Kinetics

1. Consider this balanced chemical equation:

\[
\text{H}_2\text{O}_2 (aq) + 3\text{I}^- (aq) + 2\text{H}^+ (aq) \rightarrow \text{I}_3^- (aq) + 2\text{H}_2\text{O} (l)
\]

In the first 10.0 seconds of the reaction, the concentration of \( \text{I}^- \) drops from 1.000M to 0.868M.

(a) Calculate the average rate of this reaction in this time interval.

(b) Determine the rate of change in the concentration of \( \text{H}^+ \) (that is, \( \Delta[\text{H}^+]/\Delta t \)) during this time interval.
2. Consider the equation:

$$\text{CHCl}_3 \ (g) + \text{Cl}_2 \ (g) \rightarrow \text{CCl}_4 \ (g) + \text{HCl} \ (g)$$

The initial rate of reaction is measured at several different concentrations of the reactants with the following results:

<table>
<thead>
<tr>
<th>[CHCl₃] (M)</th>
<th>[Cl₂] (M)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>0.010</td>
<td>0.0035</td>
</tr>
<tr>
<td>0.020</td>
<td>0.010</td>
<td>0.0069</td>
</tr>
<tr>
<td>0.020</td>
<td>0.020</td>
<td>0.0098</td>
</tr>
<tr>
<td>0.040</td>
<td>0.040</td>
<td>0.027</td>
</tr>
</tbody>
</table>

From the data, determine the rate law for the reaction.
3. Consider the combustion of propane:

$$C_3H_8 (g) + 5O_2 (g) \rightarrow 3CO_2 (g) + 4H_2O (g)$$

When $O_2$ is reacting at a rate of 0.3 M/s, at what rate is $CO_2$ being formed?
(a) 0.5 M/s
(b) 0.18 M/s
(c) 0.3 M/s
(d) 3 M/s

4. The reaction is first-order in cyclopropene and has a measured rate constant of $3.36 \times 10^{-5}$ s$^{-1}$ at 720K. If the initial cyclopropane concentration is 0.0445M, what is the cyclopropane concentration after 235.0 minutes?
5. A certain first-order reaction has a half-life of $1.2 \times 10^3$ s.
   (a) Calculate the rate constant for this reaction

   (b) How much time is required for this reaction to be 75% complete?

6. Consider the reaction between nitrogen dioxide and carbon monoxide:

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

   The rate constant at 701K is measured as $2.57 \text{ M}^{-1}\text{s}^{-1}$, and that at 895K is measured as $567 \text{ M}^{-1}\text{s}^{-1}$. Find the activation energy for the reaction in kJ/mol.
7. Which statement most accurately describes the behavior of a catalyst?
   a. A catalyst increases the \( \Delta G \) of a reaction and hence the forward rate.
   b. A catalyst reduces the \( \Delta H \) of a reaction and hence the temperature needed to produce products.
   c. A catalyst reduces the activation energy for a reaction and increases the rate of a reaction.
   d. A catalyst increases the equilibrium constant and final product concentrations.

8. A proposed mechanism for a reaction is

\[
C_4H_9Br \rightarrow C_4H_9^+ + Br^- \quad \text{(slow)}
\]

\[
C_4H_9^+ + H_2O \rightarrow C_4H_9OH^+ \quad \text{(fast)}
\]

\[
C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+ \quad \text{(fast)}
\]

Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction? What are the intermediates in the proposed mechanism?
9. Consider the reaction

\[ \text{Cl}_2 (aq) + H_2S (aq) \rightarrow S(s) + 2H^+ (aq) + 2\text{Cl}^- (aq) \]

The rate equation for this reaction is

\[ \text{Rate} = k \left[ \text{Cl}_2 \right] \left[ H_2S \right] \]

Which of these mechanisms is (or are) consistent with this rate equation?

I. \[ \text{Cl}_2 + H_2S \rightarrow H^+ + \text{Cl}^- + \text{Cl}^+ + HS^- \] (slow)
   \[ \text{Cl}^+ + HS^- \rightarrow H^+ + \text{Cl}^- + S \] (fast)

II. \[ H_2S \Leftrightarrow H^+ + HS^- \] (fast equilibrium)
   \[ \text{Cl}_2 + HS^- \rightarrow 2\text{Cl}^- + H^+ + S \] (slow)

a. I only
b. II only
c. Both I and II
d. Neither I or II
10. Nitrogen monoxide can be reduced with hydrogen gas to give nitrogen and water vapor.

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

(overall equation)

A proposed mechanism is

\[
\begin{align*}
2\text{NO} & \xrightleftharpoons[k_1]{k_2} \text{N}_2\text{O}_2 \\
\text{N}_2\text{O}_2 + \text{H}_2 & \xrightarrow[k_2]{k_3} \text{N}_2\text{O} + \text{H}_2\text{O} \\
\text{N}_2\text{O} + \text{H}_2 & \xrightarrow[k_3]{k_4} \text{N}_2 + \text{H}_2\text{O}
\end{align*}
\]

(fast, equilibrium)

(slow)

(fast)

What rate law is predicted by this mechanism?

