

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)

We rewrite the expression for the Lindemann rate constant

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

and calculate the difference between the measurements at two different pressures

$$\Delta \frac{1}{k_{uni}} = \frac{1}{k_1} \Delta \frac{1}{[M]} \text{ ma}$$

(2 points)

we find

$$k_1 = \frac{\Delta \frac{1}{[M]}}{\Delta \frac{1}{k_{uni}}}$$

(1 point)

and with the ideal gas law

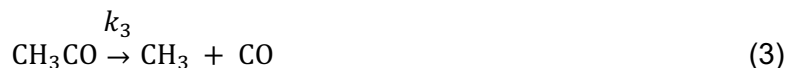
$$\frac{n}{V} = \frac{p}{RT}$$

we obtain

$$k_1 = \frac{\Delta \frac{1}{[M]}}{\Delta \frac{1}{k_{uni}}} = RT \frac{\Delta \frac{1}{p}}{\Delta \frac{1}{k_{uni}}} = 16.8 \left(\frac{\text{mol}}{\text{l}} \right)^{-1} \text{ s}^{-1}$$

(2 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)

- (1) initiation
- (2+3) propagation
- (4) termination

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)

$$\frac{d[\text{CO}]}{dt} = k_3[\text{CH}_3\text{CO}]$$

(1 point)

We make the steady-state approximation for CH_3 and for CH_3CO .

$$0 = \frac{d[\text{CH}_3\text{CO}]}{dt} = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}] - 2k_4[\text{CH}_3\text{CO}]^2$$

(1 point)

$$0 = \frac{d[\text{CH}_3]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}]$$

Adding both equations up gives

$$0 = k_1[\text{CH}_3\text{CHO}] - 2k_4[\text{CH}_3\text{CO}]^2$$

and

$$[\text{CH}_3\text{CO}] = \left(\frac{k_1}{2k_4}\right)^{\frac{1}{2}} [\text{CH}_3\text{CHO}]^{\frac{1}{2}}$$

(1 point)

so that

$$\frac{d[\text{CO}]}{dt} = k_3 \left(\frac{k_1}{2k_4}\right)^{\frac{1}{2}} [\text{CH}_3\text{CHO}]^{\frac{1}{2}}$$

(1 point)

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)

The kinetic chain length can be calculated as

$$\lambda = \frac{\text{rate of monomer consumption}}{\text{rate of activated center production}}$$

(1 point)

The rate at which monomers are consumed and converted into new CH_3 radicals that can participate in the propagation of the chain is equal to the rate at which CO is produced, therefore

$$\lambda = \frac{k_3 \left(\frac{k_1}{2k_4}\right)^{\frac{1}{2}} [\text{CH}_3\text{CO}]^{\frac{1}{2}}}{k_1 [\text{CH}_3\text{CHO}]} = k_3 \left(\frac{1}{2k_1k_4}\right)^{\frac{1}{2}} [\text{CH}_3\text{CO}]^{-\frac{1}{2}}$$

We obtain a similar expression if instead we use $k_2[\text{CH}_3][\text{CH}_3\text{CHO}]$ for the rate of monomer consumption and then make suitable substitutions using the steady state approximation for the radical intermediates. (Same points awarded.)

(2 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)

The observed rate constant for the production of CO is

$$k_{obs} = k_3 \left(\frac{k_1}{2k_4}\right)^{\frac{1}{2}}$$

(1 point)

With $k_1 = A_1 e^{-\frac{E_1}{kT}}$, $k_2 = A_1 e^{-\frac{E_2}{kT}}$, and $k_3 = A_3 e^{-\frac{E_3}{kT}}$

(1 point)

we find

$$k_{obs} = \frac{1}{\sqrt{2}} A_3 A_1^{\frac{1}{2}} A_4^{-\frac{1}{2}} e^{-\frac{E_3 + \frac{1}{2}E_1 - \frac{1}{2}E_4}{kT}}$$

so that

$$A_{obs} = \frac{1}{\sqrt{2}} A_3 A_1^{\frac{1}{2}} A_4^{-\frac{1}{2}}$$

and

$$E_{obs} = E_3 + \frac{1}{2}E_1 - \frac{1}{2}E_4$$

(2 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)

The modified rate law is

$$\frac{dn_A}{dt} = -2kn_A(n_A - 1)$$

(2 points)

$$\int_{n_{A,0}}^{n_A} \frac{dn_A}{n_A(n_A - 1)} = -2k \int_0^t dt$$

With the method of partial fractions

$$\int_{n_{A,0}}^{n_A} \frac{1}{(n_A - 1)} - \frac{1}{n_A} dn_A = -2kt$$

$$\frac{(n_A - 1)n_{A,0}}{n_A(n_{A,0} - 1)} = e^{-2kt}$$

$$n_A = \frac{n_{A,0}}{n_{A,0} + (1 - n_{A,0})e^{-2kt}}$$

(4 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)

