Introduction to Chemical Reactors

Exercises

Part 2: Design of isothermal reactors

2.1

(a) In a batch reactor of constant volume, a first order irreversible reaction halved the initial reactant concentration in 40 minutes at a temperature of $20^{\circ}C$. Calculate the reaction rate constant.

(b) Repeating the experiment at $30\ ^{\circ}C$ reduced the time to halve the initial concentration of reactant to 25 minutes. What is the apparent activation energy for the reaction? ($R = 8.315$ kJ kmol^{-1} K^{-1}).

2.2

A liquid phase reaction A $\rightarrow$ B has the rate expression

$$r = kC_A^n$$

where k is the reaction constant, n is the order of the reaction, and C_A is the concentration of reactant A.

(a) Starting from a general mass balance equation, show that the residence time τ for a CSTR carrying out this reaction is

$$\tau = \frac{C_{A0} - C_A}{kC_A^n}$$

where C_{A0} is the feed concentration.

(b) Two CSTRs with identical volume are connected in series. Denoting the concentrations of the feed, intermediate and output streams as C_{A0}, C_{A1} and C_{A2} respectively, show that the order of reaction n can be determined from

$$n = \frac{\ln\left[\dfrac{C_{A1} - C_{A2}}{C_{A0} - C_{A1}}\right]}{\ln\left[\dfrac{C_{A2}}{C_{A1}}\right]}$$

(c) Find the value for k when the residence time for each CSTR is $\tau = 18$ min, and the concentrations are $C_{A0} = 4.0$ mole litre^{-1}, $C_{A1} = 2.0$ mole litre^{-1}, $C_{A2} = 0.9$ mole litre^{-1}.

2.3

(a) Show that for a continuous stirred tank reactor (CSTR) in which reaction occurs isothermally and without change in volume, the conversion for a first order irreversible reaction is given by:

$$\frac{C_j}{C_{j0}} = \frac{1}{1 + k\tau}$$

where C_{j0}, C_j are the reactant concentrations in the reactor feed and product streams respectively, k is the first order rate constant, τ is the mean residence time of fluid in the reactor.

(b) A first order irreversible reaction in a CSTR achieves 50% conversion with $\tau = 10$ min. A pump failure causes flow through the reactor to cease but stirring and temperature are maintained. The flow is restored after 10 minutes.
What is the reactant concentration in the reactor effluent immediately after the flow is restarted?

(c) What time after the restart will be required for the reactant concentration in the product stream to exceed 49% of the initial concentration?


Part 3: Multiple reactions

3.1

(a) Show that the optimum residence time to maximise the yield of an intermediate product B in two first order, irreversible series reactions (A $\rightarrow$ B and B $\rightarrow$ C) in a PFR is

$$\tau_{opt} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

(b) The catalysed liquid phase production of a pharmaceutical intermediate B from reactant A is a first order irreversible reaction:

$$A \rightarrow B \qquad r_1 = k_1 C_A ; \qquad k_1 = 2 \text{ hr}^{-1}$$

However, B also suffers a first order decomposition under the reaction conditions to C:

$$B \rightarrow C \qquad r_2 = k_2 C_B ; \qquad k_2 = 0.4 \text{ hr}^{-1}$$
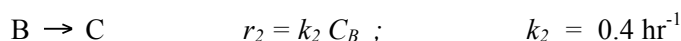
If the reaction is to be carried out using a solution of 1 kmol m^{-3} of A, isothermally and without change in volume, in a PFR, calculate the residence time that maximises the yield of B, and the maximum concentration of B.

(c) If the reaction in part (b) were to be carried out in a CSTR, calculate the maximum possible yield of B, and the mean residence time to achieve this maximum yield.

3.2

The following system of reactions is to be run in a liquid phase CSTR:

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$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad r_1 = k_1 C_A$$
$$B \xrightarrow{k_3} D \qquad r_2 = k_2 C_B$$
$$r_3 = k_3 C_B$$
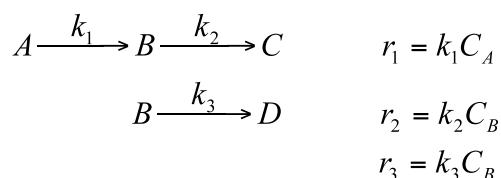
All the reactions in the system are first order.

(a) The design equation for species j in a multiple reaction system in a CSTR is

$$C_{j0} - C_j = -\tau \sum_{i=1}^{R} \nu_{ij} r_i$$

where τ is the residence time and ν_{ij} is the stoichiometric coefficient of component j in reaction i, and R is the total number of reactions.

