Dynamics and Kinetics – Final Exam

January 19, 2024

Name:

Total 51 points, 3 h 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 are not permitted. Do not write with a pencil or a fountain pen that can be erased. Please have your photo ID 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 $n = 0, 1, 2, \ldots$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

1) The gas phase reaction between CO and Cl_2 to form phosgene (Cl_2CO)

$$\mathrm{Cl_2 + CO \xrightarrow{k_{obs}} Cl_2CO}$$

has the rate law

$$\frac{d[\mathrm{Cl_2CO}]}{dt} = k_{obs}\,[\mathrm{Cl_2}]^{3/2}[\mathrm{CO}]$$

(6 points total)

a) Show that the following mechanism is consistent with this rate law.

$\mathrm{Cl_2 + M}$	$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$	$\mathrm{2\,Cl + M}$	(fast)
$\mathrm{Cl + CO + M}$	$\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$	$\mathrm{ClCO + M}$	(fast)
$\mathrm{ClCO + Cl_2}$	$\overset{k_3}{\rightarrow}$	$\mathrm{Cl_2CO + Cl}$	(slow)

where M is any gas molecule present in the reaction container. Express k_{obs} in terms of the rate constants for the individual steps of the reaction mechanism.

(3 points)

b) An alternative mechanism that has been proposed for this reaction is

$$\mathbf{Cl_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl + M} \qquad \textbf{(fast)}$$

$$\mathbf{Cl + Cl_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Cl_3} \qquad \textbf{(fast)}$$

$$\mathbf{Cl_3 + CO \xrightarrow{k_3} Cl_2CO + Cl} \qquad \textbf{(slow)}$$

Show that this mechanism also gives the observed rate law.

(3 points)

2) Consider the following reaction mechanism.

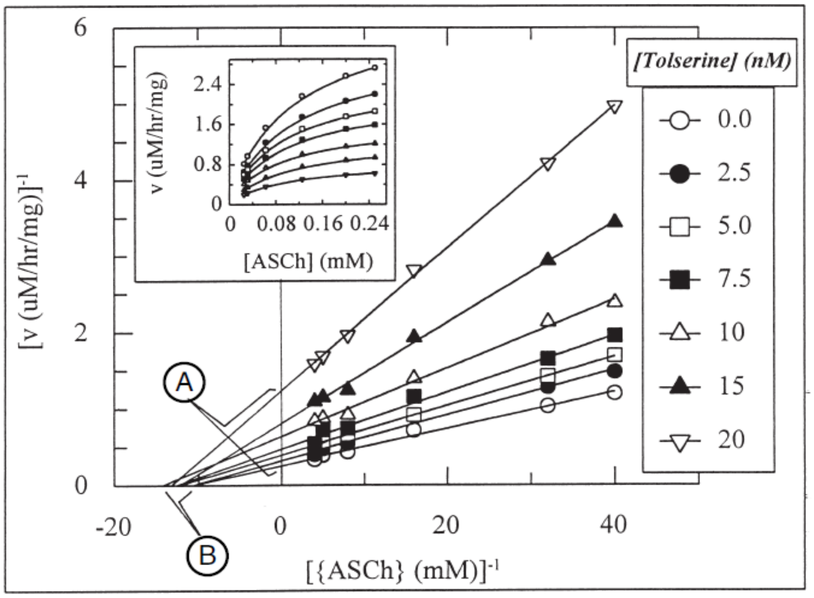
$$\mathbf{2\,A} \xrightarrow{k_1} \mathbf{B} \qquad (1)$$

$$\mathbf{B + C} \xrightarrow{k_2} \mathbf{A + D} \qquad (2)$$

Describe an algorithm (no need to write proper code) that uses the stochastic method to simulate the reaction above. (8 points)

3) Enzyme kinetics (8 points total)

a) Acetylcholinesterase catalyzes the conversion of acetylthiocholine (ASCh) into thiocholine. Reaction rates v were measured as a function of the substrate concentration in the presence of different concentrations of the inhibitor tolserine.



Which quantities can be obtained from the intercept with the y-axis (A) as well as the intercept with the x-axis (B)? Based on these data, what conclusions can you draw about the type of inhibition?

