Dynamics and Kinetics – Final Exam

December 17, 2019

Name:

Total 61 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) For the reversible reaction

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

derive the time-dependent concentrations of A and B by means of the matrix method. Assume that the initial concentration of B is zero. (18 points)

2) The gas-phase reaction

$$\mathbf{K + Br_2 \rightarrow KBr + Br}$$

proceeds by the so-called harpoon mechanism. (Total, 7 points)

a) Explain the harpoon mechanism and how it relates to the steric factor. (3 points)

b) The ionization energy of K is $E_I = 420\ \mathrm{kJ/mol}$, and the electron affinity of Br_2 is $E_{ea} = 250\ \mathrm{kJ/mol}$. The distance of nearest approach between both collision partners is about 400 pm. Estimate the steric factor for the reaction. (4 points)

3) The recombination of iodine atoms in the presence of argon is a third order reaction, that has been extensively studied using techniques such as flash photolysis.

$$\mathbf{I + I + Ar \xrightarrow{k} I_2 + Ar}$$

(Total, 16 points)

a) In an experiment, the concentration of argon is $1*10^{-2}$ mol/l, and the initial concentration of iodine atoms is $6*10^{-5}$ mol/l. At a temperature of 298 K, the half-life of the iodine atoms is 238 μs. Calculate the rate constant. (6 points)

b) At a temperature of 350 K, but otherwise identical initial conditions as in a), the half-life of the iodine atoms is 342 μs. Calculate the activation energy of the reaction. (4 points)

c) The following reaction mechanism has been suggested for the recombination of iodine atoms. First, the van-der-Waals complex IAr is formed in a weakly exothermic reaction that is reversible.

$$\mathbf{I} + \mathbf{Ar} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathbf{IAr}$$

In a second step, collision with another iodine atom leads to the formation of I_2.

$$\mathbf{IAr} + \mathbf{I} \overset{k_2}{\rightarrow} \mathbf{I_2} + \mathbf{Ar}$$

The activation energy for this second step is zero. Since this second step is rate limiting, a pre-equilibrium exists for the formation of the complex IAr in the first step.

Write down the rate equation for the formation of I_2 under the assumption of a pre-equilibrium for the complex IAr and explain why the recombination of iodine atoms has a negative activation energy. Hint: Consider the temperature dependence of the effective rate constant. (6 points)

4) Lindemann-Hinshelwood theory. (Total, 12 points)

a) Derive the expression for the rate constant of unimolecular reactions according to the Lindemann theory and explain. (6 points)

b) Discuss how the predictions of the reactive hard spheres model and the Hinshelwood theory differ and why. (2 points)

c) Describe the assumptions of the Hinshelwood theory for the activation rate constant and the approach for calculating it. (4 points)

5) Describe an algorithm (no need to write proper code) to simulate the reaction 2A → products with the stochastic method. (8 points)

Hint: In a first step, determine the probability that in a short time interval $\Delta\tau$, no reaction has occurred. Then, use this expression to set up a differential equation for the probabilty that of n molecules, none has reacted. Then, integrate the differential equation to obtain the probability as a function of time. Finally, write down an algorithm that uses random numbers to decide when the next reaction occurs, based on that probability.