CH-310 – Dynamics and Kinetics: Final Exam

January 17th, 2025

Name:

65 points in total, 3 hours to complete the exam.

Please note that this is not an open-book exam. You are allowed to use a non-programmable calculator as well as a formula sheet, A5, single-sided, and handwritten. The calculator and formula sheet will be checked during the exam. Computers or other electronic devices are not permitted. Do not write with a pencil or an erasable pen. Please have your Photo ID or Camipro Card ready.

$\int_0^\infty e^{-ax^2}dx = \frac{\sqrt{\pi}}{2\sqrt{a}} \quad (a > 0)$

$\int_0^\infty xe^{-ax^2}dx = \frac{1}{2a} \quad (a > 0)$

$\int_0^\infty x^2e^{-ax^2}dx = \frac{\sqrt{\pi}}{4a^{\frac{3}{2}}} \quad (a > 0)$

$\int_0^\infty x^{2n}e^{-ax^2}dx = \frac{(2n)!\sqrt{\pi}}{2^{2n+1}n!a^{n+\frac{1}{2}}} \quad (a > 0)$

$\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2a^{n+1}} \quad (a > 0)$

$\Gamma(z+1) = \int_0^\infty x^z e^{-x}dx$

$\Gamma(z+1) = z\Gamma(z)$, for any real z

$\Gamma(n+1) = n!$, for integer $n = 0, 1, 2, \ldots$

$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$

$\cos(2\alpha) = \cos^2(\alpha) - \sin^2(\alpha)$

$\sin(2\alpha) = 2\sin(\alpha)\cos(\alpha)$

$\cos^2\left(\frac{\alpha}{2}\right) = \frac{1+\cos(\alpha)}{2}, \quad \sin^2\left(\frac{\alpha}{2}\right) = \frac{1-\cos(\alpha)}{2}$

$\int \frac{1}{\sqrt{r^2 - x^2}}dx = \arcsin\left(\frac{x}{r}\right) + C$

$\arccos(-x) = \pi - \arccos(x)$

$\arcsin(x) = \pi/2 - \arccos(x)$

$\cos(\arcsin(x)) = \sin(\arccos(x)) = \sqrt{1 - x^2}$

Coulomb's law $\quad \boldsymbol{F}_1 = \frac{q_1 q_2}{4\pi\varepsilon_0}\frac{\boldsymbol{r}_{12}}{|\boldsymbol{r}_{12}|^2}$

$k_B = 1.38 \cdot 10^{-23}\ \mathrm{J \cdot K^{-1}}$

$R = 8.31\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$

$N_A = 6.02 \cdot 10^{23}\ \mathrm{mol^{-1}}$

$e = 1.60 \cdot 10^{-19}\ \mathrm{C}$

$h = 6.63 \cdot 10^{-34}\ \mathrm{J \cdot s}$

$\epsilon_0 = 8.85 \cdot 10^{-12}\ \mathrm{F \cdot m^{-1}}$

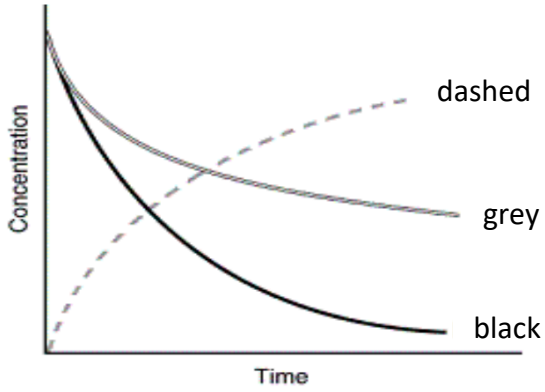
$c = 3.00 \cdot 10^8\ m \cdot s^{-1}$

$1\ amu = 1.66 \cdot 10^{-24}\ g$

<u>Problem 1: Multiple choice and short answers</u> (10 points in total)

(each question per 1 point)

1. **The following graph shows the kinetics curves for the reaction of oxygen with hydrogen to form water: $\mathbf{O_2(g) + 2H_2(g) \rightarrow 2\,H_2O(g)}$ for all species. Which curve corresponds to hydrogen?**



a) the dashed curve
b) the grey curve
c) the black curve
d) either the gray or the black curve

Shortly justify your answer.

c) Hydrogen gets used up at double the rate of oxygen, which is indicated only in the black curve.

2. **For the reaction $\mathbf{A + 3B \rightarrow 2C}$, how does the rate of consumption of B compare to the rate of production of C?**

a) the rate of consumption of B is 1/2 the rate of production of C
b) the rate of consumption of B is 3/2 the rate of production of C
c) the rate of consumption of B is 2/3 the rate of production of C
d) the rate of consumption of B is 1/3 the rate of production of C

Shortly justify your answer.

b) The stoichiometry indicates that 3B is consumed as fast as 2C is formed. Thus, the rate of consumption is higher, by a factor of 3/2 compared to the rate of production.

3. The half-life of a first-order reaction is 0.1 s. What is the rate constant?

$6.93\ s^{-1}$. The rate constant is given by $\frac{\ln(2)}{t_{1/2}}$.

4. What is the steric factor? What does a steric factor smaller than 1 mean?

A factor accounting for the fact that even at sufficient energy, not every collision might be reactive due to geometric limitations of molecular orientations. When the steric factor *P* is smaller than one, this is as expected, since the reaction needs certain orientation of the reactants to occur.

5. What does the Lindemann mechanism propose to be necessary for a successful reaction? Write down the simplest reaction scheme as well.

