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

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

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)

In matrix form, the coupled differential equations for the concentrations a_1 and a_2 can be written as

$$\dot{\boldsymbol{a}} = \boldsymbol{M}\boldsymbol{a}$$

$$\begin{pmatrix} \dot{a_1} \\ \dot{a_2} \end{pmatrix} = \begin{pmatrix} -k_1 & k_{-1} \\ k_1 & -k_{-1} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

(2 points).

Using the matrix method, the concentrations are then obtained as

$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \boldsymbol{X} \begin{pmatrix} c_1 e^{\lambda_1 t} \\ c_2 e^{\lambda_2 t} \end{pmatrix}$$

Where $\boldsymbol{X}$ is the matrix of the eigenvectors of $\boldsymbol{M}$, λ_1 and λ_2 are the corresponding eigenvalues, and c_1 and c_2 are coefficients to be determined from the boundary conditions. (2 points)

We first find the eigenvalues of $\boldsymbol{M}$. For the characteristic equation, we find

$$\begin{vmatrix} -k_1 - \lambda & k_{-1} \\ k_1 & -k_{-1} - \lambda \end{vmatrix} = 0$$

so that $\lambda_1 = 0$ and $\lambda_2 = -(k_1 + k_{-1})$. (2 points)

We find the corresponding eigenvector $\begin{pmatrix} x_{i,1} \\ x_{i,2} \end{pmatrix}$ from the equations

$$\begin{pmatrix} -k_1 - \lambda_i & k_{-1} \\ k_1 & -k_{-1} - \lambda_i \end{pmatrix} \begin{pmatrix} x_{i,1} \\ x_{i,2} \end{pmatrix} = 0$$

And obtain

$$\begin{pmatrix} x_{1,1} \\ x_{1,2} \end{pmatrix} = \begin{pmatrix} 1 \\ \frac{k_1}{k_{-1}} \end{pmatrix}$$

$$\begin{pmatrix} x_{2,1} \\ x_{2,2} \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

(4 points).

We apply the boundary conditions in order to determine the coefficients c_1 and c_2. At time $t = 0$, we find

$$\boldsymbol{a}(\boldsymbol{t} = \boldsymbol{0}) = \begin{pmatrix} a_{1,0} \\ 0 \end{pmatrix} = \boldsymbol{X} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ \frac{k_1}{k_{-1}} & -1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

where $a_{1,0}$ is the initial concentration of A (2 points)

which leads to

$$c_1 = \frac{a_{1,0}}{1 + \frac{k_1}{k_{-1}}}$$

$$c_2 = \frac{a_{1,0}}{1 + \frac{k_{-1}}{k_1}}$$

(2 points).

Finally, we obtain for the concetrations

$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \boldsymbol{X} \begin{pmatrix} c_1 e^{\lambda_1 t} \\ c_2 e^{\lambda_2 t} \end{pmatrix} = a_{1,0} \begin{pmatrix} 1 & 1 \\ \frac{k_1}{k_{-1}} & -1 \end{pmatrix} \begin{pmatrix} \frac{k_{-1}}{k_1 + k_{-1}} \\ \frac{k_1}{k_1 + k_{-1}} e^{-(k_1 + k_{-1})t} \end{pmatrix}$$

$$= a_{1,0} \begin{pmatrix} \frac{k_{-1} + k_1 e^{-(k_1 + k_{-1})t}}{k_1 + k_{-1}} \\ \frac{k_1}{k_1 + k_{-1}} \left(1 - e^{-(k_1 + k_{-1})t}\right) \end{pmatrix}$$

(4 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)

Reactions involving electron transfer can proceed by the so-called harpoon mechanism. Since electron transfer can occur over a distance that is larger than the collision cross sections of the reaction partners would suggest, this leads to a steric factor that is larger than one.

