

# Chemical Reaction Engineering Exam - WS2020

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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 reaction 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  $1600 \text{ mol m}^{-3}$  with a volume flow of  $2.300 \text{ m}^3 \text{ h}^{-1}$ . The temperature of the feed mixture shall be  $T_a = 70^\circ\text{C}$ . In the steady state, the operating temperature should be  $118^\circ\text{C}$ . The average coolant temperature  $T_K$  should be  $95^\circ\text{C}$ . With the selected reaction conditions and operating parameters, a conversion of the reactant of 98 % can be achieved.

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

- Determine the area that must be provided for additional heat dissipation by installing cooling coils. Establish the heat balance of the stationary CSTR. What is the total area for heat exchange.
- Give the relative cooling intensity (Stanton number) for the steady state. Also calculate the adiabatic temperature increase.

The heat balance of the CSTR:

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

The adiabatic temperature increase can be calculated by:

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

By rearranging Eq. 1 the Stanton number can be calculated

$$St = \frac{T_a - T + \Delta T_{ad} \cdot X}{T - T_K} = 1.253 \quad (3)$$

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

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

## Question 2

During the execution of a radical polymerization at 125 °C with an initial initiator concentration of  $c_{I0} = 0.001 \text{ mol L}^{-1}$ , 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):

$$\ln\left(\frac{c_M}{c_{M0}}\right) = \frac{2 \cdot k_{Br} \cdot \sqrt{c_{I0}}}{k_z} \cdot \left[ \exp\left(\frac{-k_z \cdot t}{2}\right) - 1 \right] \quad (1)$$

The conversion in constant reaction volume is defined by:

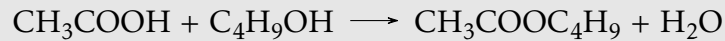
$$X = \frac{c_{M0} - c_M}{c_{M0}} \Rightarrow \frac{c_M}{c_{M0}} = 1 - X \quad (2)$$

Thus Eq. 1 can be rearranged to:

$$\begin{aligned} \ln(1 - X) &= \frac{2 \cdot k_{Br} \cdot \sqrt{c_{I0}}}{k_z} \cdot \left[ \exp\left(\frac{-k_z \cdot t}{2}\right) - 1 \right] \\ \Rightarrow t &= -\frac{2}{k_z} \cdot \ln \left[ \frac{\ln(1 - X) \cdot k_z}{2 \cdot k_{Br} \cdot \sqrt{c_{I0}}} + 1 \right] = 12\,321.348 \text{ s} \end{aligned} \quad (3)$$

### Question 3

Butyl acetat shall be produced at 100 °C from acetic acid and butanol with sulphuric acid as catalyst.



After a first approximation, it is a 2nd order reaction:

$r = k \cdot c_A \cdot c_B$  with  $k = 0.030 \text{ L mol}^{-1} \text{ min}^{-1}$ . 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  $109 \text{ kg h}^{-1}$ . 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  $c_{A0} = 2 \text{ mol L}^{-1}$

- Calculate the Damköhler number.
- Calculate the residence time  $\tau$ .
- 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:

$$\begin{aligned} Da &= \int_0^{X_A} \frac{1}{\Phi(X)} dX = \int_0^{X_A} \frac{1}{(1-X)^2} dX \\ &= \frac{X_A}{1-X_A} = 2.226 \end{aligned} \quad (1)$$

The residence time can be calculated by:

$$\tau = \frac{Da \cdot c_{A0}}{-v_A \cdot r_0} = \frac{Da}{-v_A \cdot k \cdot c_{A0}} = 37.097 \text{ min} \quad (2)$$

The selectivity towards the product can be calculated by:

$$S_P = \frac{n_P - n_{P0}}{n_{A0} - n_A} \cdot \frac{-v_A}{v_P} \implies n_{A0} - n_A = \frac{n_P - n_{P0}}{S_P} \cdot \frac{-v_A}{v_P} \quad (3)$$

The conversion of educt A is defined by:

$$\begin{aligned} X_A &= \frac{n_{A0} - n_A}{n_{A0}} = \frac{n_P - n_{P0}}{n_{A0} \cdot S_P} \cdot \frac{-v_A}{v_P} \\ \implies n_P - n_{P0} &= \frac{v_P}{-v_A} \cdot n_{A0} \cdot S_P \cdot X_A \end{aligned} \quad (4)$$

The production rate is defined by:

$$\dot{n}_P = \frac{n_P}{M_P} = \frac{n_P - n_{P0}}{\tau + t_d} = \frac{v_P}{-v_A} \cdot n_{A0} \cdot S_P \cdot X_A \cdot \frac{1}{\tau + t_d} \quad (5)$$

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

$$V_R = \frac{\dot{n}_P}{M_P} \cdot \frac{-v_A}{v_P} \cdot \frac{\tau + t_d}{c_{A0} \cdot S_P \cdot X_A} = 591.220 \text{ L} \quad (6)$$