Lindemann proposed that we need a collision partner M to activate or deactivate the reactant A.

$$\begin{aligned} A + M &\xrightarrow{k_1} A^* + M \\ A^* + M &\xrightarrow{k_{-1}} A + M \\ A^* &\xrightarrow{k_2} P \end{aligned}$$

6. What is the characteristic shift in Doppler broadening? Shortly explain.

If molecule moves towards us: blue-shift/frequency increase of light. If molecule moves away from us: red-shift/frequency decrease of light.

7. What is an autocatalytic reaction? Write down the reaction scheme of the simplest autocatalytic reaction.

It occurs, when a product of a reaction appears as a reactant of either the same reaction or a coupled reaction. Simplest case:

$$\mathrm{A} + \mathrm{B} \xrightarrow{\mathrm{k}} 2\mathrm{B}$$

8. Which plot can you use to determine the order of a reaction? Sketch on the same axes the graph for a first-, second- and third-order reaction and label the axes.

Van t'Hoff plot. For the rate

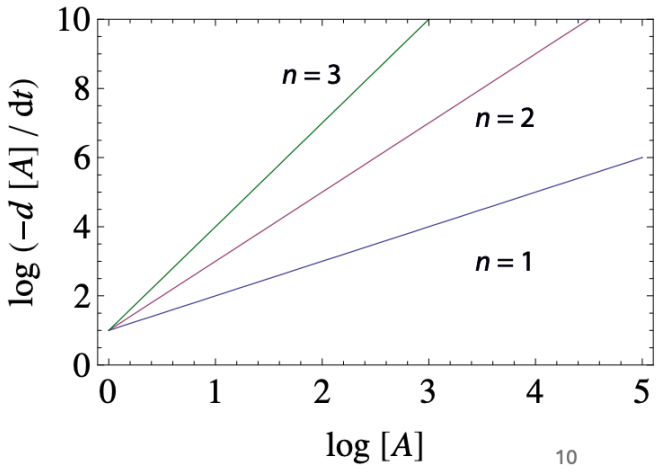
$$R = -\frac{1}{a}\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A]^n,$$

which after solving gives us (for $n \neq 1$):

$$\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} = akt(n-1)$$

Van't Hoff plot is of a form

$$\ln\left(-\frac{d[A]}{dt}\right) = n\ln[A] + \ln ak$$



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9. Derive an expression for the time evolution $[A]_t$ for an elementary reaction of second order: $2A \rightarrow B$.

Rate equation is $R = -\frac{1}{2}\frac{d[A]}{dt} = k[A]^2$.

We integrate:

$$\int_{[A]_0}^{[A]_t} \frac{1}{[A]^2} \mathrm{d}[A] = -2k \int_0^t \mathrm{d}t'$$

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt$$

$$[A]_t = \frac{[A]_0}{1 + 2kt[A]_0}$$

10. Shortly explain the concept of Förster resonance energy transfer, including how the transfer efficiency changes with distance.

Excitons can ‘diffuse’ to lower energy sites via Förster resonance energy transfer (FRET). FRET necessitates dipole-dipole coupling, and can be a long-range interaction (few nm), it falls off with $1/R^6$ (R being the distance between donor and acceptor). It can be very fast (sub-ps).

Problem 2: Kinetics of reactions (15 points in total)

1. We examine the elementary reactions:

$$\mathbf{Br_2 + H \rightarrow HBr + Br} \qquad \textbf{(R1)}$$

$$\mathbf{D + D + He \rightarrow D_2 + He} \qquad \textbf{(R2)}$$

$$\mathbf{^{22}_{11}Na^{11+} \rightarrow {}^{22}_{10}Ne^{10+} + e^{+} + \nu_e} \qquad \textbf{(R3)}$$

$$\mathbf{Br_2 + H + Ar \rightarrow HBr + Br + Ar} \qquad \textbf{(R4)}$$

Here, we assume that non-reactive collision partners are always present in excess.
For each of these reactions, provide the following information:

- **(i) The molecularity,**
- **(ii) The rate equations for all species of the reaction and the concentration dependence of the reaction rate,**
- **(iii) The reaction order with respect to all substances in the reaction equation and the overall reaction order.**

(4 points)

R1: Bimolecular reaction with two molecules colliding. The rate law is

$$v_c = -\frac{\mathrm{d}[\mathrm{Br_2}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Br}]}{\mathrm{d}t} = k_1[\mathrm{Br_2}][\mathrm{H}]$$

The reaction is of order $m = 1$ for Br_2 and $m = 1$ for H. The total reaction order is 2.

(1 point)

R2: Trimolecular reaction with atomic recombination. The rate law is

$$v_c = -\frac{1}{2}\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{D_2}]}{\mathrm{d}t} = k_2[\mathrm{D}]^2[\mathrm{He}] = k_{eff}[D]^2$$

The reaction is of order $m = 2$ for D and $m = 1$ for He. The total reaction order is 3.

(1 point)

R3: Unimolecular reaction, radioactive decay. The rate law is

$$v_c = -\frac{\mathrm{d}[^{22}_{11}\mathrm{Na}^{11+}]}{\mathrm{d}t} = \frac{\mathrm{d}[^{22}_{10}\mathrm{Ne}^{10+}]}{\mathrm{d}t} = k_4[^{22}_{11}\mathrm{Na}^{11+}]$$

The reaction is of order $m = 1$ for Na^{11+} and the total order is also 1.

