

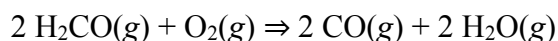
Worksheet 7

Chemical kinetics is the area of chemistry concerned with reaction rates. A **reaction rate** is defined as the increase in the concentration of a product, or the decrease in the concentration of a reactant, per unit time. It can be expressed as the average rate during a given time interval, the **instantaneous rate** at a particular time, or the **initial rate** at the beginning of the reaction.

Reaction rates depend on reactant concentrations, temperature, and the presence of catalysts. The concentration dependence is given by the **rate law**, $\text{rate} = k[A]^m[B]^n$, where k is the **rate constant**, m and n specify the reaction order with respect to reactants A and B, and $m + n$ is the overall reaction order. The values of m and n must be determined by experiment. They cannot be deduced from the stoichiometry of the overall reaction.

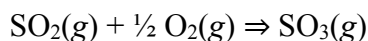
The **integrated rate law** is a concentration-time equation that makes it possible to calculate concentrations at any time t or the time required for an initial concentration to reach any particular value. For a **first-order reaction**, the integrated rate law is $\ln [A]_t = -kt + \ln [A]_0$. A graph of $\ln [A]$ versus time is a straight line with a slope equal to $-k$. For a **second-order reaction**, the integrated rate law is $1/[A]_t = kt + 1/[A]_0$. A graph of $1/[A]$ versus time is linear with a slope equal to k . For a **zero-order reaction**, the integrated rate law is $[A] = -kt + [A]_0$, and the graph of $[A]$ versus time is linear with a slope equal to $-k$. The **half-life** ($t_{1/2}$) of a reaction is the time required for the reactant concentration to drop to one-half its initial value.

1. Give four related expressions for the rate of the reaction



assuming that the concentrations of any intermediates are constant and that the volume of the reaction vessel does not change.

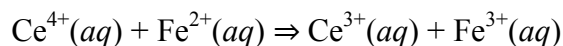
2. In the presence of vanadium oxide, $\text{SO}_2\text{(g)}$ reacts with an excess of oxygen to give $\text{SO}_3\text{(g)}$:



This reaction is an important step in the manufacture of sulfuric acid. It is observed that tripling the SO_2 concentration increases the rate by a factor of 3, but tripling the SO_3 concentration *decreases* the rate by a factor of $1.7 \cong \sqrt{3}$. The rate is insensitive to the O_2 concentration as long as an excess of oxygen is present.

- (a) Write the rate expression for this reaction, and give the units of the rate constant k .
(b) If $[\text{SO}_2]$ is multiplied by 2 and $[\text{SO}_3]$ by 4 but all other conditions are unchanged, what change in the rate will be observed?

3. The rate for the oxidation of iron(II) by cerium(IV)



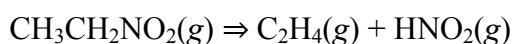
is measured at several different initial concentrations of the two reactants:

Worksheet 7

$[\text{Ce}^{4+}] \text{ (mol L}^{-1}\text{)}$	$[\text{Fe}^{2+}] \text{ (mol L}^{-1}\text{)}$	Rate $\text{(mol L}^{-1} \text{ s}^{-1}\text{)}$
1.1×10^{-5}	1.8×10^{-5}	2.0×10^{-7}
1.1×10^{-5}	2.8×10^{-5}	3.1×10^{-7}
3.4×10^{-5}	2.8×10^{-5}	9.5×10^{-7}

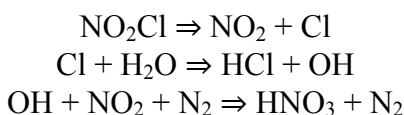
- (a) Write the rate expression for this reaction.
 (b) Calculate the rate constant k , and give its units.
 (c) Predict the initial reaction rate for a solution in which $[\text{Ce}^{4+}]$ is $2.6 \times 10^{-5} \text{ M}$ and $[\text{Fe}^{2+}]$ is $1.3 \times 10^{-5} \text{ M}$.

4. At 600 K, the rate constant for the first-order decomposition of nitro ethane



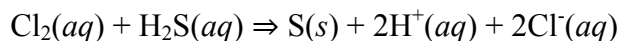
is $1.9 \times 10^{-4} \text{ s}^{-1}$. A sample of $\text{CH}_3\text{CH}_2\text{NO}_2$ is heated to 600 K, at which point its initial partial pressure is measured to be 0.078 atm. Calculate its partial pressure after 3.0 hours.

5. Consider the following reaction mechanism:



- (a) Write the overall equation for the reaction.
 (b) Identify the reaction intermediate(s).

6. Chlorine reacts with hydrogen sulfide in aqueous solution



in a second-order reaction that follows the rate expression

$$\text{rate} = k[\text{Cl}_2][\text{H}_2\text{S}]$$

Which, if any, of the following mechanisms are consistent with the observed rate expression?

- (a) $\text{Cl}_2 + \text{H}_2\text{S} \Rightarrow \text{H}^+ + \text{Cl}^- + \text{Cl}^+ + \text{HS}^-$ (slow)
 $\text{Cl}^+ + \text{HS}^- \Rightarrow \text{H}^+ + \text{Cl}^- + \text{S}$ (fast)
 (b) $\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$ (fast equilibrium)
 $\text{HS}^- + \text{Cl}_2 \Rightarrow 2 \text{Cl}^- + \text{S} + \text{H}^+$ (slow)
 (c) $\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$ (fast equilibrium)
 $\text{H}^+ + \text{Cl}_2 \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{Cl}^+$ (fast equilibrium)
 $\text{Cl}^+ + \text{HS}^- \Rightarrow \text{H}^+ + \text{Cl}^- + \text{S}$ (slow)