Chemical Reaction Engineering - Exam Questions

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Question 1

In an indirectly cooled CSTR with a heat exchange surface of $F_W = 7\,\text{m}^2$, a strongly exothermic irreversible 1st order rection takes place. Initial investigations showed that the heat exchange surface must be increased by installing cooling coils inside the reactor so that the amount of heat produced can be sufficiently dissipated. The reactant is to be fed into the CSTR at a concentration of $1600\,\text{mol}\,\text{m}^{-3}$ with a volume flow of $2.300\,\text{m}^3\,\text{h}^{-1}$. The temperature of the feed mixture shall be $T_a = 70\,°\text{C}$. In the steady state, the operating temperature should be $118\,°\text{C}$. The average coolant temperature T_K should be $95\,°\text{C}$. With the selected reaction conditions and operating parameters, a conversion of the reactant of $98\,\%$ can be achieved.

Further material data: Heat transfer coefficient $k_W = 4.750 \times 10^5\,\text{J}\,\text{m}^{-2}\,\text{h}^{-1}\,\text{K}^{-1}$, reaction enthalpy $\Delta H = -195\,\text{kJ}\,\text{mol}^{-1}$, mean density $\rho = 1800\,\text{kg}\,\text{m}^{-3}$ and mean specific heat capacity $c_p = 2200\,\text{J}\,\text{K}^{-1}\,\text{kg}^{-1}$.

a) Determine the area that must be provided for additional heat dissipation by installing cooling coils. Establish the heat balance of the statinary CSTR. What is the total area for heat exchange.

b) Give the relative cooling intensity (Stanton number) for the steady state. Also calculate the adiabatic temperature increase.

The heat balance of the CSTR:

$$T - T_a + St \cdot (T - T_k) = \Delta T_{ad} \cdot X \tag{1}$$

The adiabatic temperature increase can be calculated by:

$$\Delta T_{ad} = \frac{-\Delta H \cdot c_{A0}}{-\nu_A \cdot \rho \cdot c_p} = 78.396\,\text{K} \tag{2}$$

By rearranging Eq. 1 the Stanton number can be calculated

$$St = \frac{T_a - T + \Delta T_{ad} \cdot X}{T - T_k} = 1.253 \tag{3}$$

The heat exchange surface still to be installed can be calculated according to:

$$F_{W,add} = \frac{St \cdot \dot{V} \cdot \rho \cdot c_p}{k_W} - F_W = 17.154\,\text{m}^2 \tag{4}$$

Question 2

During the execution of a radical polymerization at 125 °C with an initial initiator concentration of $c_{I0} = 0.001\,\text{mol}\,\text{L}^{-1}$, the following kinetic data were determined: The rate constant of the initiator decomposition reaction $k_z = 1.090 \times 10^{-11}\,\text{s}^{-1}$, the gross rate constant $k_{Br} = 3.090 \times 10^{-3}\,\text{L}^{1/2}\,\text{mol}^{-1/2}\,\text{s}^{-1}$

a) Calculate the polymerisation time until a monomer conversion of 70 % is reached. Write down the formulae you used for this calculation.

The logarithmic ratio of the monomer concentration to the initial concentration can be calculated by (CRE exercise 6):

$$\ln\left(\frac{c_M}{c_{M0}}\right) = \frac{2 \cdot k_{Br} \cdot \sqrt{c_{I0}}}{k_z} \cdot \left[\exp\left(\frac{-k_z \cdot t}{2}\right) - 1\right] \tag{1}$$
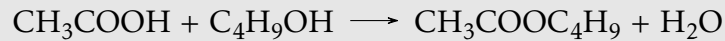
The conversion in constant reaction volume is defined by:

$$X = \frac{c_{M0} - c_M}{c_{M0}} \implies \frac{c_M}{c_{M0}} = 1 - X \tag{2}$$

Thus Eq. 1 can be rearranged to:

$$\ln\left(1 - X\right) = \frac{2 \cdot k_{Br} \cdot \sqrt{c_{I0}}}{k_z} \cdot \left[\exp\left(\frac{-k_z \cdot t}{2}\right) - 1\right]$$

$$\implies t = -\frac{2}{k_z} \cdot \ln\left[\frac{\ln(1 - X) \cdot k_z}{2 \cdot k_{Br} \cdot \sqrt{c_{I0}}} + 1\right] = 12\,321.348\,\text{s} \tag{3}$$

Question 3

Butyl acetat shall be produced at $100\,°C$ from acetic acid and butanol with suphuric acid as catalyst.

$$CH_3COOH + C_4H_9OH \longrightarrow CH_3COOC_4H_9 + H_2O$$

After a first approximation, it is a 2nd order reaction:
$r = k \cdot c_A \cdot c_B$ with $k = 0.030\,L\,mol^{-1}\,min^{-1}$. The reaction should be terminated at a conversion of $X_A = 0.69$. The component react only in the desired form to form the butyl ester, so that the selectivity can be set to one. The production rate of the butyl ester should be $109\,kg\,h^{-1}$. The dead time of the batch reactor for filling, heating, cooling and emptying is $15\,min$ (additional to the reaction time). The initial concentration of acetic acid is $c_{A0} = 2\,mol\,L^{-1}$

a) Calculate the Damköhler number.

b) Calculate the residence time τ.

c) Calculate the reaction volume V_R of the batch reactor.