(1 point)

R4: Trimolecular reaction consuming a hydrogen radical and producing a bromine radical. The rate law is

$$v_c = -\frac{\mathrm{d}[\mathrm{Br_2}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{H}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{HBr}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{Br}]}{\mathrm{d}t} = k_1[\mathrm{Br_2}][\mathrm{H}][\mathrm{Ar}] = k_{eff}[\mathrm{Br_2}][\mathrm{H}]$$

The reaction is of order $m = 1$ for Br_2 as well as for H and Ar. The total reaction order is 3.

(1 point)

2. In an argon atmosphere, is reaction R1 or R4 more likely to occur? Why?

(1 point)

Even in an argon atmosphere, R1 is more likely. Trimolecular reactions are orders of magnitude less likely to run than bimolecular ones. Moreover, the released energy does not necessarily have to be dissipated by a collision partner, but can be converted into kinetic energy of HBr and Br, as well as rovibronic excitations.

(1 points)

Consider the thermal decomposition of gaseous $\mathbf{OClO}$ into atomic $\mathbf{Cl}$ and molecular $\mathbf{O_2}$, including the reverse reaction as described by the reaction scheme:

$$\mathbf{OClO(g) \rightleftarrows Cl(g) + O_2(g).} \qquad \textbf{(RTOT)}$$

The mechanism of this reaction is described by two sequential elementary reactions (with reverse reactions):

$$\mathbf{OClO\ (g) \overset{k_7}{\rightarrow} ClOO\ (g)} \qquad \textbf{(+R7)}$$

$$\mathbf{ClOO\ (g) \overset{k_{-7}}{\longrightarrow} OClO\ (g)} \qquad \textbf{(–R7)}$$

$$\mathbf{ClOO\ (g) \overset{k_8}{\rightarrow} Cl(g) + O_2\ (g)} \qquad \textbf{(+R8)}$$

and

$$\mathbf{Cl\ (g) + O_2(g) \overset{k_{-8}}{\longrightarrow} ClOO\ (g).} \qquad \textbf{(–R8)}$$

3. Write the rate equations for all substances involved in the reaction. Then simplify the rate equations using the assumption that $v_7 \gg v_{-7}$ and $v_8 \gg v_{-8}$.

(3 points)

We can write:

$$v_{\mathrm{OClO}} = \frac{\mathrm{d[OClO]}}{\mathrm{d}t} = -k_7[\mathrm{OClO}] + k_{-7}[\mathrm{ClOO}],$$

$$v_{\mathrm{ClOO}} = \frac{\mathrm{d[ClOO]}}{\mathrm{d}t} = +k_7[\mathrm{OClO}] - k_{-7}[\mathrm{ClOO}] - k_8[\mathrm{ClOO}] + k_{-8}[\mathrm{Cl}][\mathrm{O_2}],$$

$$v_{\mathrm{Cl}} = v_{O_2} = \frac{\mathrm{d[Cl]}}{\mathrm{d}t} = \frac{\mathrm{d[O_2]}}{\mathrm{d}t} = +k_8[\mathrm{ClOO}] - k_{-8}[\mathrm{Cl}][\mathrm{O_2}],$$

(2 points)

By assuming the rate of the forward reactions to be much faster than the back-reactions, we can write the equations in a simplified form:

$$\frac{\mathrm{d[OClO]}}{\mathrm{d}t} = -k_7[\mathrm{OClO}],$$

$$\frac{\mathrm{d[ClOO]}}{\mathrm{d}t} = +k_7[\mathrm{OClO}] - k_8[\mathrm{ClOO}],$$

$$\frac{\mathrm{d[Cl]}}{\mathrm{d}t} = \frac{\mathrm{d[O_2]}}{\mathrm{d}t} = +k_8[\mathrm{ClOO}]$$

(1 point)

4. Using the assumptions made in Task 3, derive an expression for concentration $[\mathrm{Cl}]$ as a function of time and initial concentration $[\mathrm{OClO}]_0$. Assume that at $t = 0$, only the reactant OClO is present.

(7 points)

First, we solve an ODE for OClO:

$$\frac{\mathrm{d}[\mathrm{OClO}]}{\mathrm{d}t} = -k_7[\mathrm{OClO}] \Leftrightarrow [\mathrm{OClO}](t) = [\mathrm{OClO}]_0 e^{-k_7 t},$$

(1 point)

Which we then insert into an ODE for ClOO:

$$\frac{\mathrm{d}[\mathrm{ClOO}]}{\mathrm{d}t} = k_7[\mathrm{OClO}]_0 e^{-k_7 t} - k_8[\mathrm{ClOO}].$$

This equation is solvable using e.g., variation of constants:

Step 1:

$$\frac{\mathrm{d}[\mathrm{ClOO}]}{\mathrm{d}t} = -k_8[\mathrm{ClOO}] \Leftrightarrow [\mathrm{ClOO}](t) = c(t)e^{-k_8 t}$$

Step 2:

$$\frac{\mathrm{d}[\mathrm{ClOO}]}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left(c(t)e^{-k_8 t}\right) = \dot{c}(t)e^{-k_8 t} - k_8 c(t)e^{-k_8 t} = k_7[\mathrm{OClO}]_0 e^{-k_7 t} - k_8 c(t)e^{-k_8 t}$$

$$\dot{c}(t)e^{-k_8 t} = k_7[\mathrm{OClO}]_0 e^{-k_7 t}$$

$$\dot{c}(t) = k_7[\mathrm{OClO}]_0 e^{(k_8 - k_7)t}$$

We integrate, setting $c(0) = 0$ (because of the boundary conditions), and we obtain

$$c(t) = k_7[\mathrm{OClO}]_0 \frac{e^{(k_8 - k_7)t} - 1}{k_8 - k_7}.$$

This results in

$$[\mathrm{ClOO}](t) = c(t)e^{-k_8 t} = \left(k_7[\mathrm{OClO}]_0 \frac{e^{(k_8 - k_7)t} - 1}{k_8 - k_7}\right) e^{-k_8 t} = \frac{k_7[\mathrm{OClO}]_0}{k_8 - k_7}\left(e^{-k_7 t} - e^{-k_8 t}\right).$$