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)

We can estimate that electron transfer occurs at a distance r at which the energy cost of transferring an electron is compensated by the Coulomb energy of the ion pair that is created in the process, *i.e.*

$$E_I - E_{ea} - \frac{e^2}{4\pi\epsilon_0 r} = 0$$

$$r = \frac{e^2}{4\pi\epsilon_0 (E_I - E_{ea})} \approx 817\ \mathrm{pm}$$

We obtain the steric factor

$$p = \frac{\sigma_{\mathrm{exp}}}{\sigma_{\mathrm{theor}}} = \frac{\pi r^2}{\pi d^2_{\mathrm{nearest\ approach}}} \approx 4.17$$

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)

The rate equation is

$$v = -\frac{1}{2}\frac{d[\mathrm{I}]}{dt} = k\,[\mathrm{I}]^2\,[\mathrm{Ar}]$$

(2 points)

which we can integrate ($[\mathrm{Ar}] = const$)

$$\int_{[\mathrm{I}]_0}^{[\mathrm{I}]} \frac{d[\mathrm{I}]}{[\mathrm{I}]^2} = -2k[\mathrm{Ar}] \int_0^t dt$$

to obtain

$$t = \frac{\frac{1}{[\mathrm{I}]} - \frac{1}{[\mathrm{I}]_0}}{2k[\mathrm{Ar}]}$$

(1 point)

With

$$[\mathrm{I}]\left(t = t_{\frac{1}{2}}\right) = \frac{1}{2}\,[\mathrm{I}]_0$$

we find

$$t_{\frac{1}{2}} = \frac{1}{2k[\mathrm{Ar}][\mathrm{I}]_0}$$

(1 point)

With [Ar] = 1*10^{-2} mol/l, $[I]_0$ = 6*10^{-5} mol/l and $t_{\frac{1}{2},298\ \mathrm{K}}$ = 238 µs, we obtain a rate constant

$$k_{298\ \mathrm{K}} = \frac{1}{2t_{\frac{1}{2},298\ \mathrm{K}}[\mathrm{Ar}][\mathrm{I}]_0} = 3.50 \cdot 10^9 \frac{l^2}{mol^2 s}$$

(2 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)

For $t_{\frac{1}{2},350\ \mathrm{K}}$ = 342 µs, the rate constant is

$$k_{350\ \mathrm{K}} = \frac{1}{2t_{\frac{1}{2},350\ \mathrm{K}}[\mathrm{Ar}][\mathrm{I}]_0} = 2.44 \frac{l^2}{mol^2 s}$$

(1 point)

With the Arrhenius equation

$$k = A\, e^{-\frac{E_A}{RT}}$$

it follows that

$$E_A = \frac{\ln(\frac{k_{350\ \mathrm{K}}}{k_{298\ \mathrm{K}}})\ R}{\frac{1}{298\ \mathrm{K}} - \frac{1}{350\ \mathrm{K}}} = -6.05 \frac{kJ}{mol}$$

(3 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.

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

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

$$\mathbf{IAr + I \xrightarrow{k_2} I_2 + Ar}$$

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)

The rate equation for the pre-equilibrium is

$$v = \frac{d[\mathrm{I_2}]}{dt} = k_2 K [\mathrm{I}]^2 [\mathrm{Ar}]$$

with

$$K = \frac{k_1}{k_{-1}}$$

(3 points)

We thus obtain an effective rate constant for the reaction

$$k_{\mathrm{effective}} = k_2 K$$

(1 point)

The temperature dependence of $k_2 = A e^{-\frac{E_a}{RT}} = A$ is small. In contrast, the equilibrium is increasingly shifted to the reactant side with increasing temperature since $K = e^{-\frac{\Delta \mathrm{G}^0}{RT}}$ and $\Delta \mathrm{G}^0$ is negative. This leads to a negative activation energy.

$$E_a = RT^2 \frac{d\, lnk}{dT} \approx \Delta \mathrm{G}^0$$

(2 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)

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_2} \text{products}$$

(3 points)