The Damköhler number for a batch reactor and a reaction of 2nd order can be calculated by:

$$Da = \int_0^{X_A} \frac{1}{\Phi(X)}\,dX = \int_0^{X_A} \frac{1}{(1-X)^2}\,dX \tag{1}$$
$$= \frac{X_A}{1-X_A} = 2.226$$

The residence time can be calculated by:

$$\tau = \frac{Da \cdot c_{A0}}{-\nu_A \cdot r_0} = \frac{Da}{-\nu_A \cdot k \cdot c_{A0}} = 37.097\,min \tag{2}$$

The selectivity towards the product can be calculated by:

$$S_P = \frac{n_P - n_{P0}}{n_{A0} - n_A} \cdot \frac{-\nu_A}{\nu_P} \implies n_{A0} - n_A = \frac{n_P - n_{P0}}{S_P} \cdot \frac{-\nu_A}{\nu_P} \tag{3}$$

The conversion of educt A is defined by:

$$X_A = \frac{n_{A0} - n_A}{n_{A0}} = \frac{n_P - n_{P0}}{n_{A0} \cdot S_P} \cdot \frac{-\nu_A}{\nu_P} \tag{4}$$
$$\implies n_P - n_{P0} = \frac{\nu_P}{-\nu_A} \cdot n_{A0} \cdot S_P \cdot X_A$$

The production rate is defined by:

$$\dot{n}_P = \frac{\dot{m}_P}{M_P} = \frac{n_P - n_{P0}}{\tau + t_d} = \frac{\nu_P}{-\nu_A} \cdot n_{A0} \cdot S_P \cdot X_A \cdot \frac{1}{\tau + t_d} \tag{5}$$

With $n_{A0} = c_{A0} \cdot V_R$ the reactor volume V_R can be calculated by rearranging Eq. 5:

$$V_R = \frac{\dot{m}_P}{M_P} \cdot \frac{-\nu_A}{\nu_P} \cdot \frac{\tau + t_d}{c_{A0} \cdot S_P \cdot X_A} = 591.220\,L \tag{6}$$

Question 4

For a zero order reaction, the following applies: $X = Da$

    a) What conversion do you expect with $Da = 2$

    b) Is the Damköhler number at this reaction order depended on the temperature?

    c) How do you explain this? Use equations for the explanation!

The conversion can only be $100\,\%$ even if $Da = 2$. The higher Damköhler number can be attributed to the temperature.

$$Da = \frac{-\nu_A \cdot r_0 \cdot \tau}{c_{A0}} \tag{1}$$

The reaction rate r_0 at the begin of the reaction ($X = 0$):

$$r_0 = k(T) = k_\infty \cdot \exp\left(\frac{-E_A}{R \cdot T}\right) \tag{2}$$
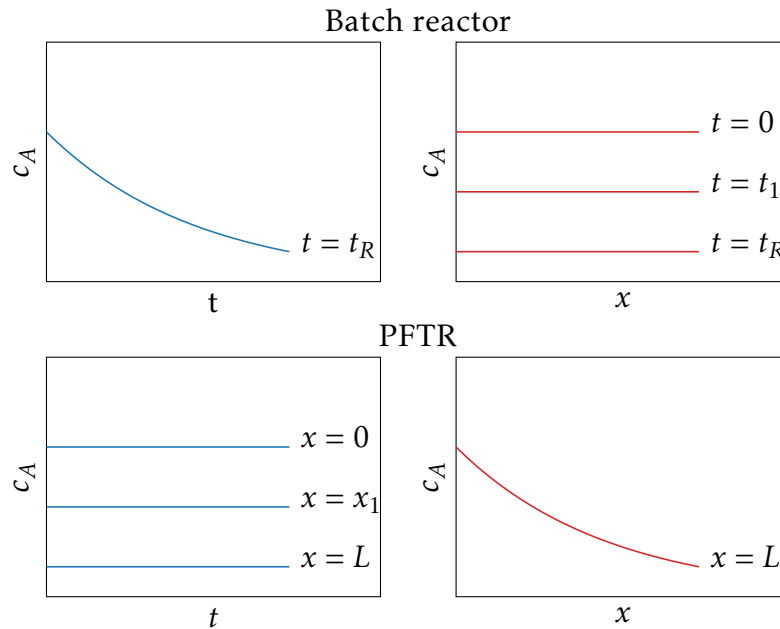
Question 5

