, March 8 will result in an automatic deduction of 50%. Submission on Tuesday will result in zero credit. Do your own work!!! While you may consult each other in your study groups, the submitted assignment should represent your own sole efforts.

Question ONE: [30 points; 10 each]

(a) The concentration of a reactant is $1.275 \times 10^{-3}$ M at the start of the following first order reaction. After $0.00801$ s the concentration falls to $0.0004639$ M. Calculate the rate constant, the half-life as well as the time taken for the reactant to fall to 1.00% of its initial value.

(b) By observing only the initial rates of a reaction, one can use these data to evaluate reaction order. Prove this statement. Clearly describe the type of data you expect, and how you would manipulate the data to deduce reaction order. Use hypothetical reaction $A + B \rightarrow$ Products; with Rate = $k[A]^x[B]^y$

©) The following reaction is known to be first order in bromine:

$$4\text{Br}_2(aq) + \text{SC(NH}_2)_2 + 5\text{H}_2\text{O} \rightarrow \text{C(NH}_2)_2 + \text{SO}_4^{2-} + 8\text{Br}^- + 10\text{H}^+$$

such that Rate = $-\frac{1}{4}\frac{d[\text{Br}_2]}{dt} = k[\text{Br}_2(aq)][\text{SC(NH}_2)_2]^x$

The following initial rate data were obtained for a fixed initial concentration of 0.0130 M aqueous bromine: (data represent rate of disappearance of bromine)

<table>
<thead>
<tr>
<th>$[\text{SC(NH}_2)_2]_0$/M</th>
<th>0.01</th>
<th>0.02</th>
<th>0.03</th>
<th>0.04</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial rate/mol s$^{-1}$</td>
<td>4.12x10$^{-3}$</td>
<td>1.65x10$^{-2}$</td>
<td>3.71x10$^{-2}$</td>
<td>6.60x10$^{-2}$</td>
<td>0.103</td>
</tr>
</tbody>
</table>

Evaluate the order with respect to thiourea, x, and deduce the value of the rate constant, $k$ (remember the units)
Question TWO: [40 points; 5, 5, 15, 15 resp.]

(a) What physical parameters do you know that can be altered to effect a relaxation spectrum? (full points will be obtained from mentioning 5 correct parameters).

(b) What is the prerequisite for a reaction to show a temperature jump spectrum? Give a relevant equation that shows how this constraint affect the reaction’s equilibrium.

©) Consider the reaction system: A + B ⇆ C. Prove that the relaxation time for such a reaction system is given by: \( J = \left[ k_1(a + b) + k_{-1} \right]^{-1} \); where \( J \) is the relaxation time; \( a, b \) represent equilibrium concentrations of A and B and \( k_1, k_{-1} \) are the forward and reverse rate constants for the reaction.

(d) The following reaction was studied by Laser-Raman temperature-jump techniques using a temperature-jump of 8.8 °C and Joule-heating across a capacitor of capacitance 0.1 :F:

\[ \text{I}_2(\text{aq}) + \text{Br}^- (\text{aq}) \rightleftharpoons \text{I}_2\text{Br}^- (\text{aq}); \quad k_1, k_{-1} \]

The following relaxation time data were obtained:

<table>
<thead>
<tr>
<th>( I_2(\text{aq}) )</th>
<th>( \Gamma(\text{aq}) )</th>
<th>( J ) (relax. time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0x10^-4 M</td>
<td>8.0x10^-4 M</td>
<td>5.71x10^-7 s</td>
</tr>
<tr>
<td>4.0x10^-4 M</td>
<td>1.1x10^-3 M</td>
<td>5.02x10^-7 s</td>
</tr>
<tr>
<td>5.0x10^-4 M</td>
<td>1.5x10^-3 M</td>
<td>4.40x10^-7 s</td>
</tr>
<tr>
<td>1.0x10^-3 M</td>
<td>2.0x10^-3 M</td>
<td>3.58x10^-7 s</td>
</tr>
<tr>
<td>1.5x10^-3 M</td>
<td>2.5x10^-3 M</td>
<td>3.03x10^-7 s</td>
</tr>
</tbody>
</table>

Evaluate \( k_1, k_{-1} \) and \( K_{eq} \)

Question THREE: [20 points; 10 each]

(a) How does the time required for a first order reaction to go to 99% completion compare (or relate) to the half-life for the reaction?

(b) The rate constant for the neutralization reaction \( \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \) \( 1.3 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). Calculate
the half-life for the neutralization process if (a) \([H^+] = [OH^-] = 0.10\ M\) and (b) \([H^+] = [OH^-] = 0.0001\ M\)?

Question FOUR: [10 points]

Since we reside in Oregon, then this question will be very appropriate:

In the field of chemical oscillations, one of the most important models used to describe the Belousov-Zhabotinski chemical oscillator is the ‘Oregonator Model’. Briefly describe the qualitative aspects of this model.

**PS:** Search databases for scientific journals written on the Oregonator model, or read modern p-chem text books that profile this topic.