If the solid or liquid is in equilibrium with the gas phase, the rate at which molecules detach from the surface (evaporate) and the rate at which molecules attach to the surface (condense) must be equal. **(1 point)**

Not every collision of a molecule with the surface of the solid or liquid will cause the molecule to stick to the surface. In other words, the molecule may have a sticking coefficient α smaller than one. **(1 point)**

The rate of condensation, which is equal to the rate of evaporation, then becomes

$$k_{\text{condensation}} = k_{\text{evaporation}} = \alpha \frac{p}{\sqrt{2\pi mk_B T}}$$

where p is the vapor pressure of the compound and m its mass.

(1 point)

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/cm³.) (4 points)

We assume that at such low temperature, every collision with the surface leads the molecule to stick, *i.e.* the sticking coefficient is $\alpha = 1$. (1 point)

For the rate of evaporation, we therefore obtain

$$k_{\text{evaporation}} = 1.24 \cdot 10^{17} \text{ s}^{-1} \text{ m}^{-2}$$

(1 point)

The evaporated thickness d of the ice sheet within a time interval Δt is

$$d = \frac{k \Delta t m}{\rho}$$

and

$$\Delta t = \frac{d \rho}{k m} = 2.48 \cdot 10^4 \text{ s}$$

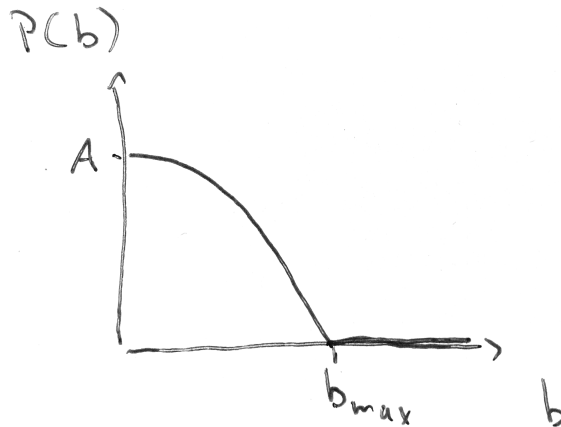
(2 points)

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)

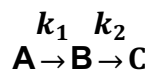
We obtain the reaction cross section σ_r from the integral **(2 points)**

$$\sigma_r = \int_0^{b_{max}} 2\pi b \cdot A \cos\left(\frac{\pi}{2} \cdot \frac{b}{b_{max}}\right) db$$

With partial integration, we find **(3 points)**

$$\begin{aligned} \sigma_r &= \frac{2b_{max}}{\pi} \sin\left(\frac{\pi}{2} \cdot \frac{b}{b_{max}}\right) b \Big|_0^{b_{max}} + \left(\frac{2b_{max}}{\pi}\right)^2 \cos\left(\frac{\pi}{2} \cdot \frac{b}{b_{max}}\right) \Big|_0^{b_{max}} \\ &= 4Ab_{max}^2 \left(1 - \frac{2}{\pi}\right) \end{aligned}$$

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)

We know that the decay of A is described by

$$[A] = [A]_0 e^{-k_1 t'}$$

(1 point)

Therefore, the quantity $d[B]$ that is being created at any given point in time during a time interval dt' is given by

$$d[B(t')] = -\frac{d[A(t')]}{dt'} dt' = k_1 [A]_0 e^{-k_1 t'} dt'$$

(2 points)

A small quantity of B that has been created at time t' decays according to

$$d[B(t)] = d[B(t')] e^{-k_2(t-t')}$$

(2 points)

The total concentration of B can therefore be described by the integral

$$[B(t)] = \int_0^t d[B(t)] = \int_0^t k_1 [A]_0 e^{-k_1 t'} e^{-k_2(t-t')} dt'$$

(2 points)

which after integration yields the same result that we obtained in class.

$$[B(t)] = \frac{k_1[A]_0}{k_1 - k_2} e^{-k_2 t} (1 - e^{-(k_1 - k_2)t}) = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

(2 points)

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

The method can only be applied if the response of the system is linear in the concentration of the intermediate. In other words, the total rate of decay of the intermediate is linear in the concentration of the intermediate. And of course, we have to know the time-dependence of the reaction of the intermediate. The method will also not work if there is a back reaction of the intermediate to the reactants or another intermediate that precedes it in the reaction sequence.