CH353 – Physical Chemistry I
Spring 2015, Unique 51170

Homework, Week 13

1. We have defined rates of reactions in terms of molar concentration.

    a) What implicit assumption does this definition require?
    b) Derive an expression for the rate of a reaction in terms of the molar concentration of reactant A for the case in which this assumption is not valid.

2. In biological systems, certain proteins called enzymes (E) catalyze the reaction of small molecules called substrates (S) to form the desired products (P). A proposed reaction mechanism involves two elementary steps; 1) one substrate binds to one enzyme in a slow step to form an enzyme-substrate complex (ES), and 2) the enzyme-substrate complex reacts quickly to form one product.

a) Write the overall reaction and the elementary reactions described by this proposed mechanism.

b) Assuming that the steady-state approximation holds, determine the rate law for the overall reaction, in terms of the concentration of reactants, concentration of products, and any rate constant.

3. Consider the following reaction:

$$Cr(H_2O)_6^{3+}(aq) + SCN^-(aq) \rightarrow Cr(H_2O)_5(SCN)^{2+}(aq) + H_2O(l)$$

The following initial rate data were obtained at 298 K:

$[Cr(H_2O)_6^{3+}]_0$ (mol/L)	$[SCN^-]_0$ (mol/L)	v_0 (mol/Ls)
1.21×10^{-4}	1.05×10^{-5}	2.11×10^{-11}
1.46×10^{-4}	2.28×10^{-5}	5.53×10^{-11}
1.66×10^{-4}	1.02×10^{-5}	2.82×10^{-11}
1.83×10^{-4}	3.11×10^{-5}	9.44×10^{-11}

Determine the rate law and rate constant for this reaction. Assuming integer reaction orders.

4. Consider the reaction of A to form either product B:

$$A \rightarrow B$$

Derive an expression for [A] at any time as a function of the initial concentration $[A]_0$ and the rate constant of the reaction.

5. Suppose you could measure the concentration of species A, [A], at any time *t* along a reaction. Explain, in words and figures, how you would use the integrated rate law you derived in problem 4 to determine the rate constant of the reaction.