(3 points)

Finally, considering $[\mathrm{Cl}]_0 = 0$, the concentration of chlorine is

$$[\mathrm{Cl}] = \int_o^t k_8[\mathrm{ClOO}](t')dt' = \frac{k_8 k_7[\mathrm{OClO}]_0}{k_8 - k_7} \cdot \left(\frac{1}{k_7}\left(1 - e^{-k_7 t}\right) - \frac{1}{k_8}\left(1 - e^{-k_8 t}\right)\right)$$
$$= \frac{[\mathrm{OclO}]_0}{k_8 - k_7} \cdot \left(k_8 - k_8 e^{-k_7 t} - k_7 + k_7 e^{-k_8 t}\right)$$
$$= [\mathrm{OclO}]_0 \left(\frac{k_8}{k_7 - k_8} e^{-k_7 t} - \frac{k_7}{k_7 - k_8} e^{-k_8 t} + 1\right)$$

(2 points)

Production of O_2 follows the same law, since

$$\frac{\mathrm{d}[\mathrm{Cl}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t},$$

and both initial concentrations are $[\mathrm{Cl}]_0 = [\mathrm{O_2}] = 0$. Therefore

$$[\mathrm{O_2}] = [\mathrm{OClO}]_0 \left(\frac{k_8}{k_7 - k_8} e^{-k_7 t} - \frac{k_7}{k_7 - k_8} e^{-k_8 t} + 1\right)$$

(1 point)

<u>Problem 3: Enzyme kinetics</u> (12 points in total)

Cyclo-oxygenase (COX) enzymes are expressed at sites of inflammation. COXs serve as targets for anti-inflammation drugs, such as ibuprofen or aspirin. Studies with a different inhibitor – valdecoxib – were carried out.
In Fig. 1, reaction rates v (expressed by consumption of oxygen) for two isoforms of the enzyme (COX-1 and COX-2) are shown as a function of substrate concentration.
In Fig. 2, enzymatic activity was measured as a function of pre-incubation time. It was found that the Michaelis constant K_M is 35 μM for COX-1 and 20 μM for COX-2.

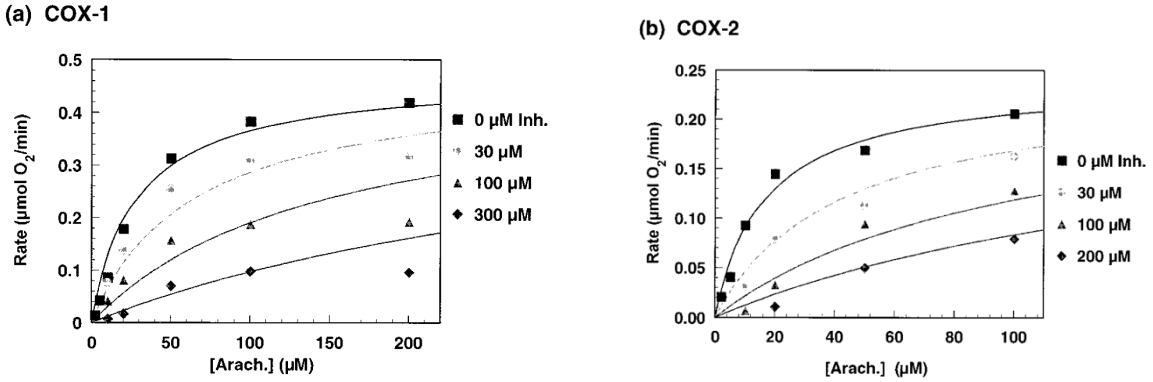


Figure 1: Direct plots of the reaction rate as a function of the substrate (arachidonate) concentration. Different curves correspond to different inhibitor concentrations.

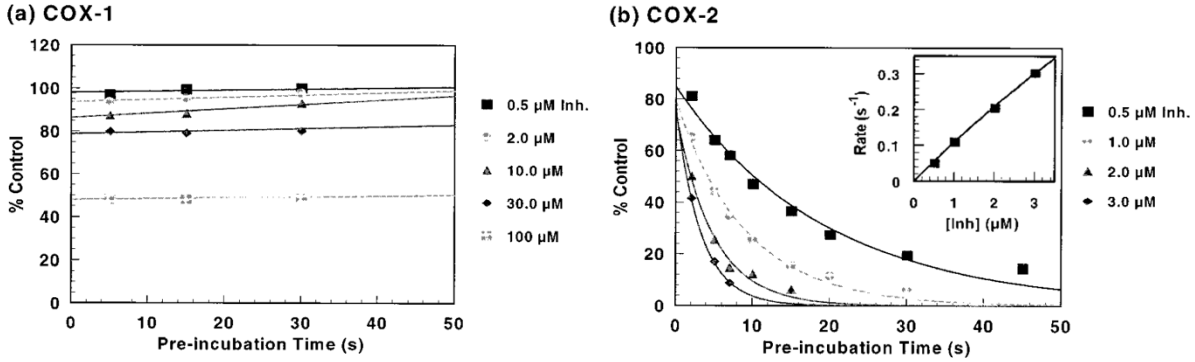


Figure 2: Time-dependent inhibition by valdecoxib. Enzyme and inhibitor (Inh) were mixed and incubated for the indicated time, before adding 100 μM of arachidonate (substrate). The activity is expressed relative to a control sample without inhibitor. The inset in (b) shows the dependence of the rate constant of the decay on the inhibitor concentration.

