# Dynamics and Kinetics – Final Exam

## January 19, 2023

**Name:**

**Total 50 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 $n = 0, 1, 2, \ldots$

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

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

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

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

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

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

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

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

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

**1) For the gas-phase reaction of nitric oxide with molecular hydrogen**

$$2\ H_2\ (g) + 2\ NO\ (g) \xrightarrow{k_{obs}} N_2\ (g) + 2\ H_2O\ (g)$$

**the observed rate law is**

$$\frac{d[N_2]}{dt} = k_{obs}[H_2][NO]^2$$

**(8 points total)**

**a) The following mechanism has been proposed.**

$$H_2\ (g) + NO\ (g) + NO\ (g) \overset{k_1}{\rightarrow} N_2O\ (g) + H_2O\ (g)$$

$$H_2\ (g) + N_2O\ (g) \overset{k_2}{\rightarrow} N_2\ (g) + H_2O\ (g)$$

**Under which circumstances does this mechanism yield the observed rate law? And which expression do you obtain for $k_{obs}$ under these circumstances? (3 points)**

**b) A different mechanism has been proposed as well.**

$$NO\ (g) + NO\ (g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2\ (g)$$

$$H_2\ (g) + N_2O_2\ (g) \overset{k_2}{\rightarrow} N_2O\ (g) + H_2O\ (g)$$

$$H_2\ (g) + N_2O\ (g) \overset{k_3}{\rightarrow} N_2\ (g) + H_2O\ (g)$$

**Under which circumstances does this mechanism yield the observed rate law? And which expression do you obtain for $k_{obs}$ under these circumstances? (4 points)**

**c) Which of the two proposed mechanisms is more likely to be correct? Explain your reasoning. (1 point)**

**2) Describe an algorithm (no need to write proper code) that uses the stochastic method to simulate an enzymatically catalyzed reaction that follows the Michaelis-Menten mechanism. (8 points)**

**3) Consider the following reversible reaction:**

$$\mathbf{A + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,X}$$

**(8 points total)**

**a) Derive an expression for the relative concentrations of A and X at equilibrium. (1 point)**

**b) Assume that for a given set of conditions, the concentration of A barely changes over the course of the reaction, so that it can be treated as constant to good approximation. Using this approximation, calculate the concentration of X as a function of time. (6 points)**

**c) Under which circumstances is the approximation justified that the concentration of A is constant? (1 point)**

**4) Transition State Theory. (11 points total)**

**a) The contour plot below shows the potential energy surface of the reaction**

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

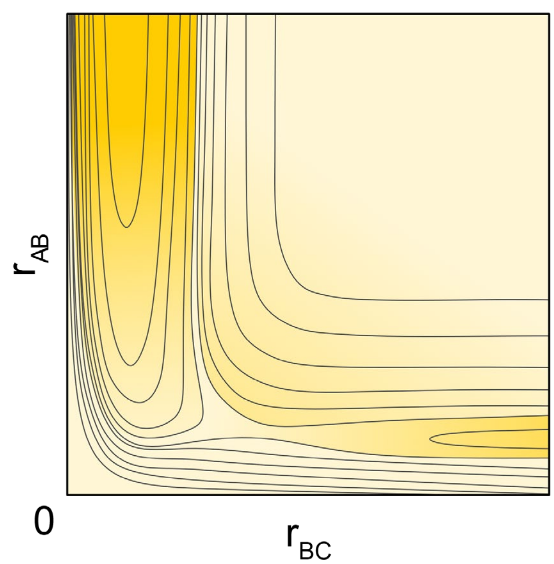
**with the reaction constrained to a linear geometry. Here, A, B, and C are atoms, and $r_{AB}$ and $r_{BC}$ are interatomic distances.**

**Draw the minimum energy path of the reaction and indicate where the reactants and the products are located.**

**Draw the path on the potential energy surface that the system follows as the reactant AB molecule undergoes bond vibrations (without the distance to the C atom changing).**

**Indicate the transition state of the reaction and provide a definition of the transition state. At the transition state, what are the relative distances of the three atoms?**

**(5 points)**



**b) Use the transition state theory to estimate the rate constant of the reaction**

$$F + H_2 \rightarrow HF + H$$

**at 300 K.**

**The activation energy of the reaction is 1.7 kJ/mol. A flurine atom has a mass of 19 amu, and a hydrogen atom of 1 amu. The $H_2$ molecule has a rotational constant of B = 61.6 $cm^{-1}$ and a vibrational frequency corresponding to $\nu$ = 4395 $cm^{-1}$. The transition state has a rotational constant of $B^{\ddagger}$ = 2.3 $cm^{-1}$ and vibrational frequencies corresponding to $\nu_{stretch}$ = 4007 $cm^{-1}$, $\nu_{bend,1}$ = 392 $cm^{-1}$, and $\nu_{bend,2}$ = 397 $cm^{-1}$. (6 points)**

**5) The reaction cross section of a bimolecular gas-phase reaction has the following dependence on the collision energy $E$**

$$\boldsymbol{\sigma_R(E) = \begin{cases} 0 & \text{for } E < E^* \\ \pi d^2 p \dfrac{\sqrt{E - E^*}}{E} \sqrt{E^*} & \text{for } E \geq E^* \end{cases}}$$

**where $\pi d^2$ is the hard-spheres collision cross section, $p$ is a steric factor, and $E^*$ is a threshold energy, below which the reaction cross section drops to zero.**

**Determine the thermal rate coefficient $k(T)$. (7 points)**

**6) Derive the relative speed distribution of two particles in a two-dimensional gas. In order to do so, follow these steps. First write down the combined velocity distribution of two particles, then transform into center of mass coordinates. Integrate out the center-of-mass part to obtain the distribution of the relative velocities. Finally, transform into polar coordinates and integrate out the angular part to obtain the relative speed distribution. (8 points)**