(2 points)

b) The following mechanism has been proposed for the conversion of acetylthiocholine (S) into thiocholine (P) by the enzyme acetylcholinesterase (E) in the presence of the inhibitor tolserine (I). Note that this is a variant of the mechanisms for inhibition that we have discussed in class.

$$
\begin{array}{ccccc}
\mathbf{E + S + I} & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & \mathbf{ES + I} & \xrightarrow{k_2} & \mathbf{E + P + I} \\
\downharpoonleft\upharpoonright \; K_{EI} & & & & \\
\mathbf{EI + S} & \overset{K_{ESI}}{\leftrightharpoons} & \mathbf{ESI} & \xrightarrow{k_3} & \mathbf{E + P + I}
\end{array}
$$

a) Find an expression for the rate of the reaction in analogy to our treatment of inhibited enzymatic reactions that we have discussed in class. The expression should only depend on the concentrations of the substrate $[S]$, the inhibitor $[I]$, and the initial enzyme concentration $[E]_0$. Explain the approximations you have to make in your derivation.

(4 points)

c) Show how this result changes in the limit of

- **the complex EI binding the substrate only very weakly?**
- **the inhibitor I binding only weakly to the enzyme E?**

What scenario or type of inhibition do you obtain in either case?

(2 points)

4) Kinetic theory of gases. (13 points total)

a) Calculate the probability $P(u_{x0})$ that the x-component of the velocity u_x of a molecule lies in the range $-u_{x0} \leq u_x \leq u_{x0}$. Express the probability $P(u_{x0})$ in terms of the error function $erf(z)$.

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-x^2} dx$$

Sketch the probability $P(u_{x0})$.

(4 points)

b) Derive the speed distribution $F(u)du$ of a two-dimensional ideal gas.

Hint: Start from a one-dimensional velocity distribution to derive a two-dimensional distribution of the velocities, and then do a suitable coordinate transformation. (6 points)

c) Calculate the most frequent speed with which gas molecules strike a surface. Also calculate the most probable speed of a gas molecule. Finally, calculate the ratio of both.

(3 points)

5) Reaction dynamics

(8 points total)

a) Potential energy surfaces. Sketch the contour plot of a typical potential energy surface of a reaction

$$AB + C \rightarrow A + BC$$

with the reaction constrained to a linear geometry. Here, A, B, and C are atoms. Assume that the reaction has a so-called "late" transition state, *i.e.* at the transition state, the configuration of the atoms is more similar to the products than the reactants. Draw the minimum energy path of the reaction and indicate where the reactants, the products, and the transition state are located.

(4 points)

b) Unimolecular reactions. Explain qualitatively how the Hinshelwood rate constant and the RRK rate constant depend on the size of the molecule.

(4 points)

6) Bimolecular collisions

(8 points total)

a) In class, we have derived the deflection function for hard spheres collsions by first deriving an expression for the trajectory of a particle scattered by an arbitrary central potential.

Show that one can also derive this deflection function simply from geometric considerations of the collision geometry. Use the trigonometric identities given on page 1 to arrive at the expression we obtained in class.

(2 points)

b) Consider bimolecular collisions with a central potential

$$\boldsymbol{U(r) = \left(\frac{c}{r}\right)^{12}}$$

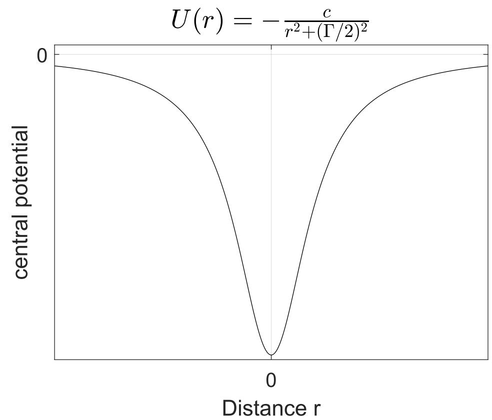
where c is a constant and r is the distance between the two particles.

Sketch representative trajectories that illustrate the scattering for small, intermediate, and large impact parameters. Sketch the deflection function together with the deflection function for a hard spheres collision. Explain qualitatively how the differences between these two deflection functions arise.

(3 points)

c) Consider bimolecular collisions in a central potential defined by a negative Lorentzian

$$U(r) = -\frac{c}{r^2 + \left(\frac{1}{2}\Gamma\right)^2}$$



where c is a constant, r is the distance between the two particles, and Γ relates to the width of the Lorentzian.

Sketch representative trajectories that illustrate the scattering for small, intermediate, and large impact parameters. Sketch the deflection function together with the deflection function for a hard spheres collision. Explain qualitatively how the differences between these two deflection functions arise.

(3 points)