	COX-1	COX-2
Steady-state K_I (μM)	**24.0 ± 5.5**	**20.0 ± 3.1**
Time-dependent K_I (μM)	**-**	**35.0 ± 6.1**

Table 1: Kinetic constants for inhibition of COX-1 and COX-2 by valdecoxib.

1. **What type of inhibition is observed for both COX-1 and COX-2? Shortly explain your reasoning. What inhibitor concentration is needed to inactivate 95% of COX-2 after 10 seconds of incubation time? The initial substrate concentration is 100 μM.**

Hint: Activity decays exponentially with respect to the incubation time, as seen in Fig. 2b, following the law $A(t) = A_0 e^{-kt}$.

(3 points)

In both cases we observe mixed inhibition, as seen in Figure 1. Both v_{max} and k_M change when inhibitor is added, ruling out pure competitive and non-competitive inhibition, respectively. For pure uncompetitive inhibition, k_M would decrease, which is not the case. Since v_{max} decreases and k_M increases with the addition of an inhibitor, we must conclude that the plots suggest a mixed inhibition.

(2 points)

Decay of activity:

$$A(t) = A_0 e^{-kt}$$

$$k = -\frac{1}{t} \ln \frac{A(t)}{A_0}$$

For $t = 10\ s$, $\frac{A(t)}{A_0} = 0.05$:

$$k = 0.3\ s^{-1}$$

This decay rate constant corresponds to inhibitor concentration of 3 μM, as seen in the inset of Fig. 2B.

Alternatively, it can be also seen directly from main Fig. 2.

(1 point)

2. Two possible mechanisms for inhibition were suggested. Here, EI* marks the stable enzyme-inhibitor complex. Assign the two mechanisms below to COX-1 and COX-2 based on the results shown in Fig. 2. Explain your reasoning.

(1)

$$\mathbf{E + S + I} \rightleftharpoons \mathbf{ES} \rightleftharpoons \mathbf{E + P}$$

$$\mathbf{EI} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{EI^*}$$

(2)

$$\mathbf{E + S + I} \rightleftharpoons \mathbf{ES} \rightleftharpoons \mathbf{E + P}$$

$$\mathbf{EI} \overset{k_2}{\rightarrow} \mathbf{EI^*}$$

(3 points)

Reasoning can be seen in Fig. 2.

COX-1 follows the scheme (1) with the reversible inhibition. The activity does not change with a different incubation time, enzyme is free to bind the inhibitor and then release it.

COX-2 follows the scheme (2) with the irreversible second step to EI*. Once this complex is formed, the enzyme is no longer available for the reaction. With longer incubation time, more EI* is irreversibly formed, decreasing the remaining activity.

(1 point for correct assignment, 2 points for reasoning)

3. The mechanism of enzyme inhibition is in fact best explained by a three-step scheme with an unstable EI enzyme-inhibitor complex, a stable modification EI*, and a fully inactivated enzyme EX. Based on this, calculate the rate of enzyme inactivation expressed as a function of available enzyme concentration [E] and inhibitor concentration [I]. Explain the approximations you are using and why it is legitimate to do so.
What will be the concentration of inactivated enzyme [EX] at the start of the reaction and after reaching equilibrium?

$$\mathbf{E + I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{EI} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathbf{EI^*} \xrightarrow{k_{inact}} \mathbf{EX}$$

(5 points)

We are looking for $v = \frac{\mathrm{d[EX]}}{\mathrm{d}t} = k_{in}[\mathrm{EI}^*]$.

We can apply two steady state approximations on EI and EI*, since both are intermediate states and fulfill all requirements of the approximation.

$$\frac{\mathrm{d}[\mathrm{EI}^*]}{\mathrm{d}t} = -k_{in}[\mathrm{EI}^*] - k_{-2}[\mathrm{EI}^*] + k_2[\mathrm{EI}] = 0 \qquad (1)$$

$$\frac{\mathrm{d}[\mathrm{EI}]}{\mathrm{d}t} = k_1[\mathrm{E}][\mathrm{I}] - k_{-1}[\mathrm{EI}] - k_2[\mathrm{EI}] + k_{-2}[\mathrm{EI}^*] = 0 \qquad (2)$$

(2 points)

From (1), we get $[\mathrm{EI}^*] = \frac{k_2}{k_{in}+k_{-2}}[\mathrm{EI}]$, which we plug into (2) to obtain

$$[\mathrm{EI}] = \frac{k_1}{k_{-1}+k_2-\frac{k_2 k_{-2}}{k_{in}+k_{-2}}}[\mathrm{E}][\mathrm{I}],$$

and finally

$$v = k_{in}[\mathrm{EI}^*] = \frac{k_1 k_2 k_{in}}{k_{-1}k_{in}+k_{-1}k_{-2}+k_2 k_{in}}[\mathrm{E}][\mathrm{I}].$$

(2 points)

For short times (initiation of the reaction), $[\mathrm{EX}] \rightarrow 0$, since no enzyme is deactivated in the beginning. In equilibrium ($t \rightarrow \infty$), $[\mathrm{EX}] \rightarrow [\mathrm{E}]_0$, since all enzyme is deactivated and the reaction stops.

