Current Week's Assignment

All homework questions are from Zumdahl 4th Edition. Solutions will usually be posted by Friday, and will appear on the past homework page.

❖ READING --- Zumdahl Chapter 12: 12.1 - end of chapter

❖ PROBLEMS -- Chapter 12: 8, 20, 21, 22, 23, 26, 27, 31 and the GRADED web quiz questions

Past week's assignment and solutions  |  Trial Midterms
Chapter 12: Chemical Kinetics

8. The rate of a chemical reaction varies with time. Consider the general reaction:

$$ A \rightarrow \text{Products where rate} = \frac{-\Delta[A]}{\Delta t} $$

If we graph $[A]$ vs. $t$, it would roughly look like the dark line in the following plot.

![Plot of [A] vs. time](image)

An instantaneous rate is the slope of a tangent line to the graph of $[A]$ vs. $t$. We can determine the instantaneous rate at any time during the reaction. On the plot, tangent lines at $t = 0$ and $t = t_1$ are drawn. The slope of these tangent lines would be the instantaneous rates at $t \approx 0$ and $t = t_1$. We call the instantaneous rate at $t \approx 0$ the initial rate. The average rate is measured over a period of time. For example, the slope of the line connecting points a and c is the average rate of the reaction over the entire length of time 0 to $t_2$. The rate which is largest is the initial rate. At $t \approx 0$, the slope of the tangent line is greatest which means the rate is largest at $t \approx 0$.

20. \[ \frac{\Delta[H_2]}{\Delta t} = 3 \frac{\Delta[N_2]}{\Delta t} \quad \text{and} \quad \frac{\Delta[NH_3]}{\Delta t} = -2 \frac{\Delta[N_2]}{\Delta t} \]; So, \( -\frac{1}{3} \frac{\Delta[H_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[NH_3]}{\Delta t} \)

or \[ \frac{\Delta[NH_3]}{\Delta t} = -\frac{2}{3} \frac{\Delta[H_2]}{\Delta t} \]

Ammonia is produced at a rate equal to $2/3$ of the rate of consumption of hydrogen.
21. a. The units for rate are always mol/L•s.
   b. Rate = k; k must have units of mol/L•s
   c. Rate = k[A], \( \frac{\text{mol}}{\text{L} \cdot \text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right) \)
   d. Rate = k[A]^2, \( \frac{\text{mol}}{\text{L} \cdot \text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)^2 \)
   e. \( \text{L}^2/\text{mol}^2 \cdot \text{s} \)

22. Rate = k[Cl]^{1/2}[CHCl_3], \( \frac{\text{mol}}{\text{L} \cdot \text{s}} = k \left( \frac{\text{mol}}{\text{L}} \right)^{1/2} \left( \frac{\text{mol}}{\text{L}} \right), \) k must have units of \( \text{L}^{1/2}/\text{mol}^{1/2} \cdot \text{s} \).

**Rate Laws from Experimental Data: Initial Rates Method**

23. a. In the first two experiments, [NO] is held constant and [Cl_2] is doubled. The rate also doubled. Thus, the reaction is first order with respect to Cl_2. Or mathematically: \( \text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y \)

\[
\frac{0.36}{0.18} = \frac{k(0.10)^x(0.20)^y}{k(0.10)^x(0.10)^y} = \frac{(0.20)^y}{(0.10)^y}, \quad 2.0 = 2.0^y, \quad y = 1
\]

We can get the dependence on NO from the second and third experiments. Here, as the NO concentration doubles (Cl_2 concentration is constant), the rate increases by a factor of four. Thus, the reaction is second order with respect to NO. Or mathematically:

\[
\frac{1.45}{0.36} = \frac{k(0.20)^x(0.20)}{k(0.10)^x(0.20)} = \frac{(0.20)^x}{(0.10)^x}, \quad 4.0 = 2.0^x, \quad x = 2; \quad \text{So}, \quad \text{Rate} = k[\text{NO}]^2[\text{Cl}_2]
\]

Try to examine experiments where only one concentration changes at a time. The more variables that change, the harder it is to determine the orders. Also, these types of problems can usually be solved by inspection. In general, we will solve using a mathematical approach, but keep in mind, you probably can solve for the orders by simple inspection of the data.

b. The rate constant k can be determined from the experiments. From experiment 1:

\[
\frac{0.18 \text{ mol}}{\text{L min}} = k \left( \frac{0.10 \text{ mol}}{\text{L}} \right)^2 \left( \frac{0.10 \text{ mol}}{\text{L}} \right), \quad k = 180 \text{ L}^2/\text{mol}^2 \cdot \text{min}
\]

From the other experiments:

\[
k = 180 \text{ L}^2/\text{mol}^2 \cdot \text{min} \text{ (2nd exp.)}; \quad k = 180 \text{ L}^2/\text{mol}^2 \cdot \text{min} \text{ (3rd exp.)}
\]