For an exothermic reaction, draw the expected course of reaction of the educt A (c_A) as a functiuon of time (t) and location (x) espacially for the measurement location z_0 and z_1. The reaction proceeds according to the scheme
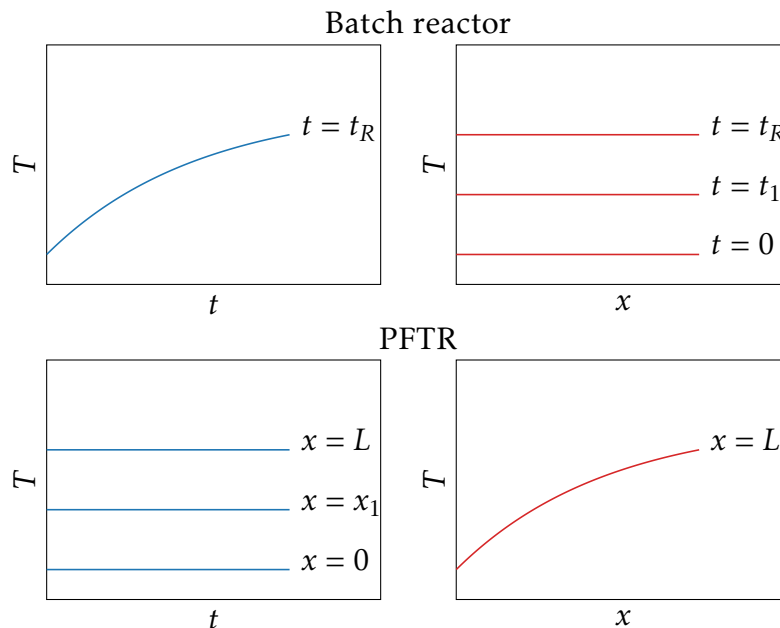
$$A \longrightarrow P$$

No cooling and the reactors behave ideal.

Time and location dependence on concentration:

Batch reactor

PFTR

Time and location dependence on temperature:

Batch reactor

PFTR

Question 6

A heterogeneously catalysed reaction of two gaseous reactants (A + B) to the product C shows **Langmuir-Hinshelwood** kinetics. In an experiment, the partial pressure of component B is kept constant, while that of component A is steadily increased. Describe the course of the reaction rate and explain it using a suitable formula. For this purpose, assign the areas of the curve exactly to the explained cases (in the diagram)!

The Langmuir-Hinshelwood model states that both reactants are chemisorpt on the surface of the catalyst.

$$A_{ch} + B_{ch} \longrightarrow C$$

The reaction rate can be described by:

$$r = k \cdot \Theta_A \cdot \Theta_B \tag{1}$$

The coverage Θ can be calculated by:

$$\Theta_A = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A + K_B \cdot p_B} \qquad \Theta_B = \frac{K_B \cdot p_B}{1 + K_A \cdot p_A + K_B \cdot p_B} \tag{2}$$

Thus the reaction rate can be rearranged to:

$$r = k \cdot \frac{K_A \cdot p_A \cdot K_B \cdot p_B}{(1 + K_A \cdot p_A + K_B \cdot p_B)^2} \tag{3}$$
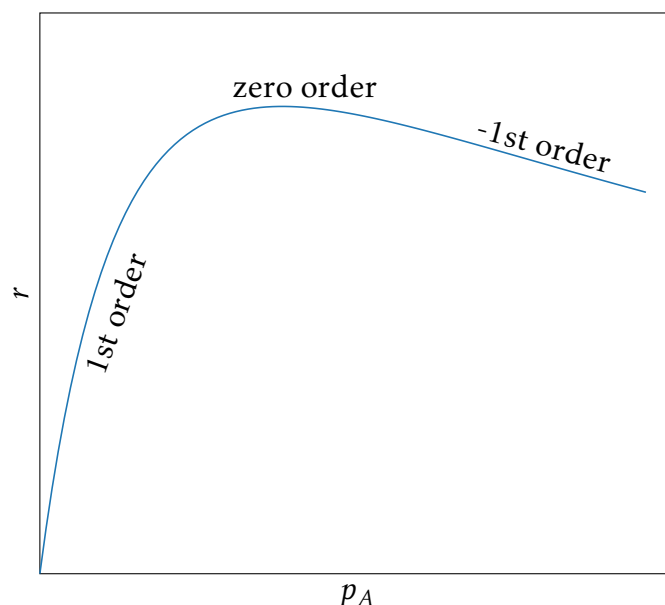
In the case of a low partial pressure of A ($K_A \cdot p_A \ll 1 + K_B \cdot p_B$), Eq. 3 can be simplified to:

$$r = k \cdot \frac{K_A \cdot K_B \cdot p_B}{(1 + K_B \cdot p_B)^2} \cdot p_A = k' \cdot p_A \tag{4}$$

The rate behaves 1st order in p_A. In the case of a heigh partial pressure of A ($K_A \cdot p_A \gg 1 + K_B \cdot p_B$), Eq. 3 can be simplified to:

$$r = k \cdot \frac{K_B \cdot p_B}{K_A} \cdot \frac{1}{p_A} \tag{5}$$

The rate behaves -1st order in p_A.

Question 7

True or false.

a) You investigate the product formation rate in a reaction of a dissolved substance with gaseous hydrogen. Which quantities (see table) are important for the kinetics.

b) An exothermic reaction is carried out adiabatically in a CSTR. Which variables are important when calculating the temperature T in the reactor?

c) Mass transport limitation in heterogeneous catalysis: pore diffusion and film diffusion

d) Free radical polymerization: Rate the following statements as true or false. (The statements refere exclusivly to ideal kinetics.)

