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.

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

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

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

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

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

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

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

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

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

Coulomb's law $\boldsymbol{F}_1 = \frac{q_1q_2}{4\pi\varepsilon_0}\frac{\boldsymbol{r}_{12}}{|\boldsymbol{r}_{12}|^2}$

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

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

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

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

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

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

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

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

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

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

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

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

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

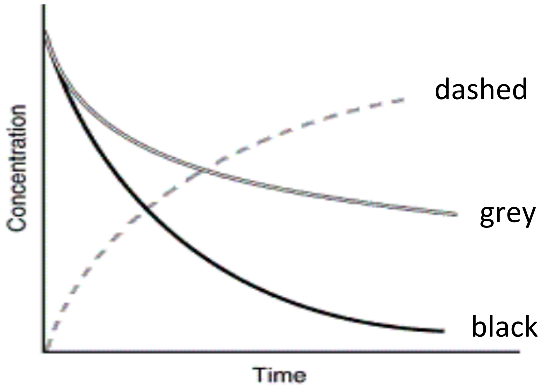
$c = 3.00\ \cdot 10^8\ m \cdot s^{-1}$

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

<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: $\mathrm{O_2(g) + 2H_2(g) \rightarrow 2\,H_2O(g)}$ 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.

2. **For the reaction $\mathrm{A + 3B \rightarrow 2C}$, 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.

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

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

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

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

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

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.**

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

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

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

1. We examine the elementary reactions:

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

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

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

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

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 differential 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)

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

(1 point)

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:

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

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

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

$$\mathbf{ClOO\ (g) \xrightarrow{k_{-7}} OClO\ (g)} \tag{–R7}$$

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

and

$$\mathbf{Cl\ (g) + O_2(g) \xrightarrow{k_{-8}} ClOO\ (g).} \tag{–R8}$$

3. **Write the differential 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)

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)

Problem 3: Enzyme kinetics **(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.

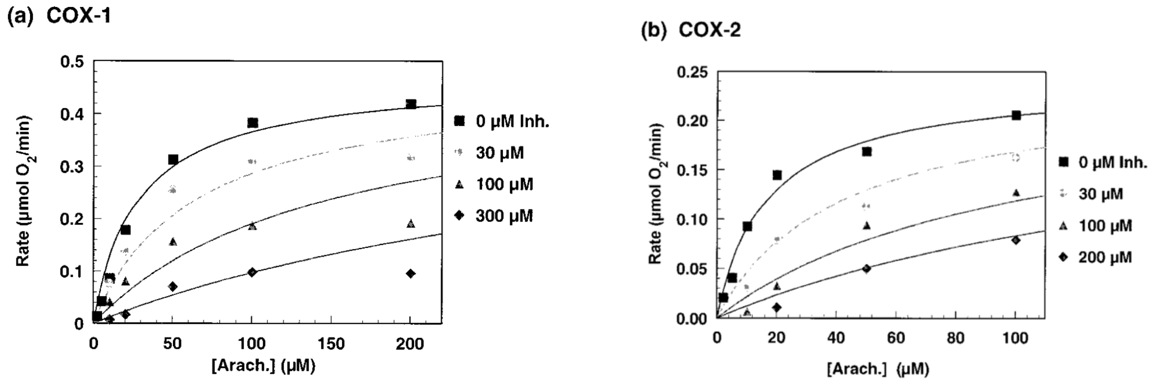


Figure 1: Direct plots of the reaction rate as a function of the substrate (arachidonate) concentration. Different curves correspond to different inhibitor concentrations.

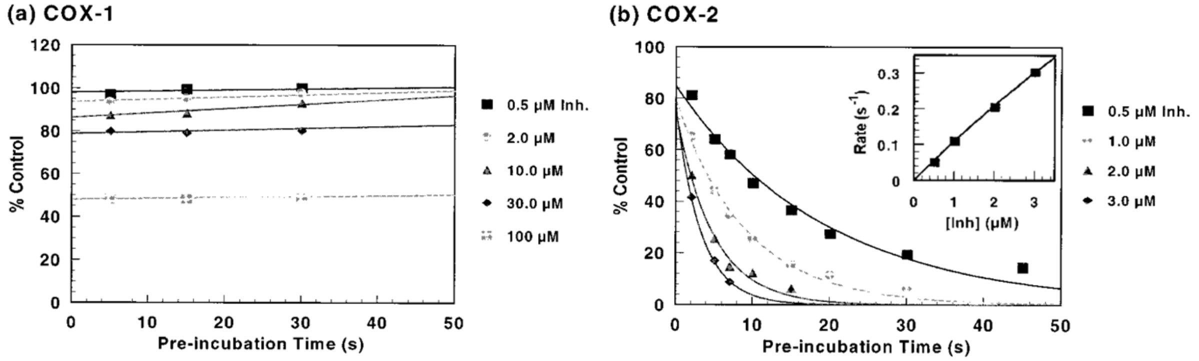


Figure 2: Time-dependent inhibition by valdecoxib. Enzyme and inhibitor (Inh) were mixed and incubated for the indicated time, before adding 100 μM of arachidonate (substrate). The activity is expressed relative to a control sample without inhibitor. The inset in (b) shows the dependence of the rate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

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)

$$\begin{tikzcd}
\mathbf{E + S + I} \arrow[r, rightleftharpoons] \arrow[d, shift right, "k_1"'] & \mathbf{ES} \arrow[r, rightleftharpoons] & \mathbf{E + P} \\
\mathbf{EI} \arrow[u, shift right, "k_{-1}"'] \arrow[r, rightleftharpoons, "k_2", "k_{-2}"'] & \mathbf{EI^*} &
\end{tikzcd}$$

(2)

$$\begin{tikzcd}
\mathbf{E + S + I} \arrow[r, rightleftharpoons] \arrow[d, shift right, "k_1"'] & \mathbf{ES} \arrow[r, rightleftharpoons] & \mathbf{E + P} \\
\mathbf{EI} \arrow[u, shift right, "k_{-1}"'] \arrow[r, "k_2"] & \mathbf{EI^*} &
\end{tikzcd}$$

(3 points)

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?

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

(5 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.**

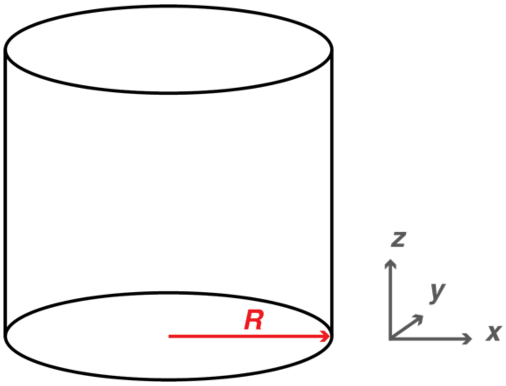
(1 point)

Problem 4: Kinetic theory of gases. (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)



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

(4 points)

Problem 5: Electron harpooning (8 points in total)

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

(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. Calculate 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 harpooning distance and activation potential in the plot.

(6 points)

<u>Problem 6: Transition state theory</u> (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)

Which assumptions do we make in transition state theory?

(2 points)