11. Identify the molecularity of each of the following elementary reactions.

e. \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \)

f. \( \text{NOCl}_2 + \text{NO} \rightarrow 2\text{NOCl} \)

g. \( \text{O}_3 \rightarrow \text{O}_2 + \text{O} \)

h. \( \text{H} + \text{H} + \text{N}_2 \rightarrow \text{H}_2 + \text{N}_2 \)
12. Write the expression for the equilibrium constant $K_c$ for each of the following equations:

a. $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

b. $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

c. $Na_2CO_3(s) + SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons Na_2SO_4(s) + CO_2(g)$

d. $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

13. A mixture containing nitrogen, hydrogen, and iodine established the following equilibrium at $400^\circ C$:

$$2NH_3(g) + 3I_2(g) \rightleftharpoons N_2(g) + 6HI(g)$$

Use the information below to calculate $K_c$ for this reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad Kc1 = 0.50 \text{ at } 400^\circ C$$

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad Kc2 = 50 \text{ at } 400^\circ C$$
14. Calculate $K_c$ for the following reaction:

$$\text{I}_2 (g) + \text{Cl}_2 (g) \rightleftharpoons 2\text{ICl} (g), \quad K_p = 81.9 \text{ (at 298 K)}$$

15. Consider the reaction:

$$\text{Fe}^{3+} (aq) + \text{SCN}^- (aq) \rightleftharpoons \text{FeSCN}^{2+} (aq)$$

A solution is made containing an initial [Fe$^{3+}$] concentration of $1.0 \times 10^{-3}$ M and an initial [SCN$^-$] of $8.0 \times 10^{-4}$ M. At equilibrium, [FeSCN$^{2+}$] = $1.7 \times 10^{-4}$ M. Calculate the value of the equilibrium constant ($K_c$).
16. At a certain temperature, the $K_p$ for the decomposition of $\text{H}_2\text{S}$ is 0.864.

$$\text{H}_2\text{S} (g) \rightleftharpoons \text{H}_2 (g) + \text{S} (g)$$

Initially, only $\text{H}_2\text{S}$ is present at a pressure of 0.245 atm in a closed container. What is the total pressure in the container at equilibrium?

17. Consider the reaction for the decomposition of Dihydrogen Sulfide:

$$2\text{H}_2\text{S} (g) \rightleftharpoons 2\text{H}_2 (g) + \text{S}_2 (g), K_c = 1.67 \times 10^{-7} \text{ at } 800 \, ^\circ\text{C}$$

A reaction vessel has a concentration of $[\text{H}_2\text{S}] = 0.025 \, \text{M}$ initially present. Assuming there is no initial amount of $\text{S}_2$ or $\text{H}_2$ present, find the equilibrium concentration of $[\text{S}_2]$.

- a. $5.11 \times 10^{-6} \, \text{M}$
- b. $2.97 \times 10^{-4} \, \text{M}$
- c. $4.71 \times 10^{-4} \, \text{M}$
- d. $5.94 \times 10^{-4} \, \text{M}$
18. Silver Sulfate dissolves in water according to the following reaction:

\[ \text{Ag}_2\text{SO}_4 (s) \rightleftharpoons 2\text{Ag}^+ (aq) + \text{SO}_4^{2-} (aq), \text{K}_c = 1.1 \times 10^{-5} \text{ at 298 K} \]

A 1.5 L solution contains 6.55 g of dissolved Silver Sulfate. If additional solid Silver Sulfate is added to the solution, will it dissolve?

19. Coal, which is primarily carbon, can be converted to natural gas, primarily CH\(_4\), by the exothermic reaction:

\[ \text{C(s)} + 2\text{H}_2 (g) \rightleftharpoons \text{CH}_4 (g) \]

Which of the following disturbances favor the formation of CH\(_4\) to re-establish equilibrium, if any?

a. Adding more H\(_2\) to the reaction mixture.
b. Adding more C to the reaction mixture.

c. Raising the temperature of the reaction mixture.

d. Lowering the volume of the reaction mixture.

e. Adding a catalyst to the reaction mixture.

f. Adding Ne gas to the reaction mixture.

20. Consider the reaction:

\[ \text{CO (g)} + 2\text{H}_2 \text{ (g)} \rightleftharpoons \text{CH}_3\text{OH (g)}, \quad K_p = 2.26 \times 10^4 \text{ at } 25 \, ^\circ\text{C} \]

Calculate \( \Delta G_{\text{rxn}} \) for the reaction at 25 °C under the following conditions:

a. standard conditions

b. at equilibrium

c. when \( P_{\text{CH}_3\text{OH}} = 1.0 \text{ atm}; \quad P_{\text{CO}} = P_{\text{H}_2} = 0.010 \text{ atm} \)