Topics to be covered on the quiz:

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Practice problems:

1) (a) During a reaction, what happens to the concentrations of the reactants? the products?
(b) Why do the rates of reactions decrease as concentrations decrease?

   (a) During a reaction, the concentrations of the reactants decrease and the products increase.
   (b) With a lower concentration, there are less atoms/molecules available for collisions.

2) (a) Define reaction rate.
(b) Distinguish between initial rate, average rate, and instantaneous rate of a chemical reaction.

   Initial rate = rate near time 0
   Average rate = rate between two times
   Instantaneous rate = rate at a specific time

(c) Which of the three rates is usually the fastest? Initial rate
(d) The initial rate is usually used. Give a possible explanation why it is usually used.

   Highest rate due to largest concentrations of reactants

3) (a) Distinguish between the differential rate law and the integrated rate law.
(b) Which one is usually just called the rate law?
(c) What is k in a rate law?
(d) What is meant by order in a rate law?

   (a) The differential rate law deals with rate vs. concentration. The integrated rate law deals with concentration vs. time.
   (b) The differential rate law is usually called the rate law.
   (c) The k in a rate law is the rate constant.
   (d) Order for a rate law is the exponents of the concentrations of the reactants, determined by experiment.

4) Consider zero-, first-, and second-order integrated rate laws. If you have concentration vs. time data for a reactant in a reaction, what graphs would you make to “prove” a reaction is either zero-, first-, or second-order? How can the rate constant be determined from such a plot? What does the y-intercept equal in each plot?

   0 order = [molarity] vs. time
   1st order = ln [molarity] vs. time
   2nd order = 1/[molarity] vs. time

   Rate constant k = [slope] from graph
   y-intercept is related to the initial concentration

5) Hydrogen reacts explosively with oxygen. However, a mixture of H₂ and O₂ can exist indefinitely at room temperature. Explain why H₂ and O₂ do not react under these conditions.

   There is not enough activation energy for the reaction to occur. (Bonds are pretty stable already!)

6) Consider the combustion of ethene, C₂H₄(g) + 3 O₂(g) —> 2 CO₂(g) + H₂O(g). If the concentration of C₂H₄ is decreasing at a rate of 0.025 M/s, what are the rates of change in the concentrations of CO₂ and H₂O?

   Change of CO₂ and H₂O = 0.050 M/s due to equation coefficients
7) Consider a hypothetical reaction between A, B, and C that is first order in A, zero order in B, and second order in C. (a) Write the rate law for the reaction. (b) How does the rate change when [A] is doubled and the other reactant concentrations are held constant? How does the rate change when [B] is tripled and the other reactant concentrations are held constant? How does the rate change when [C] is tripled and the other reactant concentrations are held constant? (e) By what factor does the rate change when the concentrations of all three reactants are tripled?

(a) \[ \text{rate} = k[A]^1[B]^0[C]^2 \]
(b) if [A] is doubled, rate doubles; if [B] is tripled, rate stays the same; if [C] is tripled, rate increases by a factor of 9
(c) \[ \text{rate} = k[3A]^1[3B]^0[3C]^2 = x 27! \]

8) The central idea of the collision model is that molecules must collide in order to react. Give two reasons why not all collisions of reactant molecules result in product formation.
- not enough energy (lower than activation energy)
- incorrect molecular orientation during collisions

9) Consider the reaction

\[ 4 \text{ PH}_3 (g) \rightarrow \text{ P}_4 (g) + 6 \text{ H}_2 (g) \]

If, in a certain experiment, over a specific time period, 0.0048 moles of \text{ PH}_3 are consumed in a 2.0 L container each second of reaction, what are the rates of production of \text{ P}_4 and \text{ H}_2?

\[ \text{PH}_3 = - 0.0024 \text{ M/s} \quad \text{P}_4 = + 6.0 \times 10^{-4} \text{ M/s} \quad \text{H}_2 = + 3.6 \times 10^{-3} \text{ M/s} \]

10) At 40 °C, hydrogen peroxide will decompose according to the following reaction:

\[ 2 \text{ H}_2\text{O}_2 (aq) \rightarrow 2 \text{ H}_2\text{O (l)} + \text{ O}_2 (g) \]

The following data were collected for the concentration of hydrogen peroxide at various times:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[H$_2$O$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.000</td>
</tr>
<tr>
<td>2.16 x 10$^4$</td>
<td>0.500</td>
</tr>
<tr>
<td>4.32 x 10$^4$</td>
<td>0.250</td>
</tr>
</tbody>
</table>

(a) Calculate the average rate of decomposition of H$_2$O$_2$ between 0 and 2.16 x 10$^4$ s. Use this rate to calculate the average rate of production of O$_2$ over the same time period.
(b) What are those same rates for the time period from 2.16 x 10$^4$ s to 4.32 x 10$^4$ s?