Task a)

Quantity	✓ or –
Mass transfer coefficient	✓
Free enthalpy of formation	–
Reaction entropy	–
Frequency factor	✓
Activation energy	✓
Rate constant	✓
Reaction enthalpy	–
Reaction order	✓
Temperature	✓
Equilibrium constant	–

Task b)

| Quantity	✓ or –
Stanton number	–
Conversion	✓
Inlet temperature of the reactant stream	✓
Reaction enthalpy	✓
Cooling surface	–
Density of the reaction mixture	✓
Temperature of the cooling medium	–
Heat capacity of the reaction mixture	✓
Heat transfer coefficient of the cooling jacket	–
Initial concentration of the reactant	✓

Task c)

Statement	$\checkmark$ or –
Mass transfer inhibition can be caused in parallel by pore and film diffusion.	$\checkmark$
In heterogeneous catalysis, a high value for the Thiele module is desirable	–
In the case of transport inhibition due to film diffusion, the effective velocity constant k_{eff} at very high temperatures is independent of temperature.	$\checkmark$
Pore diffusion-based transport limitations result in an effective activation energy that is half the value of the purely chemical activation energy.	$\checkmark$
An increase in the diffusion coefficient D_{eff} leads to lower pore efficiency	–

Task d)

Statement	$\checkmark$ or –
The Bodenstein principle states that the concentration of radicals ($R^\bullet$ and $P^\bullet$) equals zero.	–
The formation of radicals $R^\bullet$ from the initiator can only be done by UV radiation	–
The radical efficiency factor takes into account the proportion of the primarily formed radicals leading to polymerization	$\checkmark$
Termination reactions in radical polymerization are always disproportinations.	–
If the conversion of the monomer increases, the degree of polymerization decreases.	$\checkmark$

Question 8

The reaction of the gaseous educt A with a dissolved educt B to product C is carried out in a isothermally operated batch reactor.

$$A_g + B_{fl} \longrightarrow C_{fl}$$
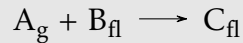
The reaction rate r was determined experimentally as a function of the concentration of B. The partial pressure of the gaseous educt A in the reactor was constant at $1500\,\text{hPa}$ in all experiments. The Henry coefficient for A in the solvent is $3.820 \times 10^{-3}\,\text{mmol}\,\text{L}^{-1}\,\text{Pa}^{-1}$.

a) Determine the rate constant k and the value for $\beta_L \cdot a$

b) What is the concentration of the gaseous educt A in the liquid under the respective reaction conditions? Calculate how large the concentration of A in the liquid is when no reaction takes place.

c) Compare the values of $\beta_L \cdot a$ and $k \cdot c_B$ for the highest stated concentration c_B. Is it possible to simplify the macrokinetic equation to determine the reaction rate r? Compare the given value r with the value determined after simplification.

The values for the concentration of B $c_{B,fl}$ and the reaction rate r are given in Tab. 1.

The rate of such a type of reaction is defined by:

$$r = k \cdot H_A \cdot \frac{a \cdot \beta_L}{a \cdot \beta_L + k \cdot c_{B,fl}} \cdot p_A \cdot c_{B,fl} \tag{1}$$

Rearranging Eq. 1 leads to:

$$\frac{1}{r} = \underbrace{\frac{1}{k \cdot H_A \cdot p_A}}_{\text{slope } m} \cdot \frac{1}{c_{B,fl}} + \underbrace{\frac{1}{H_A \cdot p_A \cdot a \cdot \beta_L}}_{\text{intercept } d} \tag{2}$$

The slope and intercept can be determined by a linear regression $r^{-1} = f\left(c_{B,fl}^{-1}\right)$.

Table 1: Given values and their reciprocal values

$c_{B,fl}/\text{mol}\,\text{L}^{-1}$	$r/\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$	$c_{B,fl}^{-1}/\text{L}\,\text{mol}^{-1}$	$r^{-1}/\text{L}\,\text{s}\,\text{mol}^{-1}$
0.025	4.54×10^{-4}	40.00	2204.26
0.150	1.58×10^{-3}	6.67	631.78
0.600	2.53×10^{-3}	1.67	395.91
1.200	2.80×10^{-3}	0.83	356.61
4.000	3.04×10^{-3}	0.25	329.11
6.000	3.08×10^{-3}	0.17	325.17
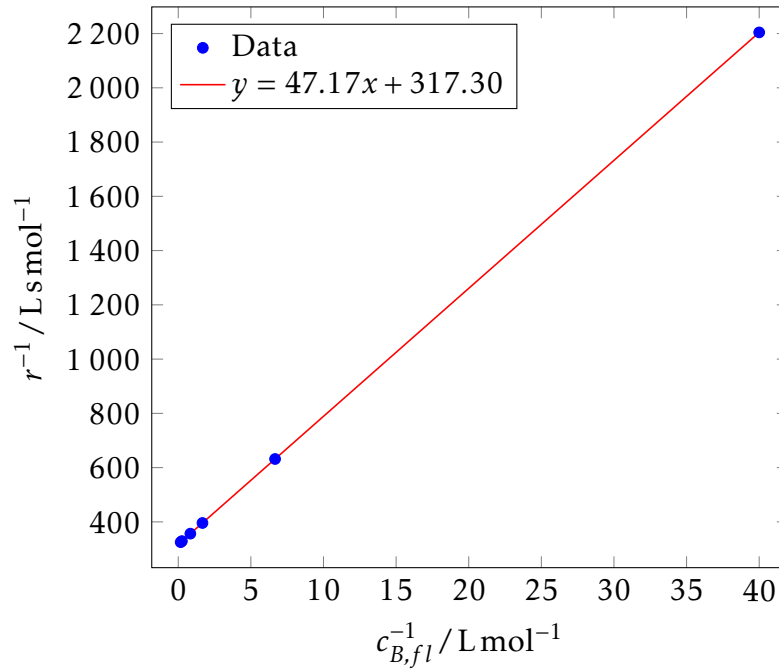
The rate constant k can be calculated by ($[m]$ = second):

$$k = \frac{1}{m \cdot H_A \cdot p_A} = 0.036 \, \text{L mol}^{-1} \, \text{s} \tag{3}$$