(1 points)

4. Simplify the formula for the rate of inactivation from Task 3 for the case of an irreversible step between stable and unstable enzyme-inhibitor complex.

(1 point)

Taking

$$v = k_{in}[\mathrm{EI}^*] = \frac{k_1 k_2 k_{in}}{k_{-1}k_{in} + k_{-1}k_{-2} + k_2 k_{in}}[\mathrm{E}][\mathrm{I}],$$

and setting $k_{-2} = 0$ (no backwards step between EI* and EI), we get

$$v = \frac{k_1 k_2}{k_{-1} + k_2}[\mathrm{E}][\mathrm{I}].$$

(1 point)

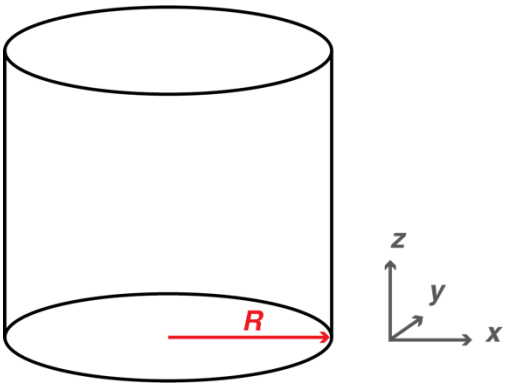
The figures and data from this problem were adapted from: M.C. Walker *et al.*: A three-step kinetic mechanism for selective inhibition of cyclo-oxygenase-2 by diarylheterocyclic inhibitors. Biochemical Journal (357), 2001.

<u>Problem 4: Kinetic theory of gases</u>. (11 points in total)

1. **Consider an ideal gas confined in a cylindrical container, as shown in the sketch below. Derive the speed distribution $F(u_z)du_z$ along the *z* axis of the container.**

Hint: Derive the three-dimensional distribution of the velocities from its one-dimensional form. Then perform a suitable coordinate transformation, considering the vessel. Write the transformation down (no need to write the Jacobi matrix).

(7 points)



We begin with the one-dimensional distribution of the velocity

$$f(u_i) = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\frac{mu_i^2}{2k_B T}},$$

which gives us the three-dimensional velocity distribution

$$f^{3D}(u_x, u_y, u_z)\mathrm{d}u_x\mathrm{d}u_y\mathrm{d}u_z = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{m\left(u_x^2+u_y^2+u_z^2\right)}{2k_B T}}\mathrm{d}u_x\mathrm{d}u_y\mathrm{d}u_z.$$

(1 point)

We do a coordinate transformation to cylindrical coordinates:

$$u_x = u\cos\phi$$
$$u_y = u\sin\phi$$
$$u_z = u_z$$

$$u_x^2 + u_y^2 + u_z^2 = u^2 + u_z^2$$

$$\mathrm{d}u_x\mathrm{d}u_y\mathrm{d}u_z = u\mathrm{d}u\mathrm{d}\phi\mathrm{d}u_z$$

(2 points)

We obtain:

$$\widetilde{f^{3D}}(u,\phi,u_z)\,\mathrm{d}u\,\mathrm{d}\phi\,\mathrm{d}u_z = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{mu^2}{2k_B T}} e^{-\frac{mu_z{}^2}{2k_B T}}\, u\,\mathrm{d}u\,\mathrm{d}\phi\,\mathrm{d}u_z.$$

(1 point)

Finally, integrate over u, ϕ:

$$\begin{aligned} F(u_z)\mathrm{d}u_z &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{mu_z{}^2}{2k_B T}} \int_0^{2\pi} \mathrm{d}\phi \int_0^{R} u\, e^{-\frac{mu^2}{2k_B T}} \mathrm{d}u\ \mathrm{d}u_z \\ &\triangleq \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{mu_z{}^2}{2k_B T}}\, 2\pi \frac{k_B T}{m}\left(1 - e^{-\frac{mR^2}{2k_B T}}\right)\mathrm{d}u_z \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{mu_z{}^2}{2k_B T}} \left(1 - e^{-\frac{mR^2}{2k_B T}}\right)\mathrm{d}u_z, \end{aligned}$$

which gives you a final result. It is a modified speed distribution of a one-dimensional gas.

Δ: The second integral is solved with a simple substitution

$$s = \frac{mu^2}{2k_B T}$$

$$\mathrm{d}s = \frac{mu}{k_B T}\,\mathrm{du}$$

Boundaries of the integral after the substitution are $\left(0\,;\,\frac{mR^2}{2k_B T}\right)$.

(3 points)

2. How will the distribution $F(u_z)du_z$ from Task 1 change for $R \to 0$ and $R \to +\infty$? What conclusions can you draw from this?

