

Chem132A Discussion 7 Solutions

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1 Chemical Kinetics

Reaction to Consider

The reaction for the decomposition of F_2O is :



After various experiments, the following reaction mechanism was published :



1.1 Steady-State Approximation

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

$$\frac{-d[F_2O]}{dt} = k_r[F_2O]^2 + k'_r[F_2O]^{\frac{3}{2}} \quad (6)$$

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

$$\frac{d[I]}{dt} = 0 \quad (7)$$

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

Solution:

I will start by writing down all of the rates associated with each step in the mechanism. Because the mechanism is written with only forward arrows, we can simply define the rates in terms of the products.

$$\begin{aligned} \text{Rate}_1 &= k_a[F_2O]^2 \\ \text{Rate}_2 &= k_b[F][F_2O] \\ \text{Rate}_3 &= k_c[OF]^2 \\ \text{Rate}_4 &= k_d[F]^2[F_2O] \end{aligned} \quad (8)$$

The overall problem is to determine the rate law for F_2O , to do this we can look at all of the steps within the mechanism that generate/consume F_2O .

RECALL: This is the overall rate of a molecule in the original equation. We can use any reactant or product to define the overall rate, but we must account for the stoichiometry in this step! For example: if the reaction were $A + 2B \longrightarrow 3C + D$, then we know

$$\frac{1}{3} \frac{d}{dt}[C] = \frac{d}{dt}[D] = -\frac{d}{dt}[A] = -\frac{1}{2} \frac{d}{dt}[B] \quad (9)$$

In the same way we will write the overall rate in terms of F_2O .

$$\frac{1}{2} \frac{d}{dt}[F_2O] = -k_a[F_2O]^2 - k_b[F][F_2O] \quad (10)$$

Where step 1 of the mechanism is overall negative wrt F_2O and step 4 is overall neutral and does not play a factor in the rate. Again the RHS (the individual rates) do not have any stoichiometry included it is accounted for by the rate law itself (raising the concentrations to various powers). This result looks similar to the rate law we are trying to prove, however, it is in terms of the intermediate F.

To remove this intermediate dependence we make a steady state approximation and write down the rate of formation of the intermediates in a similar manner. Please note: we are no longer writing rates of an overall reaction, these are rates associated with the mechanism, therefore no coefficients are used, simply the rate law.

From the mechanism we see that F is formed in steps 1/3, and F is consumed in steps 2/4.

$$\frac{d[F]}{dt} = 0 = k_a[F_2O]^2 - k_b[F][F_2O] + k_c[OF]^2 - k_d[F]^2[F_2O] \quad (11)$$

We will then write down the steady state approximation for the other intermediate in the same way.

$$\frac{d[OF]}{dt} = 0 = k_a[F_2O]^2 + k_b[F][F_2O] - k_c[OF]^2 \quad (12)$$

Remember, our goal was to remove the [F] intermediate in our overall rate of F_2O . But the intermediate F and the intermediate OF both depend on the same variables. We can therefore take the equations and combine them to reduce the overall number of variables (we have 2 intermediates, we therefore need 2 equations to solve).

If we add each intermediate equation together we see some nice cancellations!

$$2k_a[F_2O]^2 - k_d[F]^2[F_2O] = 0 \quad (13)$$

We will solve this equation for [F], so that we can substitute into our overall rate law.

$$[F] = \left(2 \frac{k_a}{k_d} [F_2O] \right)^{\frac{1}{2}} \quad (14)$$

Finally we substitute in our expression for [F] into the overall rate law of F_2O . Doing the algebra I find:

$$\begin{aligned} \frac{1}{2} \frac{d}{dt}[F_2O] &= -k_a[F_2O]^2 - k_b \left(2 \frac{k_a}{k_d} [F_2O] \right)^{\frac{1}{2}} [F_2O] \\ -\frac{d}{dt}[F_2O] &= 2k_a[F_2O]^2 + 2k_b \left(2 \frac{k_a}{k_d} \right)^{\frac{1}{2}} [F_2O]^{3/2} \end{aligned} \quad (15)$$

1.2 Arrhenius Equation

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

$$\ln k = \ln A - \frac{E}{RT} \quad (16)$$

For the decomposition determine the activation energy for elementary equation 2 in the provided mechanism. The experimentally determined Arrhenius parameters are as follows for the temperature range 501-583K:

For k_r , $A = 7.8 \times 10^{13} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_a = 1.935 \times 10^4 \text{ KJ}$.

For k'_r , $A = 2.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $E_a = 1.691 \times 10^4 \text{ KJ}$.

Where R is the gas constant. For the k_d term in the Arrhenius equation can be ignored as step 4 in the reaction mechanism is termolecular. This term means a reaction involving three molecules colliding which has a much smaller probability of occurring than two molecules colliding. Thus this term can be ignored.