The product of the specific interface and the mass transport coefficient $a \cdot \beta_L$ can be calculated by ($[d] = \text{L s mol}^{-1}$):

$$a \cdot \beta_L = \frac{1}{d \cdot H_A \cdot p_A} = 0.0054 \, \text{s}^{-1} \tag{4}$$

The concentration of the gas A in the liquid can by rearranging the mass balance $\dot{n}_{diff} = \dot{n}_{rxn}$:

$$a \cdot \beta_L \cdot V_{fl} \cdot \left(H_A \cdot p_A - c_{A,fl}\right) = k \cdot V_{fl} \cdot c_{A,fl} \cdot c_{B,fl}$$
$$\implies c_{A,fl} = \frac{a \cdot \beta_L}{a \cdot \beta_L + k \cdot c_{B,fl}} \cdot p_A \cdot H_A \tag{5}$$

The concentration of A in liquid without a further reaction can be calculated by rearranging the mass balance $\dot{n}_{diff} = 0$:

$$a \cdot \beta_L \cdot V_{fl} \cdot \left(H_A \cdot p_A - c_{A,fl}\right) = 0$$
$$\implies c_{A,fl} = H_A \cdot p_A = 0.584 \, \text{mol L}^{-1} \tag{6}$$

In the case of a high concentration of B ($k \cdot c_{B,fl} \gg a \cdot \beta_L$) Eq. 1 simplifies to:

$$r = k \cdot a \cdot \beta_L \cdot H_A \cdot p_A \tag{7}$$

Question 9

During the execution of a radical polymerization at three different temperatures, the following data were collected for the respective course of the monomer concentration c_M. In addition the rate constants of the initiator decomposition reaction k_z determined in kinetic investigations performed previously are available. The initial initiator concentrations are also given $c_{I0} = 0.002\,\text{mol}\,\text{L}^{-1}$.

a) Determine the activation energies E_z and E_{Br} as well the corresponding pre-exponential factors $k_{z\infty}$ and $k_{Br\infty}$.

b) Calculate for the different temperatures the polymerization time until a monomer conversion of 75 % is reached.

$T/^\circ$C	k_z/s^{-1}
80	4.454×10^{-13}
100	6.010×10^{-12}
120	1.275×10^{-11}

The values for the time t and monomer concentration c_M are given in Tab. 1 to 3.

The logarithmic ratio of the monomer concentration to the initial concentration can be calculated by:

$$\ln\left(\frac{c_M}{c_{M0}}\right) = \underbrace{\frac{2 \cdot k_{Br} \cdot \sqrt{c_{I0}}}{k_z}}_{\text{slope } m} \cdot \left[\exp\left(\frac{-k_z \cdot t}{2}\right) - 1\right] \tag{1}$$

The slope can be determined by linear regression $\ln\left(\frac{c_M}{c_{M0}}\right) = f\left(\exp\left(\frac{-k_z \cdot t}{2}\right) - 1\right)$. The gross rate constant can be calculated by:

$$k_{Br} = \frac{m \cdot k_z}{2 \cdot \sqrt{c_{I0}}} \tag{2}$$

Tab. 1 to 3 contain the results of the calculation of the slope and the logarithmic ratio

Table 1: At 80 °C

| t/s	$c_M/\text{mol}\,\text{L}^{-1}$	$\ln\left(\frac{c_M}{c_{M0}}\right)$	$\exp\left(\frac{-k_z \cdot t}{2}\right) - 1$
0	1.50	0.00	0.00
3000	1.45	-3.39×10^{-2}	-6.68×10^{-10}
6000	1.40	-6.90×10^{-2}	-1.34×10^{-9}
9000	1.35	-1.05×10^{-1}	-2.00×10^{-9}
12 000	1.30	-1.43×10^{-1}	-2.67×10^{-9}
18 000	1.20	-2.23×10^{-1}	-4.01×10^{-9}

Table 2: At 100 °C

t/s	$c_M/\text{mol L}^{-1}$	$\ln\left(\frac{c_M}{c_{M0}}\right)$	$\exp\left(\frac{-k_z \cdot t}{2}\right) - 1$
0	1.50	0.00	0.00
3000	1.30	-1.43×10^{-1}	-9.01×10^{-9}
6000	1.10	-3.10×10^{-1}	-1.80×10^{-8}
9000	0.95	-4.57×10^{-1}	-2.70×10^{-8}
12 000	0.80	-6.29×10^{-1}	-3.61×10^{-8}
18 000	0.60	-9.16×10^{-1}	-5.41×10^{-8}