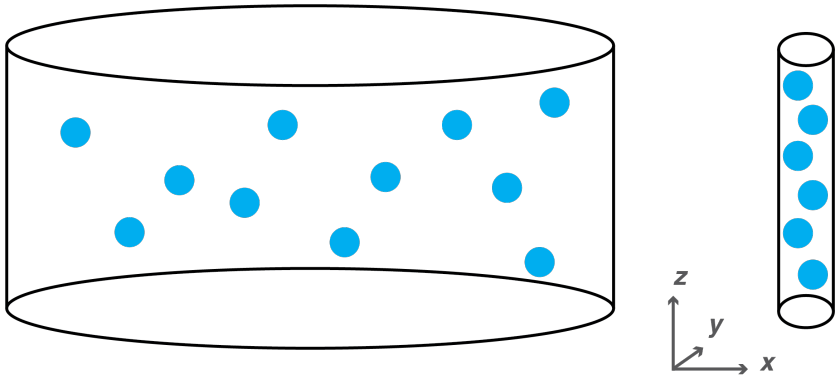
(4 points)

For $R \to +\infty$, the result from Task 1 becomes a standard 1D distribution, as $e^{-\frac{mR^2}{2k_BT}} \to 0$. The cylinder diameter is so large that it does not impose any constraints on the gas inside, which becomes a standard three-dimensional ideal gas.

(2 points)

For $R \to 0$, the result from Task 1 degenerates with the distribution $F(u_z)\mathrm{d}u_z \to 0$. The molecules of the gas are restricted to a single dimension and enter a special regime called one-dimensional gas.
Due to the dimensions of the cylinder (rather “nano tube”), the molecules collide most frequently with the walls rather than with each other, rendering the concept of a Maxwell-Boltzmann distribution of ideal gases invalid.

(2 points)



<u>Problem 5: Electron harpooning</u> (8 points in total)

1. Explain the harpoon mechanism and how it relates to the steric factor.

(2 points)

The harpoon mechanism concerns reactions that involve electron transfer. The transfer occurs over longer distances than the collision cross section of the reaction partners would suggest due to an attractive potential between the partners, thus leading to a steric factor bigger than one.

(2 points)

2. Octamethylcalix[4]pyrrole (omC4P) behaves like an alkali metal and is able to initiate electron harpooning to bind halogens, such as chlorine.
The electron affinity of Cl is 3.7 eV. From theory, the harpooning should occur at a distance of 523 pm. What is the ionization energy of omC4P?
Simulations of the potential energy surface suggest an energy balance ΔE that is shifted by -0.75 eV. What is the harpooning distance under these conditions?
Sketch the dependence of the potential energy of neutral and charged reactants (omC4P + Cl and $omC4P^+ + Cl^-$) on the distance between them. Indicate, where you can find the critical harpooning distance and activation potential in the plot.

(6 points)

Activation energy of chlorine: $EA = 3.7\ eV$.
Theoretical distance of harpooning: $d_{theo} = 5.23$ Å.

To find the ionization energy EI_{omC4P}, one sets the energy balance

$$\Delta E = EI_{\mathrm{omC4P}} - EA_{\mathrm{Cl}} + A = EI_{\mathrm{omC4P}} - EA_{\mathrm{Cl}} - \frac{e^2}{4\pi\varepsilon_0 d} = 0,$$

(1 point)

which yields

$$EI_{\mathrm{omC4P}} = 6.45\ eV.$$

(1 point)

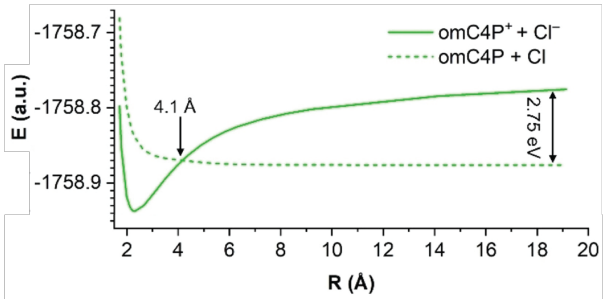
The shift in energy balance implies the existence of a new critical distance of harpooning r:

$$\Delta E = EI_{\mathrm{omC4P}} - EA_{\mathrm{Cl}} - \frac{e^2}{4\pi\varepsilon_0 r} = -0.75\ eV.$$
$$r = 4.1\ \text{Å}$$

(1 point)

Activation potential is defined as

$$E_{activ} = EI_{\mathrm{omC4P}} - EA_{\mathrm{Cl}}$$



(3 points 1 pt activation potential, 1 pt curves, 1 pt indication)

Problem inspired by the following publication: W. Cao and X.-B. Wang: Organic Molecules Mimic Alkali Metals Enabling Spontaneous Harpoon Reactions with Halogens. Chem. Eur. J. 30 (20), e202400038 (2024).

Problem 6: Transition state theory (9 points total)

1. We use transition-state theory (TST) for the nucleophilic substitution reaction:

$$\mathbf{F^- + MeBr \rightarrow MeF + Br^-}$$

For the following question, you can assume the methyl moiety to be one large quasi-particle. The most relevant bond for the reactants is the bond between the methyl and bromide. Its length is 178 pm, with a vibrational wave number of $\tilde{\nu} = 1250\,\mathrm{cm^{-1}}$. Assume the transition state to be linear across the Me-F bond, with the Me-F bond length in the transition state being 140 pm and the Me-Br bond length in the transition state being 180 pm, with vibrational wave numbers $\tilde{\nu}_{ss} = 500\,\mathrm{cm^{-1}}$ and bending vibrations: $\tilde{\nu}_{bend}$ = $400\,\mathrm{cm^{-1}}$ with a twofold degeneracy.
The molecular weight of MeBr is 94.94 g/mol, with the methyl moiety being 15.04 g/mol. The atomic mass of fluorine is 19.00 g/mol. The barrier height is E_{QM} = 30 kJ/mol (difference between zero-point energies of the transition state and reactants).
Determine the rate constant at 300 K.

