Dynamics and Kinetics: Pool of problems for self-training

Note: Problems marked with "**X**" are not required for successfully passing the course.

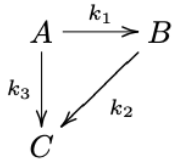
Problem 1

True or false?

a) For an elementary step the order of the reaction is equal to the molecularity of the reaction.
b) For an elementary step the order of the reaction is equal to the sum of the absolute values of the stoichiometric coefficients of the reactants.
c) The order of an overall reaction is equal to the molecularity of the reaction.
d) The molecularity of an overall reaction is equal to the sum of the absolute values of the stoichiometric coefficients of the reactants.
e) The order of a reaction can be determined from the units of the rate constant for the reaction.

Problem 2

Consider the following mechanism:



Using the sequential method find explicit expressions for $[A]_t$, $[B]_t$ and $[C]_t$ in terms of an initial concentration $[A]_0 = A_0$. Assume $[B]_0 = [C]_0 = 0$.

Problem 3

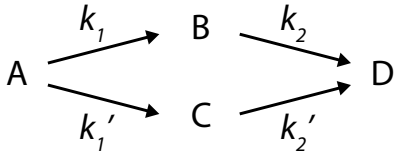
Consider an overall reversible composite reaction $A + B \rightleftharpoons E + F$ with a mechanism (in terms of elementary steps):

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + F$$

Find equilibrium constant for the overall reaction in terms of equilibrium constants K_1 and K_2 for the first and second reversible steps, respectively, and in terms of the rate constants of the elementary steps.

Problem 4

The following reaction sequence is given:



a) Derive the time-dependent concentrations of A, B, and C, assuming that all initial concentrations are zero apart from that of A.

b) Explain how one can simply calculate the time-dependent concentration of D from the results obtained above. Just describe the approach without actually calculating it.

X Problem 5

Use the matrix method to solve the reversible 1st order reaction

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

with $[B]_0 = 0$. What are the equilibrium concentrations of A and B?

X Problem 6

Describe an algorithm (no need to write proper code) to simulate the reaction $2A \rightarrow$ products with the stochastic method.

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 probability 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.

Problem 7

A sample of milk kept at 25°C is found to sour 40 times as rapidly as when it is kept at 4°C. Estimate the activation energy for the souring process.

Problem 8

The rate constant for the decomposition of a certain substance is $2.8\ 10^{-3}\ M^{-1}s^{-1}$ at 30°C and $1.38\ 10^{-2}\ M^{-1}s^{-1}$ at 50 °C. Compute the parameters in the Arrhenius equation for this reaction (i.e. E_a and A).

Problem 9

The initial rate of formation of O_2 by the action of an enzyme on a certain substrate has been measured for different substrate concentrations:

[S] (mol/l)	0.050	0.017	0.010	0.005	0.002
V_{O2} (mm^3/min)	16.6	12.4	10.1	6.6	3.3

Compute the Michaelis-Menten constant for this reaction.

Problem 10

Find the root mean square velocity v_{rms} for N_2 and H_2.

Problem 11: Measurement of vapor pressure by effusion

In the Knudsen method for measuring vapor pressure, a specimen of known quantity is heated in a container whose wall has a small hole. The loss of mass during a known period of time can be related to the pressure of saturated vapor and to the temperature.

a) Let Δm be the loss of mass through a circular hole of radius r during a time interval Δt. Express the vapor pressure p in terms of Δm and Δt.

b) The Knudsen method was used to determine the vapor pressure of germanium at 1000 °C. During a time interval of 7200s, the loss of mass through the hole of radius 0.5mm was 4.3 x 10^{-2}mg. What is the vapor pressure of germanium at 1000 °C? Assume that germanium forms a monatomic gas of molar mass 73g.

Problem 12: Arrhenius parameters by linear regression

The table below shows experimentally measured rate constants for the reaction

$$OH(g) + ClCH_2CH_2Cl(g) \longrightarrow H_2O(g) + ClCHCH_2Cl(g).$$

T (K)	292	296	321	333	343	363
K_{exp} (10^8 cm^3 /mol / s	1.24	1.32	1.81	2.08	2.29	2.76

Use linear regression in Mathematica or Maple to obtain the activation energy and the pre-exponential factor in Arrhenius equation for this reaction.

Problem 13

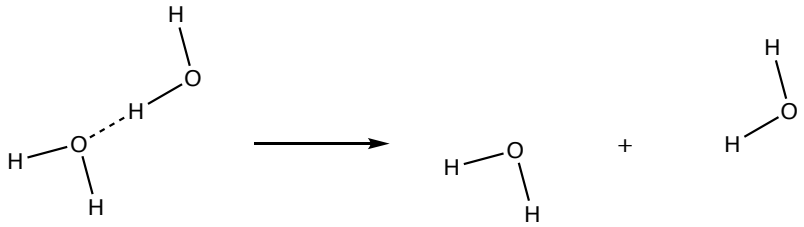
Suppose that the apparent first-order rate coefficient k^1 in the Lindemann-Christiansen theory of unimolecular reactions has reached 80% of the limiting value k^1_∞ at a concentration of 10^{-4} mol dm^{-3}. Compute k_2 / k_{-1}.

Problem 14

The apparent rate coefficient of a gas-phase reaction which follows the Lindemann mechanism is 2.5×10^{-4} s^{-1} at 1.3 kPa (partial pressure of the reactant) and 2.1×10^{-5} s^{-1} at 12 Pa. Compute the rate constant for the energization process in this mechanism (in units Pa^{-1} s^{-1}).

Problem 15: RRK theory

The water dimer is a hydrogen bonded complex that one can investigate in the gas phase. In a spectroscopic study, the water dimer is in its vibrational ground state. It is then illuminated with a laser and absorbs one photon of frequency $\nu_{\text{laser}} = 1.12 \cdot 10^{14}$ Hz and dissociates into two monomers.



The water dimer has a dissociation energy of 13.2 kJ/mol, and dissociation occurs without a barrier for the reverse reaction. The intermolecular mode of the dimer that leads to dissociation when it is excited has a frequency of $\nu_{\text{vib}} = 5.19 \cdot 10^{12}$ Hz.

Estimate the lifetime of the water dimer after laser excitation using RRK theory.

X Problem 16: Partition function of a spin

Electron spin can only have too values. If it is placed in a magnetic field, the corresponding energies are $\pm\mu_B B$ where μ_B is the Bohr magneton given by

$$\mu_B = \frac{eh}{2m_e} = 9.273 \times 10^{-24}\,\text{J T}^{-1}\,.$$

Compute the partition function of an electron spin and the populations of the two states in a magnetic field of 1 T at temperatures 4 K and 298 K.

X Problem 17: Isotope effect

Compute the isotope effect on the translational partition function (i.e., the ratio of translational partition functions) of molecules H_2 and D_2.

X Problem 18: Number of accessible states

Compute the number of vibrational and rotational states of an O_2 molecule which can be thermally occupied at 25℃. The spacing between two nearest vibrational levels is υ = 1580 cm^{-1} and the rotational constant B = 1.45 cm^{-1}.

X Problem 19: Translational, rotational, vibrational partition functions

Calculate the translational partition function for H_2 at 25 °C.

Calculate the rotational partition function of $H^{35}Cl$ at 25 °C. The bond length of $H^{35}Cl$ is 127.4 pm.

Calculate the vibrational partition function of I_2 at 25 °C. The vibrational constant of I_2 is 214.6 cm^{-1}.

Calculate the number of thermally accessible vibrational states at this temperature.