(a) \[ \Delta [\text{H}_2\text{O}_2]/\Delta t = -2.31 \times 10^{-5} \text{ M/s}; \Delta [\text{O}_2]/\Delta t = + 1.16 \times 10^{-5} \text{ M/s} \]
(b) \[ \Delta [\text{H}_2\text{O}_2]/\Delta t = -1.16 \times 10^{-5} \text{ M/s}; \Delta [\text{O}_2]/\Delta t = + 5.79 \times 10^{-6} \text{ M/s} \]

11) Define what is meant by unimolecular and bimolecular steps. Why are termolecular steps infrequently seen in chemical reactions?

unimolecular = elementary step in a reaction mechanism with one reactant molecule
bimolecular = elementary step in a reaction mechanism with two reactant molecules
termolecular = elementary step in a reaction mechanism with three reactant molecules
- infrequently seen in chemical reactions because the probability of three molecules being able to hit each other with enough energy and in the right molecular orientation, all at the same time, is pretty low
12) The decomposition of nitrosyl chloride was studied:

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

The following data were obtained, where

\[ \text{rate} = -\frac{\Delta \text{[NOCl]}}{\Delta t} \]

<table>
<thead>
<tr>
<th>[NOCl] \text{[molecules/cm}^3\text{]}</th>
<th>Initial rate [molecules/(cm}^3\cdot\text{s})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0 \times 10^{16}</td>
<td>1.06 \times 10^5</td>
</tr>
<tr>
<td>3.0 \times 10^{16}</td>
<td>5.98 \times 10^4</td>
</tr>
<tr>
<td>2.0 \times 10^{16}</td>
<td>2.66 \times 10^4</td>
</tr>
<tr>
<td>1.0 \times 10^{16}</td>
<td>6.64 \times 10^3</td>
</tr>
</tbody>
</table>

(a) What is the rate law? 
rate = k[NOCl]^2
(b) Calculate the rate constant. 
k = 6.6 \times 10^{-29}

13) The rate of the reaction

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

depends only on the concentration of nitrogen dioxide below 225 °C. At a temperature below 225 °C, the following data were collected:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[NO_2] \text{(M)}</th>
<th>I calculated: ln [NO_2]</th>
<th>1/[NO_2]</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 10^2</td>
<td>0.444</td>
<td>-0.812</td>
<td>2.252</td>
</tr>
<tr>
<td>3.00 \times 10^3</td>
<td>0.381</td>
<td>-0.965</td>
<td>2.625</td>
</tr>
<tr>
<td>4.50 \times 10^3</td>
<td>0.340</td>
<td>-1.079</td>
<td>2.941</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>5.747</td>
</tr>
</tbody>
</table>

Determine the rate law, the integrated rate law, and the value of the rate constant. Calculate [NO_2] at 2.70 \times 10^4 \text{s}.

- First, I calculated the natural log (ln) of the molarities and the reciprocals (1/molarity). (see above)
- Next, I made three graphs: (a) [NO_2] vs. time, (b) ln [NO_2] vs. time, and 1/[NO_2] vs. time
  [I made mine on graph paper and on Microsoft Excel; also works on graphing calculators]
  (see next page for examples)
- The straightest line graph was 1/[NO_2], so I knew it was a second-order reaction, so the rate law was
  rate = k[NO_2]^2 (differential rate law) or (using the one on the AP formula sheet)
  \[ 1/\text{[NO}_2] - 1/\text{[NO}_2]_0 = kt \]
- k is the |slope| of the straight-line graph, so around 2.0 \times 10^{-4}
- plugging in the given time to the integrated rate law, you get around 0.14 M for the given time
14) The rate law for a reaction can be determined only from experiment and not from the balanced equation. Two common experimental procedures exist for determining a reaction’s rate law, the method of concentration vs. time (which we did in our lab) and the method of initial rates. Briefly explain how each method is used to determine the rate law.

concentration vs. time –> Watch a reaction as it occurs, measuring the concentration over time (as we did by measuring the absorbances over time)
(Graph results to find order of reaction)
initial rates –> try a reaction several times, changing the concentrations each time (keeping some constant for comparison) and measuring the rate quickly after mixing
Do calculations to determine order of reaction for each reactant

15) The following mechanism has been proposed for the gas-phase reaction of H₂ with ICl:

\[
\begin{align*}
H_2 (g) + ICl (g) & \rightarrow HI (g) + HCl (g) \\
HI (g) + ICl (g) & \rightarrow I_2 (g) + HCl (g)
\end{align*}
\]

(a) Write the balanced equation for the overall reaction.
(b) Identify any intermediates in the mechanism.

(a) \(H_2 + 2 ICl \rightarrow I_2 + 2 HCl\)
(b) HI
16) A proposed mechanism for a reaction is

\[ \text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{B}_9 + \text{Br}^- \] slow
\[ \text{C}_4\text{B}_9 + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH}_2^- \] fast
\[ \text{C}_4\text{H}_9\text{OH}_2^- + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^+ \] fast

(a) Write the rate law expected for this mechanism.
(b) What is the overall balanced equation for this reaction?
(c) What are the intermediates in this proposed mechanism?

(a) \( \text{rate} = k[\text{C}_4\text{H}_9\text{Br}] \)
(b) \( \text{C}_4\text{H}_9\text{Br} + 2 \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^- + \text{Br}^- \)
(c) \( \text{C}_4\text{B}_9 \) and \( \text{C}_4\text{H}_9\text{OH}_2^- \)

17) Finish ChemActivity #57.