(7 points)

The rate constant is given by:

$$k_{\mathrm{TST}} = N_{\mathrm{Av}} \frac{k_B T}{h} \frac{\tilde{q}_V^{\ddagger}}{\tilde{q}_{V,\mathrm{F}} \tilde{q}_{V,\mathrm{MeBr}}}\, e^{-E_{QM}^0/k_B T}.$$

The masses of the reactants are:

$$m_{\mathrm{F}} = 3.15 \cdot 10^{-26}\ \mathrm{kg}\ ,$$
$$m_{\mathrm{MeBr}} = 1.58 \cdot 10^{-25}\ \mathrm{kg},$$
$$m_{\mathrm{Me}} = 2.50 \cdot 10^{-26}\mathrm{kg},$$
$$m_{\mathrm{Br}} = 1.33 \cdot 10^{-25}\mathrm{kg}.$$

The moment of inertia of MeBr is:

$$I = \mu d^2 = \frac{m_{\mathrm{Me}}\, m_{\mathrm{Br}}}{m_{\mathrm{Me}} + m_{\mathrm{Br}}} d_{\mathrm{MeBr}}^2 = 6.66 \cdot 10^{-46}\ \mathrm{kg\,m^2}$$

with $d_{\mathrm{MeBr}} = 178\ \mathrm{pm}$.

(1 point)

The collinear transition state has a mass of $m^{\ddagger} = m_{\mathrm{MeBr}} + m_{\mathrm{F}} = 113.94\ \mathrm{g/mol}$. The center of mass is in distance x from the fluorine atom:

$$-m_{\mathrm{F}} x - m_{\mathrm{Me}}\,(x - 140) + m_{\mathrm{Br}}(320 - x) = 0$$
$$x = 242.9\ pm$$

Therefore, the moment of inertia is:

$$I^{\ddagger} = m_{\mathrm{F}}(242.9\ \mathrm{pm})^2 + m_{\mathrm{Me}}(102.9\ \mathrm{pm})^2 + m_{\mathrm{Br}}(77.1\ \mathrm{pm})^2 = 2.91 \cdot 10^{-45}\ \mathrm{kg\,m^2}$$

(2 points)

We calculate the partition functions for the reactants. For the fluorine we have:

$$q_{V,\mathrm{F},tr} = \tilde{q}_{V,\mathrm{F},tr} = \left(\frac{2\pi m_F k_B T}{h^2}\right)^{3/2} = 8.06 \cdot 10^{31}\ \mathrm{m}^{-3}$$

Rotational and vibrational partition functions for fluorine are zero since it is a single atom.

(1 point)

For the methyl bromide we have:

$$\tilde{q}_{V,\mathrm{MeBr},tr} = \left(\frac{2\pi m_{MeBr} k_B T}{h^2}\right)^{3/2} = 9.03 \cdot 10^{32}\ \mathrm{m}^{-3}$$

$$\tilde{q}_{V,\mathrm{MeBr},rot} = \left(\frac{8\pi^2 I_{MeBr} k_B T}{h^2}\right) = 495.8$$

$$\tilde{q}_{V,\mathrm{MeBr},vib} = \frac{1}{1-e^{-x}} \approx 1,$$

Because $x = \frac{h\tilde{\nu}c}{k_B T} \approx 6.0$.

(1 point)

For the transition state, we have analogous formulae:

$$\tilde{q}^{\ddagger}_{V,tr} = \left(\frac{2\pi m_{\ddagger} k_B T}{h^2}\right)^{3/2} = 1.18 \cdot 10^{33}\ \mathrm{m}^{-3}$$

$$\tilde{q}^{\ddagger}_{rot} = \left(\frac{8\pi^2 I^{\ddagger} k_B T}{h^2}\right) = 2166.6$$

$$\tilde{q}^{\ddagger}_{vib} = \frac{1}{(1-e^{-x_{SS}})(1-e^{-x_{bend}})^2} = 1.51$$

with $x_{ss} = \frac{h\tilde{\nu}_{ss}c}{k_B T} = 2.4$ and $x_{bend} = \frac{h\tilde{\nu}_{bend}c}{k_B T} = 1.92$.

(1 point)

Finally, we multiply the partition functions, as $\tilde{q}_V = \tilde{q}_{V,tr}\tilde{q}_{V,rot}\tilde{q}_{V,vib}$.

$$\tilde{q}^{\ddagger}_V = 3.86 \cdot 10^{36}\ \mathrm{m}^{-3}$$
$$\tilde{q}_{V,F} = 8.06 \cdot 10^{31}\ \mathrm{m}^{-3}$$
$$\tilde{q}_{V,MeBr} = 4.47 \cdot 10^{35}\mathrm{m}^{-3},$$

which leads to

$$k_{TST} = N_{\mathrm{Av}} \frac{k_B T}{h} \frac{\tilde{q}^{\ddagger}_V}{\tilde{q}_{V,\mathrm{F}}\tilde{q}_{V,\mathrm{MeBr}}}\, e^{-E^0_{QM}/k_b T} = 2.4\ \frac{\mathrm{m}^3\mathrm{s}^{-1}}{\mathrm{mol}} \text{ or } 2.4 \cdot 10^3\ \mathrm{M}^{-1}\mathrm{s}^{-1}.$$

(1 point)

2. Which assumptions do we make in transition state theory?

(2 points)

In transition state theory, we make basic assumptions:

(i) Born Oppenheimer approximation
(ii) Boltzmann (thermal) distribution

(1 point)

We also assume:

(i) No re-crossing
(ii) Quasi-equilibrium
(iii) Classical motion along the reaction coordinate

(1 point)