Table 3: At 120 °C

t/s	$c_M/\text{mol L}^{-1}$	$\ln\left(\frac{c_M}{c_{M0}}\right)$	$\exp\left(\frac{-k_z \cdot t}{2}\right) - 1$
0	1.50	0.00	0.00
3000	0.90	-0.51	-1.91×10^{-8}
6000	0.55	-1.00	-3.82×10^{-8}
9000	0.30	-1.61	-5.74×10^{-8}
12 000	0.20	-2.01	-7.65×10^{-8}
18 000	0.07	-3.06	-1.15×10^{-7}

Determined regression lines:

$T = 80\,°\text{C}$

$T = 100\,°\text{C}$

$T = 120\,°\text{C}$
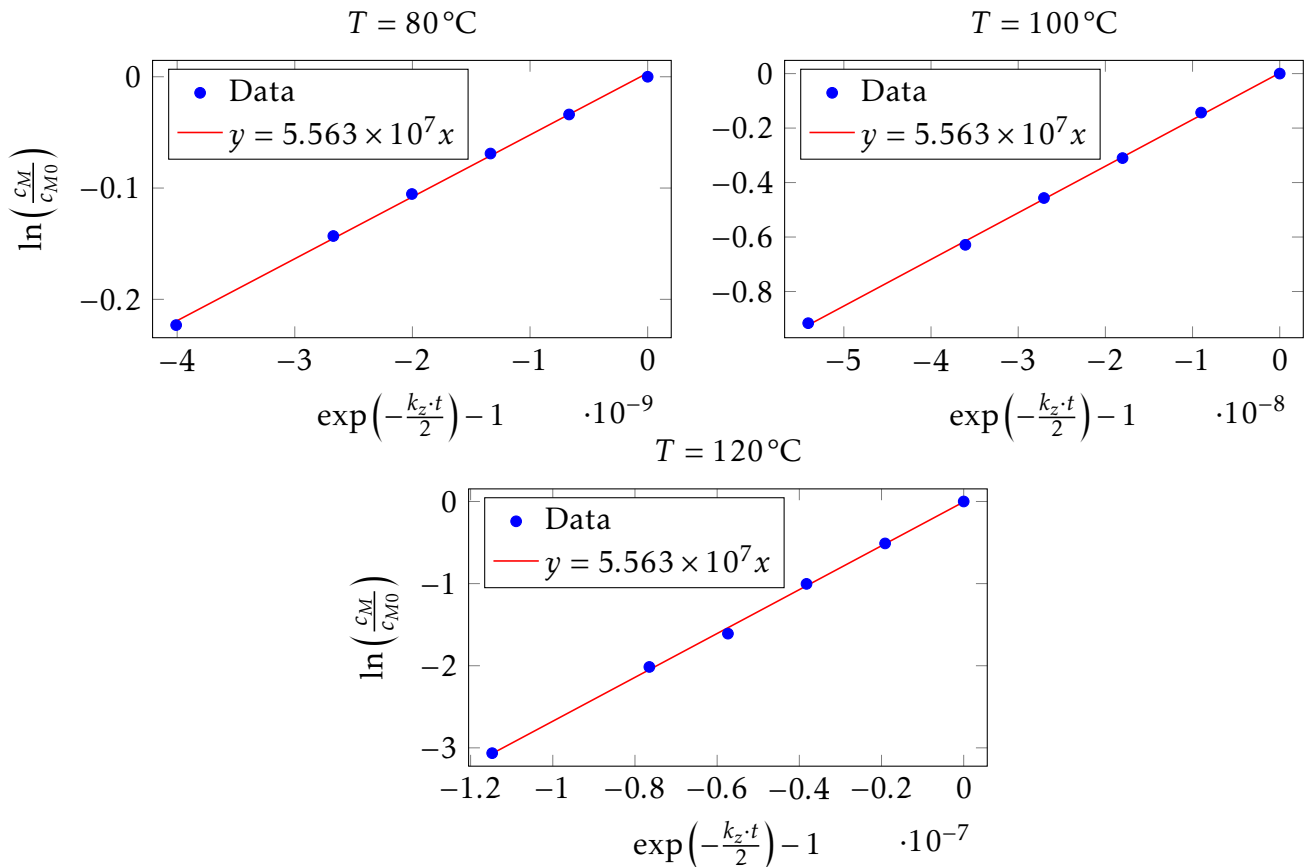
The gross rate constants from Eq. 2:

Table 4: Gross reaction constants.

$T/^\circ C$	$k_{Br}/\text{L}^{1/2}\,\text{mol}^{-1/2}\,\text{s}^{-1}$
80	2.770×10^{-4}
100	3.738×10^{-3}
120	7.930×10^{-3}

The activation energy for the gross reaction reaction can be calculated by (temperature in kelvin):

$$E_{Br} = R \cdot \ln\left[\frac{k_{Br}(T_1)}{k_{Br}(T_2)}\right] \cdot \frac{T_1 \cdot T_2}{T_1 - T_2} = 142.557\,\text{kJ} \tag{3}$$

The pre-exponential factor for the gross reaction can be calculated by:

$$k_{Br\infty} = k_{Br}(T_1) \cdot \exp\left(\frac{E_{Br}}{R \cdot T_1}\right) = 3.371 \times 10^{17}\,\text{L}^{1/2}\,\text{mol}^{-1/2}\,\text{s}^{-1} \tag{4}$$

