

Dynamics and Kinetics – Final Exam

January 13, 2021

Name:

Total 49 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.

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

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

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

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

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

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

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

$$\Gamma(n+1) = n!, \text{ for integer } n = 0, 1, 2, \dots$$

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

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

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

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

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

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

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

1) At 298 K, the apparent rate coefficient of a gas-phase reaction that follows the Lindemann mechanism is $5.5 \cdot 10^{-4} \text{ s}^{-1}$ at 2.4 kPa and $1.0 \cdot 10^{-5} \text{ s}^{-1}$ at 1.5 Pa. Calculate the rate constant for the energization process in this mechanism (in units of $(\text{mol/l})^{-1} \text{ s}^{-1}$). (5 points)

2) Acetaldehyde has been proposed to decompose according to the following mechanism. (Total, 14 points)



a) In this radical chain reaction, identify the different types of reaction steps. (3 points)

b) Derive a rate law for the formation of CO that contains only the concentration of the reactant $[\text{CH}_3\text{CHO}]$. Assume that all radical species are present only in low concentrations in order to make suitable approximations. (4 points)

c) Use the rate law derived in (b) to find an expression for the kinetic chain length λ of this radical chain reaction. (3 points)

d) How are the observed Arrhenius activation energy and Arrhenius prefactor for the production of CO related to the activation energies and prefactors of reactions (1–4)? (4 points)

3) In class, we have discussed the rate law for a bimolecular reaction



If instead of concentrations, we write the rate law in terms of number of A molecules n_A , it becomes

$$\frac{dn_A}{dt} = -2kn_A^2$$

We have made a small mistake here, since one A molecule cannot react with itself. Modify the rate law accordingly and integrate it to obtain an expression for $n_A(t)$. (6 points)

4) In class, we have derived an expression for the collision rate with the wall of a container. One can use the same approach to describe the rate of evaporation of a liquid or a solid in vacuum (Hertz-Knudsen equation). (Total, 7 points)

a) How can we link the evaporation rate of a compound with a specific vapor pressure to the collision rate of the gas with a surface? What additional considerations does one have to take into account? (3 points)

b) The vapor pressure of hexagonal ice at 150 K is $2.45 \cdot 10^{-6}$ Pa. How long does it take a 100 nm thick ice film in ultrahigh vacuum to evaporate completely? (Water has a molar mass of about 18 g/mol, and ice has a density of about 0.92 g/cm^3 .) (4 points)

5) For a reactive collision, the reaction probability $P(b)$ is a function of the impact parameter b and is described by

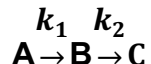
$$P(b) = \begin{cases} A \cos\left(\frac{\pi}{2} \cdot \frac{b}{b_{max}}\right) & \text{for } b < b_{max} \\ 0 & \text{for } b > b_{max} \end{cases}$$

where A and b_{max} are constants. (Total, 6 points)

a) Sketch the reaction probability as a function of the impact parameter. (1 point)

b) Calculate the reaction cross section. (5 points)

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



where the initial concentrations of B and C are zero.

Here, we would like to use a different approach that is based on the following idea. Imagine that at time t , during a small time interval dt , the first reaction step generates a small quantity $d[B(t)]$ of the intermediate B. We do know how in the following, this small quantity $d[B(t)]$ will convert into the product C. This conversion will follow the same time dependence independently of how large a quantity of B has previously been created or will still be created.

At a later time $t + dt$, during another small time interval dt , another small quantity $d[B(t + dt)]$ of the intermediate will be created and convert into C in the same manner, and so forth.

At any given point in time, the concentration of B will therefore be the sum of these small quantities $d[B]$ that have previously been created and have since partially converted into products. (Total, 11 points)

a) Use this idea to calculate the concentration of B as a function of time. (9 points)

b) Under which conditions can one calculate the concentration of an intermediate of a reaction sequence with this method. (2 points)

