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**, 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

$$2\ H_2CO(g) + O_2(g) \Rightarrow 2\ CO(g) + 2\ H_2O(g)$$

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, $SO_2(g)$ reacts with an excess of oxygen to give $SO_3(g)$:

$$SO_2(g) + \tfrac{1}{2}\ O_2(g) \Rightarrow SO_3(g)$$

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 $[SO_2]$ is multiplies by 2 and $[SO_3]$ 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)

$$Ce^{4+}(aq) + Fe^{2+}(aq) \Rightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

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

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$[Ce^{4+}]$ (mol L^{-1})	$[Fe^{2+}]$ (mol L^{-1})	Rate (mol L^{-1} s^{-1})
1.1 x 10^{-5}	1.8 x 10^{-5}	2.0 x 10^{-7}
1.1 x 10^{-5}	2.8 x 10^{-5}	3.1 x 10^{-7}
3.4 x 10^{-5}	2.8 x 10^{-5}	9.5 x 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 $[Ce^{4+}]$ is 2.6 x 10^{-5} M and $[Fe^{2+}]$ is 1.3 x 10^{-5} M.

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

$$CH_3CH_2NO_2(g) \Rightarrow C_2H_4(g) + HNO_2(g)$$

is 1.9 x 10^{-4} s^{-1}. A sample of $CH_3CH_2NO_2$ 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:

$$NO_2Cl \Rightarrow NO_2 + Cl$$
$$Cl + H_2O \Rightarrow HCl + OH$$
$$OH + NO_2 + N_2 \Rightarrow HNO_3 + N_2$$

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

6. Chlorine reacts with hydrogen sulfide in aqueous solution

$$Cl_2(aq) + H_2S(aq) \Rightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$$

in a second-order reaction that follows the rate expression

$$\text{rate} = k[Cl_2][H_2S]$$

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

(a) $Cl_2 + H_2S \Rightarrow H^+ + Cl^- + Cl^+ + HS^-$	(slow)
$Cl^+ + HS^- \Rightarrow H^+ + Cl^- + S$	(fast)
(b) $H_2S \Leftrightarrow HS^- + H^+$	(fast equilibrium)
$HS^- + Cl_2 \Rightarrow 2\ Cl^- + S + H^+$	(slow)
(c) $H_2S \Leftrightarrow HS^- + H^+$	(fast equilibrium)
$H^+ + Cl_2 \Leftrightarrow H^+ + Cl^- + Cl^+$	(fast equilibrium)
$Cl^+ + HS^- \Rightarrow H^+ + Cl^- + S$	(slow)