The activation energy for the initiator decomposition reaction can be calculated by:

$$E_z = R \cdot \ln\left[\frac{k_z(T_1)}{k_z(T_2)}\right] \cdot \frac{T_1 \cdot T_2}{T_1 - T_2} = 142.557\,\text{kJ} \tag{5}$$

The pre-exponential factor for the initiator decomposition reaction can be calculated by:

$$k_{z\infty} = k_z(T_1) \cdot \exp\left(\frac{E_z}{R \cdot T_1}\right) = 5.421 \times 10^{8}\,\text{L}^{1/2}\,\text{mol}^{-1/2}\,\text{s}^{-1} \tag{6}$$

The conversion in constant reaction volume is defined by:

$$X = \frac{c_{M0} - c_M}{c_{M0}} \implies \frac{c_M}{c_{M0}} = 1 - X \tag{7}$$

Thus the polymerization time t_p for a monomer conversion of 75 % can be calculated by rearranging Eq. 1:

$$\ln(1 - X) = \frac{2 \cdot k_{Br} \cdot \sqrt{c_{I0}}}{k_z} \cdot \left[\exp\left(\frac{-k_z \cdot t_p}{2}\right) - 1\right]$$

$$\implies t_p = -\frac{2}{k_z} \cdot \ln\left[\frac{\ln(1 - X) \cdot k_z}{2 \cdot k_{Br} \cdot \sqrt{c_{I0}}} + 1\right] \tag{8}$$

Table 5: Polymerization times

$T/^\circ C$	t_p/s
80	1.119×10^{5}
100	8.293×10^{3}
120	3.909×10^{3}

Question 10

> What is meant by stationarity in a reactor system? How does this affect the mass and heat balance?

A **stationary process** describes the movement of matter or energy in which the state variables of the considered system do not change in the course of time.

- In terms of the **mass balance**, an intermediate product of a reaction chain has a constant concentration over time during the process.

- With regard to the **heat balance**, the continuous heat transport is stationary if the temperature at any point in the system is constant in time.

This implies mathematically for the mass balance:

$$\frac{dc_A}{dt} = -\nabla \cdot \vec{j} + \nu_A \cdot r \stackrel{!}{=} 0 \tag{1}$$

And for the heat balance:

$$\frac{d(\rho \cdot c_p \cdot T)}{dt} = -\nabla \cdot \vec{q} + (-\Delta H) \cdot r \stackrel{!}{=} 0 \tag{2}$$

Question 11

Name an example of how you can reduce mass transfer limitations in a heterogeneously catalyzed reaction in the case of:

(a) pore diffusion

(b) film diffusion

To reduce **pore diffusion**, the particle size of the catalyst can be reduced.
To reduce **film diffusion**, the flow velocity of the fluid can be increased.

Question 12

Radical polymerization is a system of consecutive reactions. Intermediate products are radicals.

(a) Explain the Bodenstein quasi-staionarity principle in context with radical polymerization.

(b) What is the degree of polymerization P_n. What measures are necessary in the process of radical polymerization to achieve the highest possible degree of polymerization P_n. Neglect the gel effect.

(c) What is the meaning of the radical efficiency factor?

Bodenstein's quasi-stationary principle states that if an intermediate product (B) is formed slowly with rate constant k_1 and the final product (C) is formed quickly with rate constant k_2, it can be assumed that the concentration of the intermediate product does not change.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad \text{with } k_2 \gg k_1 \tag{1}$$
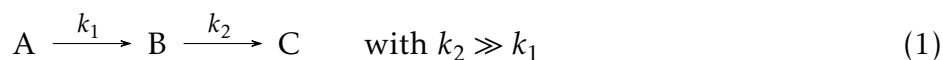
The **degree of polymerization** is the ratio of the number average of the molar mass of the macro molecule M_n and the molar mass of the basic building block M_m (monomer).

$$P_n = \frac{M_n}{M_m} \tag{2}$$

In case of a **radical polymerization** the degree of polymerization is proportional to the ratio of the rate of the propagation and the rate of the termination.
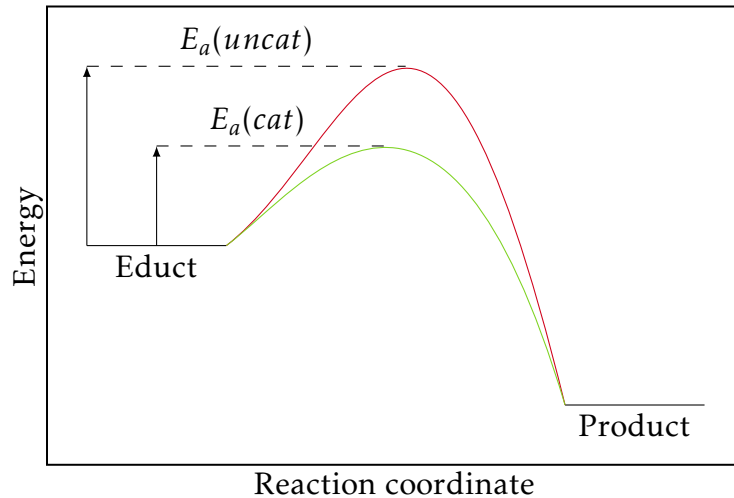
$$P_n \propto \frac{k_w}{k_a} \tag{3}$$

A high degree of polymerization requires $k_w \gg k_a$.
The **radical efficiency factor** f describes the effective radical concentration. The efficiency is ideal 1 but can be decreased due to recombination of the radical inside a solvent cage or before initiating a chain, or due to side reactions.

