Chem132A Discussion Homework

Moises Romero (moiseser@uci.edu), Shane Flynn (swflynn@uci.edu)
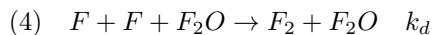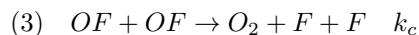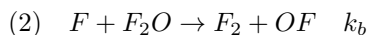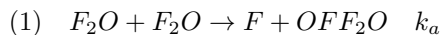
12/3/17

1 Chemical Kinetics

Chemical Kinetics is the study of reaction rates. The mathematics and experimental findings associated with chemical reactions can be combined to better understand potential mechanisms through which the reaction can occur.

Reaction to Consider

The reaction for the decomposition of F_2O is :

$$2F_2O(g) \rightarrow 2F_2(g) + O_2(g) \tag{1}$$

After various experiments, the following reaction mechanism was published :

$$(1) \quad F_2O + F_2O \rightarrow F + OFF_2O \quad k_a$$

$$(2) \quad F + F_2O \rightarrow F_2 + OF \quad k_b$$

$$(3) \quad OF + OF \rightarrow O_2 + F + F \quad k_c$$

$$(4) \quad F + F + F_2O \rightarrow F_2 + F_2O \quad k_d$$

1.1 Steady-State Approximation

Using the steady-state approximation show that the mechanism follows the experimental rate law of :

$$\frac{-d[F_2O]}{dt} = k_r[F_2O]^2 + k_r'[F_2O]^{\frac{3}{2}} \tag{2}$$

Recall: the steady state approximation assumes that the intermediate, **I** , has a constant concentration:

$$\frac{d[I]}{dt} = 0 \tag{3}$$

Hint: For the decomposition, the intermediate products are F and OF.

1.2 Arrhenius Equation

The Arrhenius equation allows us to determine the activation energies of elementary reactions.

$$\ln k_r = \ln A - \frac{E_a}{RT} \tag{4}$$

For the decomposition determine the activation energy for equation 2 in the provided mechanism.

The experimentally determined Arrhenius parameters are as follows (for the temperature range 501-583 K):

For k_r A=7.8 x 10^{13}dm^{3}mol^{-1}s^{-1} and $\frac{E_a}{R} = 1.935$ x 10^4K.

For k'_r A=2.3 x 10^{10}dm^{3}mol^{-1}s^{-1} and $\frac{E_a}{R} = 1.691$ x 10^4K.

2 Michaelis-Menten

Some of the most important biological reaction are the class of **Enzyme-Catalyzed Reactions**. Experimentally it has been shown that these reactions usually follow a rate law of the form

$$-\frac{d}{dt}[S] = \frac{k[S]}{K + [S]} \tag{5}$$

In 1913, Leonor Michaelis and Maude Menten showed that a simple mechanism could account for this rate law (in terms of as Enzyme, a Product, and a Substrate).

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P \tag{6}$$

In this question we will explore this model to understand biochemistry.

2.1 Traditional Equation

To start, we will derive the traditional M-M Equation.

2.1.1 Dissociation

What reaction will give the following rate constant, and what does it represent physically?

$$k_d = \frac{[E][S]}{[ES]} \tag{7}$$

2.1.2 Rate-Determining step

Assuming the Enzyme-Substrate complex forming the product is the rate determining step, what is the rate of product formation?

2.1.3 Enzyme Conservation

Determine the concentration of the enzyme-substrate complex by assuming total amount of enzyme $[E]_T$ is conserved.

2.1.4 Simplify

Show that the rate of product formation (r_p) is given by

$$r_p = \frac{v_{max}[S]}{[S] + k_d} \tag{8}$$

Where v_{max} is defined to be $k_2[E]_T$.

2.2 Uncompetitive Inhibition

We will now investigate a simple twist to the model, to account for an inhibitor. In general an inhibitor is a molecule that can bind to an enzyme and decrease its activity. An **Uncompetitive Inhibitor** is a molecule that can only bind to an Enzyme-Substrate complex.

2.2.1 Mechanism

Add a new equation to account for the Inhibitor. Assuming it establishes an equilibrium, write down the dissociation constant for the inhibitor complex (k_I).

2.2.2 Enzyme Concentration

Find an expression for the enzyme concentration. State all assumptions along the way.

2.2.3 Product Formation Rate

Show the rate of formation of the products simplifies to:

$$r_p = \frac{v_{max}[S]}{k_d + [S]\left(1 + \frac{[I]}{k_i}\right)} \tag{9}$$

Does your result make sense when compared to the original M-M product formation rate?

3 Final Exam

At this point you should start preparing for the final exam. Expect $\approx \frac{1}{3}$ of the final to be essentially the same material as previous exams and homework. Also expect the exam to be roughly evenly distributed over the course material (i.e. Exam 1, Exam 2, and post-Exam 2).

A final problem set and solution covering material in Chapter 21 will be posted **NEXT WEEK**. We are waiting to see how much material is covered in lecture before making the set. This final problem set **IS** part of the course and may appear again of the final.