Dynamics and Kinetics – Final Exam

January 21, 2022

Name:

Total 48 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 $n = 0, 1, 2, \ldots$

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

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

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

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

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

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

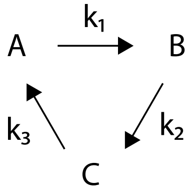
$\epsilon_0 = 8.85 \cdot 10^{-12}\ \mathrm{F \cdot m^{-1}}$

1) In class we discussed two-body classical scattering with a central interaction potential. (9 points total)

a) Sketch a typical trajectory of a scattering event. Sketch and explain the coordinate system you have chosen. Indicate and explain the masses and velocities involved. Explain the symmetry properties of the trajectory. Mark the impact parameter and deflection angle. (6 points)

b) For scattering in a Lennard-Jones potential, sketch a deflection function with the kinetic energy comparable to the well depth. With the help of your sketch, explain the salient features of the deflection function. (3 points)

2) Describe an algorithm (no need to write proper code) to simulate the reaction



with the stochastic method and explain it. (8 points)

3) In class, we have derived the RRK rate constant

$$k_2(E) = \nu \left(\frac{E - E_0}{E}\right)^{s-1}$$

under the assumptions that the s vibrational degrees of freedom can be treated as classical harmonic oscillators. Derive the same expression for s quantized oscillators. (8 points total)

a) Explain the physical meaning of the terms ν and $\left(\frac{E-E_0}{E}\right)^{s-1}$ in the context of the assumptions of the RRK theory. (2 points)

b) Assume that all oscillators have the same eigenfrequency ν and that $E = Nh\nu$. How many possibilities exist to distribute the energy E over the s oscillators? (2 points)

c) How many possibilities exist to distribute the energy E over the s oscillators if an energy of at least $E_0 = N_0 h\nu$ is stored in the critical oscillator? (2 points)

d) With the results from b) and c), derive the RRK rate constant. Which further assumptions do you have to make? (2 points)

4) Nitramide (O_2NNH_2) decomposes in water according to the following equation:

$$O_2NNH_2\,(aq) \xrightarrow{k} N_2O\,(g) + H_2O\,(l)$$

The experimentally determined rate law is the following:

$$\frac{d[N_2O]}{dt} = k_{obs}\frac{[O_2NNH_2]}{[H^+]}$$

The following mechanism has been proposed.

$$O_2NNH_2\,(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^-\,(aq) + H^+\,(aq) \qquad \text{(fast, pre-equilibrium)}$$

$$O_2NNH^-\,(aq) \xrightarrow{k_2} N_2O\,(g) + OH^-\,(aq) \qquad \text{(slow)}$$

$$H^+\,(aq) + OH^-\,(aq) \xrightarrow{k_3} H_2O\,(l) \qquad \text{(fast)}$$

(8 points total)

a) Is the proposed mechanism consistent with the rate found experimentally? If so, what is the relationship between observed rate k_{obs} and the rate constants of the elementary steps of the mechanism? (4 points)

b) To analyze the kinetics of this complex reaction, one could consider applying the steady-state approximation to O_2NNH^- (aq). Is this consistent with the rate found experimentally? Under which conditions? (4 points)

5) The rate of a bimolecular reaction in the gas phase

A + B → products

generally depends on the relative kinetic energy of the collision. Calculate the total frequency of collisions per unit volume between A and B that have a *relative* kinetic energy larger or equal than a threshold energy E_0. (8 points)

6) Given is the following reaction.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \xrightarrow{k_3} \mathrm{D} \xrightarrow{k_4} \mathrm{E}$$

(7 points total)

a) Determine the concentration of C if the concentrations of B, C, and D are initially zero.

It would certainly be possible to solve this problem sequentially. Instead, use the following approach that is more simple.

In class, we have already integrated the rate equations for the consecutive reaction

$$\mathrm{B} \xrightarrow{k_2} \mathrm{C} \xrightarrow{k_3} \mathrm{D}$$

where the initial concentrations of C and D are zero. For a given initial concentration of B, the time-dependent concentration of C is

$$[\mathrm{C}] = \frac{k_2[\mathrm{B}]_0}{k_3 - k_2}\left(e^{-k_2 t} - e^{-k_3 t}\right)$$

The difference in our problem here is that B does not start out with a fixed initial concentration $[\mathrm{B}]_0$, but is continuously being formed. However, for a very small quantity $d[\mathrm{B}(t')]$ that is formed at a given point in time t', we can calculate how much C will be formed from this amount $d[\mathrm{B}(t')]$ at a later time $t - t'$. Use this idea to solve for the concentration of C. (5 points)

b) Based on your result in a), how can you use the same approach to calculate the concentration of D in the following reaction (initial concentrations are all zero except that of A)?

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B} \xrightarrow{k_2} \mathbf{C} \xrightarrow{k_3} \mathbf{D} \xrightarrow{k_4} \mathbf{E}$$

Write down the integral for the concentration of D. There is, however, no need to solve the integral. (2 points)