Question 13

What do you understand by the term catalysis? Name three different metal catalyst and the reaction catalyzed with them.
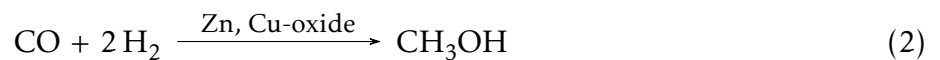
Catalysis means the lowering of the activation energy E_a. It is the process of increasing the rate of a chemical reaction by adding a catalyst, which is not consumed in the course of the reaction.
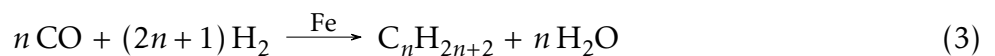

The synthesis of methane:

$$CO + 3\,H_2 \xrightarrow{\text{Ni}} CH_4 + H_2O \tag{1}$$

The synthesis of methanol:

$$CO + 2\,H_2 \xrightarrow{\text{Zn, Cu-oxide}} CH_3OH \tag{2}$$

Fischer-Tropsch synthesis:

$$n\,CO + (2n+1)\,H_2 \xrightarrow{\text{Fe}} C_nH_{2n+2} + n\,H_2O \tag{3}$$

## Question 14

A heterogeneously catalysed reaction of two gaseous reactants (A + B) to the product C shows **Eley-Rideal** kinetics. In an experiment, the partial pressure of component B is kept constant, while that of component A is steadily increased. Describe the course of the reaction rate and explain it using a suitable formula. For this purpose, assign the areas of the curve exactly to the explained cases (in the diagram)!

The Eley-Rideal model states that one reactant is chemisorpt on the surface of the catalyst.

$$A_{ch} + B_g \longrightarrow C$$
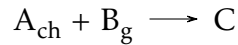
The reaction rate can be described by:

$$r = k \cdot \Theta_A \cdot p_B \tag{1}$$

The coverage Θ can be calculated by:

$$\Theta_A = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A} \tag{2}$$

Thus the reaction rate can be rearranged to:

$$r = k \cdot \frac{K_A \cdot p_A \cdot p_B}{1 + K_A \cdot p_A} \tag{3}$$

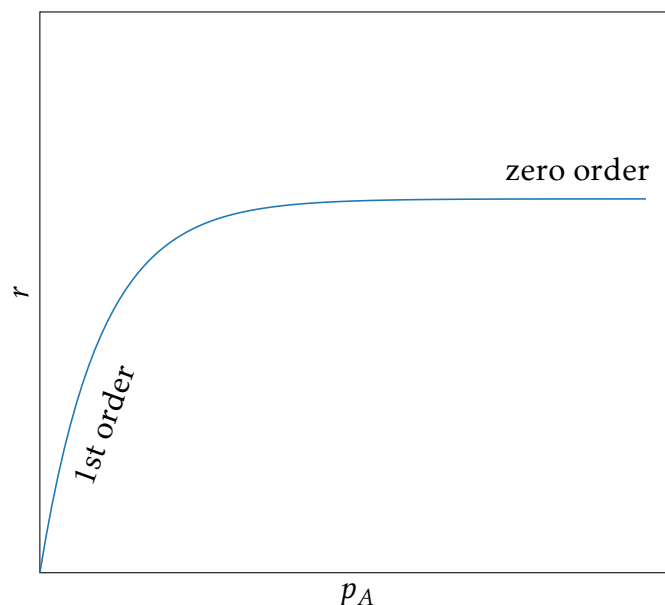In the case of a low partial pressure of A ($K_A \cdot p_A \ll 1$), Eq. 3 can be simplified to:

$$r = k \cdot K_A \cdot p_A \cdot p_B \tag{4}$$

The reaction is 2nd order and the rate behaves 1st order in p_A.
In the case of a high partial pressure of A ($K_A \cdot p_A \gg 1$), Eq. 3 can be simplified to:

$$r = k \cdot p_B \tag{5}$$

The reaction is 1st order and the rate behaves zero order in p_A.

Question 15

To determine kinetic data, the reaction rate of chemical reaction is determined

(a) What is the dimension of the reaction rate?

(b) What are the dimension of the rate constant?

The general rate law can be formulated by:

$$r = \frac{1}{\nu_i} \cdot \frac{dc_i}{dt} = k \cdot c_i^n \qquad \text{with } [r] = \text{mol}\,\text{L}^{-1}\,\text{s}^{-1} \tag{1}$$

Table 1: Rate law and dimension of k

Order	Rate law	$[k]$
0	$r = k$	$\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$
1	$r = k \cdot c_A$	$\text{L}\,\text{s}^{-1}\,\text{mol}^{-1}$
2	$r = k \cdot c_A \cdot c_B$	$\text{L}^2\,\text{s}^{-2}\,\text{mol}^{-2}$
3	$r = k \cdot c_A \cdot c_B \cdot c_C$	$\text{L}^3\,\text{s}^{-3}\,\text{mol}^{-3}$

The rate constant of a reaction with oder $n \neq 0$ has the dimension $[k] = \text{L}^n\,\text{s}^{-n}\,\text{mol}^{-n}$