#### 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.

$$Da = \frac{-\nu_A \cdot r_0 \cdot \tau}{c_{A0}} \quad (1)$$

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

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

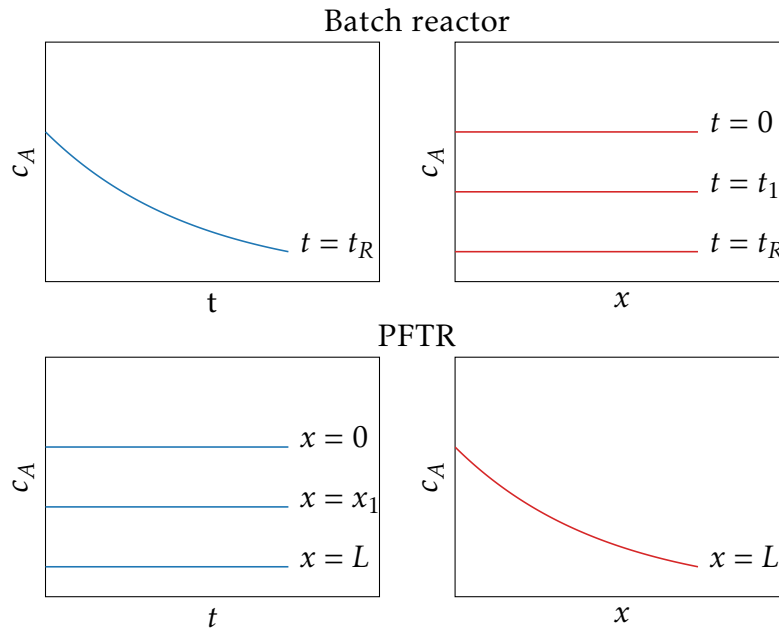
### Question 5

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

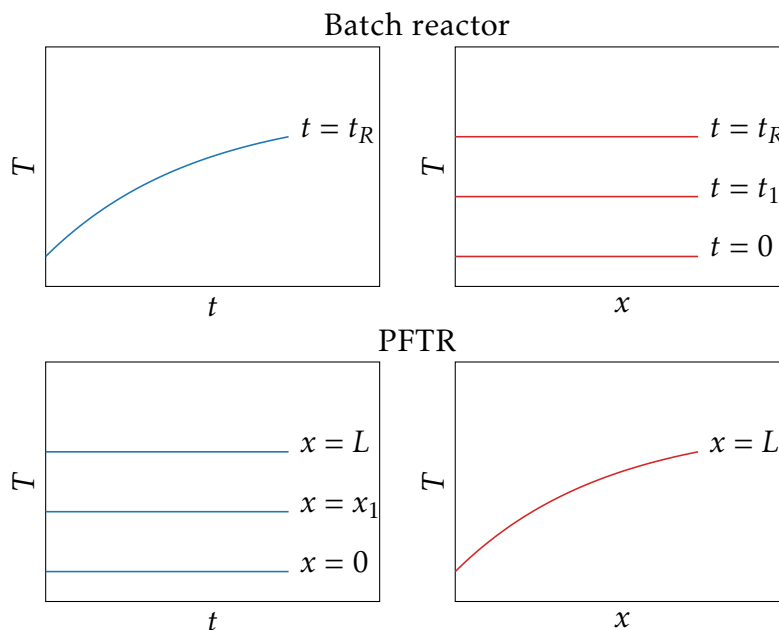


No cooling and the reactors behave ideal.

Time and location dependence on concentration:



Time and location dependence on temperature:



### 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.



The reaction rate can be described by:

$$r = k \cdot \Theta_A \cdot \Theta_B \quad (1)$$

The coverage  $\Theta$  can be calculated by:

$$\Theta_A = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A + K_B \cdot p_B} \quad \Theta_B = \frac{K_B \cdot p_B}{1 + K_A \cdot p_A + K_B \cdot p_B} \quad (2)$$

Thus the reaction rate can be rearranged to:

$$r = k \cdot \frac{K_A \cdot p_A \cdot K_B \cdot p_B}{(1 + K_A \cdot p_A + K_B \cdot p_B)^2} \quad (3)$$

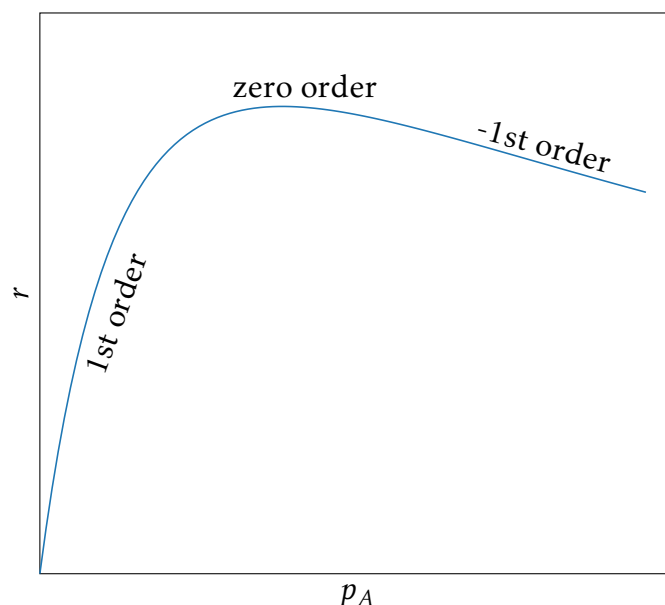
In the case of a low partial pressure of A ( $K_A \cdot p_A \ll 1 + K_B \cdot p_B$ ), Eq. 3 can be simplified to:

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

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:

$$r = \frac{K_B \cdot p_B}{K_A} \cdot \frac{1}{p_A} \quad (5)$$

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

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	✓ or –
Mass transfer inhibition can be caused in parallel by pore and film diffusion.	✓
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.	✓
Pore diffusion-based transport limitations result in an effective activation energy that is half the value of the purely chemical activation energy.	✓
An increase in the diffusion coefficient $D_{eff}$ leads to lower pore efficiency	–