Solution:

We want to solve for E_b , so we will want solve for k_b . We know the expression for k'_r contains k_b . We will want to take that expression and multiply by \ln , and then separate our logs to simplify more..

$$\ln k'_r = \ln \left[k_b \left(\frac{k_a}{k_d} \right) \right] = \ln k_b + \frac{1}{2} \ln k_a - \frac{1}{2} \ln k_d \quad (17)$$

Recall that step 4 of the mechanism is termolecular(probability of 3 compounds colliding is very small) therefore k_d term can be ignored. From our derivation in the first problem we know $k_r = k_a$. So the expression is now :

$$\ln k'_r = \ln k_b + \frac{1}{2} \ln k_r \quad (18)$$

We can rewrite using the Arrhenius equation as :

$$\ln A'_r - \frac{E'_r}{RT} = \ln A_b - \frac{E_b}{RT} + \frac{1}{2} \ln A_r - \frac{1}{2} \frac{E_r}{RT} \quad (19)$$

We can take the derivative with respect to Temperature to get the activation energies.

$$\frac{E'_r}{RT^2} = \frac{E_b}{RT^2} + \frac{1}{2} \frac{E_r}{RT^2} \quad (20)$$

We can multiply through by RT^2 and rearrange to solve for E_b

$$E_b = E'_r - \frac{1}{2} E_r = 1.691 \times 10^4 \text{KR} - \left(\frac{1}{2}\right) 1.935 \times 10^4 \text{KR} = 7235 \text{K}(R) = (7235 \text{K})(.008314 \text{kJmol}^{-1}) = 60 \text{kJmol}^{-1} \quad (21)$$

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

$$-\frac{d}{dt}[S] = \frac{k[S]}{K + [S]} \quad (22)$$

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



In this question we will explore various applications of the 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?

$$k_d = \frac{[E][S]}{[ES]} \quad (24)$$

Solution

We know that our rates are written in terms of products divided by reactions, therefore.



This is simply the reverse reaction in step 1 of Equation 23. This reaction is the dissociation of the enzyme-substrate complex into separate enzyme and substrate (ie. $k_d = k_{-1}$).

2.1.2 Rate-Determining step

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

Solution

If we assume the second half of equation 23 is the rate-determining step (i.e. it is irreversible), then the rate of product formation is simply controlled by this equation.

$$r_p = k_2[ES] \quad (26)$$

2.1.3 Enzyme Conservation

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

Solution

If the total amount of enzyme is conserved, and the enzyme can only be part of the complex or alone we can write

$$[E]_T = [E] + [ES] \quad (27)$$

Now using the dissociation process above we can substitute in an expression for $[E]$.

$$\begin{aligned} [E]_T &= \frac{k_d[ES]}{[S]} + [ES] = [ES] \left(\frac{k_d}{[S]} + 1 \right) \\ [ES] &= \frac{[E]_T}{\frac{k_d}{[S]} + 1} \end{aligned} \quad (28)$$

2.1.4 Simplify

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

$$r_p = \frac{v_{max}[S]}{[S] + k_d} \quad (29)$$

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

Solution

We just need to substitute in our previous result for r_p and solve.

$$\begin{aligned} r_p &= k_2 \left(\frac{[E]_T}{\frac{k_d}{[S]} + 1} \right) = \frac{v_{max}}{\frac{k_d}{[S]} + 1} \\ r_p &= \frac{v_{max}[S]}{k_d + [S]} \end{aligned} \quad (30)$$

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 (k_i).

Solution

As stated, the inhibitor only interacts with the ES complex, therefore



We can then write the dissociation of the complex as

$$k_I = \frac{[ES][I]}{[ESI]} \quad (32)$$

2.2.2 Enzyme Concentration

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

Solution

If we assume a low concentration of the product concentration, than the rate-determining step becomes irreversible. If we then assume the total enzyme concentration is conserved we can write.

$$[E]_T = [E] + [ES] + [ESI] \quad (33)$$

We can now substitute in our dissociation expression.

$$\begin{aligned} [E]_T &= [E] + [ES] + [ESI] \\ [E]_T &= [E] + \frac{[E][S]}{k_d} + \frac{[ES][I]}{k_I} \\ [E]_T &= [E] + \frac{[E][S]}{k_d} + \frac{[E][S][I]}{k_I} \end{aligned} \quad (34)$$

Finally we can factor out terms and solve for the concentration of the enzyme.

$$\begin{aligned} [E]_T &= [E] \left(1 + \frac{[S]}{k_d} + \frac{[S][I]}{k_d k_I} \right) \\ [E] &= \frac{[E]_T}{\left(1 + \frac{[S]}{k_d} + \frac{[S][I]}{k_d k_I} \right)} \end{aligned} \quad (35)$$

2.2.3 Product Formation Rate

Determine the rate of formation of the products (simplify as much as possible).

Solution

Again we start with r_p and simplify.

$$\begin{aligned} r_p &= k_2[ES] \\ &= k_2 \frac{[E][S]}{k_d} \\ &= k_2 \left[\frac{[E]_T[S]}{k_d \left(1 + \frac{[S]}{k_d} + \frac{[S][I]}{k_d k_I} \right)} \right] \\ r_p &= \frac{v_{max}[S]}{k_d + [S] \left(1 + \frac{[I]}{k_i} \right)} \end{aligned} \quad (36)$$

And if we compare this to our original M-M expression for the rate, the inhibitor will make this process slower.