The average rate constant is \( k_{\text{mean}} = 1.8 \times 10^2 \text{ L}^2/\text{mol}^2 \cdot \text{min} \).
26. a. Rate = k[\text{I}^\text{-}]^x[\text{OCl}^-]^y; \quad \frac{7.91 \times 10^{-2}}{3.95 \times 10^{-2}} = \frac{k(0.12)^x(0.18)^y}{k(0.060)^x(0.18)^y} = 2.0^x, \quad 2.00 = 2.0^x, \quad x = 1

\frac{3.95 \times 10^{-2}}{9.88 \times 10^{-3}} = \frac{k(0.060)^y}{k(0.030)^y}, \quad 4.00 = 2.0 \times 2.0^y, \quad 2.0 = 2.0^y, \quad y = 1

Rate = k[\text{I}^\text{-}][\text{OCl}^-]

b. From the first experiment: \quad \frac{7.91 \times 10^{-2} \text{ mol}}{L \text{ s}} = k \left( \frac{0.12 \text{ mol}}{L} \right) \left( \frac{0.18 \text{ mol}}{L} \right), \quad k = 3.7 \text{ L/mol s}

All four experiments give the same value of k to two significant figures.

27. a. Rate = k[Hb]^x[CO]^y; Comparing the first two experiments, [CO] is unchanged, [Hb] doubles, and the rate doubles. Therefore, the reaction is first order in Hb. Comparing the second and third experiments, [Hb] is unchanged, [CO] triples and the rate triples. Therefore, y = 1 and the reaction is first order in CO.

b. Rate = k[Hb][CO]

c. From the first experiment:

\[ 0.619 \mu \text{mol/L s} = k \left(2.21 \mu \text{mol/L}\right)\left(1.00 \mu \text{mol/L}\right), \quad k = 0.280 \text{ L/\mu mol s} \]

The second and third experiments give similar k values, so \( k_{\text{mean}} = 0.280 \text{ L/\mu mol s} \).

d. Rate = k[Hb][CO] = \frac{0.280 \text{ L}}{\mu \text{mol s}} \times \frac{3.36 \mu \text{mol}}{L} \times \frac{2.40 \mu \text{mol}}{L} = 2.26 \mu \text{mol/L s}

31. Assume the reaction is first order and see if the plot of ln [NO_2] vs. time is linear. If this isn’t linear, try the second order plot of 1/[NO_2] vs. time. The data and plots follow.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[NO_2] (M)</th>
<th>ln [NO_2]</th>
<th>1/[NO_2] (M^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.500</td>
<td>-0.693</td>
<td>2.00</td>
</tr>
<tr>
<td>1.20 \times 10^3</td>
<td>0.444</td>
<td>-0.812</td>
<td>2.25</td>
</tr>
<tr>
<td>3.00 \times 10^3</td>
<td>0.381</td>
<td>-0.965</td>
<td>2.62</td>
</tr>
<tr>
<td>4.50 \times 10^3</td>
<td>0.340</td>
<td>-1.079</td>
<td>2.94</td>
</tr>
<tr>
<td>9.00 \times 10^3</td>
<td>0.250</td>
<td>-1.386</td>
<td>4.00</td>
</tr>
<tr>
<td>1.80 \times 10^4</td>
<td>0.174</td>
<td>-1.749</td>
<td>5.75</td>
</tr>
</tbody>
</table>
The plot of $1/\text{[NO}_2\text{]}$ vs. time is linear. The reaction is second order in NO$_2$. The rate law and integrated rate law are: Rate = $k\text{[NO}_2\text{]}^2$ and $\frac{1}{\text{[NO}_2\text{]}} = kt + \frac{1}{\text{[NO}_2\text{]}_0}$.

The slope of the plot $1/\text{[NO}_2\text{]}$ vs. $t$ gives the value of $k$. Using a couple points on the plot:

$$\text{slope} = k = \frac{\Delta y}{\Delta x} = \frac{(5.75 - 2.00) M^{-1}}{(1.80 \times 10^{-4} - 0) s} = 2.08 \times 10^{-4} \text{ L/mole s}$$

To determine $\text{[NO}_2\text{]}$ at $2.70 \times 10^4 \text{ s}$, use the integrated rate law where $1/\text{[NO}_2\text{]}_0 = 1/0.500\text{ M} = 2.00 M^{-1}$

$$\frac{1}{\text{[NO}_2\text{]}} = kt + \frac{1}{\text{[NO}_2\text{]}_0}, \quad \frac{1}{\text{[NO}_2\text{]}} = \frac{2.08 \times 10^{-4} \text{ L}}{\text{mol s}} \times 2.70 \times 10^4 \text{ s} + 2.00 M^{-1}$$

$$\frac{1}{\text{[NO}_2\text{]}} = 7.62, \quad \text{[NO}_2\text{]} = 0.131 \text{ M}$$