We apply the steady-state approximation to the activate species A^*, so that

$$\frac{d[\mathrm{A}^*]}{dt} = k_1[\mathrm{A}][\mathrm{M}] - k_{-1}[\mathrm{A}^*][\mathrm{M}] - k_2[\mathrm{A}^*] \overset{!}{=} 0$$

$$[\mathrm{A}^*] = \frac{k_1[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}$$

$$k_{uni}[\mathrm{A}] = k_2[\mathrm{A}^*] = \frac{k_1 k_2[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}$$

$$k_{uni} = \frac{k_1 k_2[\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}$$

(3 points)

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

The reactive hard spheres model does not consider the internal energy of the molecule, but only translational energy that is available to drive a reaction. It therfore underestimates the rate constant. In contrast, the Hinshelwood theory takes into account that the molecule has energy stored in its vibrational degrees of freedom, even before an activating collision occurs.

(2 points)

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

Energized molecules are in a pre-equilibrium with the ground-state molecules, so that $\frac{k_1}{k_{-1}} = \frac{[A^*]}{[A]}$. The deactivation rate is taken to be the collision rate $k_{-1} = \sigma_{AM}\langle u_{AM}\rangle$. The fraction of activated molecules is then calculated as the probability that a molecule has an energy larger than the threshold energy E_0 of the reaction $\frac{k_1}{k_{-1}} = \frac{[A^*]}{[A]} = \int_{E_0}^{\infty} P(E)dE$. That probability is then calculated from a Boltzmann distribution.

(4 points)

5) Describe an algorithm (no need to write proper code) to simulate the reaction $2\mathbf{A} \rightarrow$ 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.

We know that reactions between two A molecules out of a total of n occur at the rate

$$R = -kn^2$$

In fact, we have made a small mistake here when we did not consider that a molecule cannot react with itself. Therefore, more accurately,

$$R = -kn(n-1)$$

The probability for a reaction to occur in a short time interval $\Delta\tau$ is therefore

$$kn(n-1)\Delta\tau$$

and the probability for no reaction is

$$1 - kn(n-1)\Delta\tau$$

We calculate the probability $P_n(\tau + \Delta\tau)$ that at time $\tau + \Delta\tau$, all n molecules have not reacted. This is the product of the probability $P_n(\tau)$ that at time τ, none had reacted and the probability that no reaction occurs in the time interval $\Delta\tau$.

$$P_n(\tau + \Delta\tau) = P_n(\tau)(1 - kn(n-1)\Delta\tau)$$

We thus obtain a differential equation for P_n

$$\frac{dP_n}{d\tau} = -kn(n-1)P_n$$

which upon integration gives an expression for the probability that for n molecules of A, none have reacted after a given time τ

$$P_n = e^{-kn(n-1)\tau}$$

(4 points)

We initially set the number of molecules to $n = n_0$ and the time to $t = 0$. We then have the computer calculate a random number r in the interval between 0 and 1 and set

$$r = P_n = e^{-kn(n-1)\tau}$$

so that

$$\tau = -\frac{\ln(r)}{kn(n-1)}$$

This way, we randomly determine the time interval τ at which the next reaction occurs. We increment the time by this value τ and reduce the number of molecules n by two. Then we repeat.

(4 points)

The following matlab code will do the trick.

```
% stochastic method for solving second order rate equation

for l = 1:6
    set(figure(l) ,'WindowStyle','docked'); clf;
end
clc; clearvars;

n0 = 1e3; % number of molecules at t0
k = 1; % bimolecular rate constant

t = 0; % vector of time steps
n = n0; % vector of corresponding number of molecules n
while n > 0 % repeat until all molecules have reacted
    % calculate next time step dt from random number 'rand'
    dt = -log(rand)/k/(n(end)*(n(end)-1));
    t = [t; t(end) + dt]; % add new time step to vector t
    n = [n; n(end) - 2]; % add new number of molecules to vector n
end



figure(1); hold on
plot(t, n); % plot result of simulation
xlabel('time'); ylabel('number of molecules')

% for comparison, plot analytical solutions for second order rate equation (just for fun)
t = linspace(0, t(end), 1e4);
plot(t, n0./(1 + 2*n0*k*t))
plot(t, n0./(n0 + (1-n0)*exp(-2*k*t)))
```