Write down the balances for each of the species and obtain expressions for their concentrations in terms of τ and the constants k_1, k_2, k_3 and C_{A0}.

Assume that $C_A = C_{A0}$ and $C_{B0} = C_{C0} = C_{D0} = 0$ at $\tau = 0$.

(b) Show that the residence time that maximises C_B is:

$$\tau_{opt} = \left(\frac{1}{k_1 (k_2 + k_3)} \right)^{\frac{1}{2}}$$

(c) Assume that you have to work with the same reaction system as the one described in part (a).
For a conversion X_A (defined as $(C_{A0} - C_A)/C_{A0}$) = 0.9, and value for the reaction rate coefficient of $k_1 = 1.5 \times 10^{-3}$ s^{-1}, and an input concentration of species A of $C_{A0} = 8000$ mol m^{-3}, calculate the required residence time, τ (note that this is not τ_{opt}).

3.3

The ingestion of ethanol into the bloodstream and its subsequent elimination can be approximated as a series reaction. The absorption rate from the gastrointestinal tract into the bloodstream is a first–order reaction with a $k_1 = 10$ h^{-1}.
The rate at which ethanol is broken down in the bloodstream is a zero–order reaction with a $k_2 = 0.192$ g h^{-1} (L of body fluid)$^{-1}$.

(a) If you take two large double shots of spirit immediately after arriving at a pub, what will be the maximum concentration of ethanol in the blood? How long must you wait to be able to drive legally?

(b) Assume that you need to leave the pub as soon as you have finished the two shots. How many minutes would you have to reach your destination without being legally intoxicated?

(c) How long must you wait after having two large double shots of spirit if the second shot is drunk 30 minutes after the first one?

Useful data, assumptions and warnings:

• The UK legal limit for drivers is 0.8 g of ethanol per litre of body fluid.

- One large double shot of spirits (40% ABV, e.g. whisky) is equivalent to 2.8 units of alcohol.
- One unit of alcohol is 10 ml (7.89 g) of ethanol.
- Assume the volume of body fluid to be 40 litres.
- Example based on data from [Fogler 05]. Warning: do not try this at home!

Part 4: Design of non-isothermal reactors

4.1

Reaction A → B is first order and exothermic with a $\Delta H_R = -135$ kJ mol^{-1}. It is to be run in aqueous solution at atmospheric pressure.

(a) Using the energy balance equation for an adiabatic reactor, show that the temperature rise in the reactor when the reactant concentration has dropped to C_A is

$$\left(T - T_0\right) = \frac{-\Delta H_R}{\rho Cp}\left(C_{A0} - C_A\right)$$

(b) If the initial temperature in the adiabatic reactor is $T_0 = 320$ K, and assuming complete conversion, determine the highest value of C_{A0} if the reactor contents are just not to reach 100 °C.

(c) It is found from experimental measurements at 320 K that the maximum conversion attainable for the reaction $X_{max} = 0.818$.
Because of a malfunction upstream, the feed concentration of the reactor becomes $C_{A0} = 2.0$ mol litre^{-1}. What would be the expected final temperature in the CSTR in the event of the reaction reaching X_{max}?

4.2

The mass and energy balance equations for a nonisothermal steady-state CSTR with external cooling are:

$$C_{A0} - C_A = \tau r$$

and

$$\left(T - T_0\right) = \frac{J \tau r}{C_{A0}} - \kappa\left(T - T_c\right)$$

respectively. The quantities J and κ are defined as $J \equiv \dfrac{-\Delta H_R \, C_{A0}}{\rho Cp}$ and $\kappa \equiv \dfrac{U A_c}{v \rho Cp}$

The meaning of each of the variables is:
C_{A0} : input concentration of species A to the reactor (mol m^{-3})
C_A : output concentration of A from the reactor (mol m^{-3})
τ : reactor residence time (s)
T : temperature of operation (K)
r : reaction rate (mol m^{-3} s^{-1})
T_0 : input temperature (K)
T_c : coolant temperature (K)
ΔH_R : enthalpy of reaction (J mol^{-1})
ρ : density of the fluid (kg m^{-3}/
c_p : specific heat capacity of the fluid (J kg^{-1} K^{-1})

U : heat transfer coefficient (W m^{-2} K^{-1})
A_c: cooling area (m2/
v : volumetric flowrate (m^3 s^{-1})

(a) Show that for a zero-order exothermic liquid-phase reaction A $\rightarrow$ B in a nonisothermal steady-state CSTR with external cooling the Energy Generation and Energy Removal equations $G(T)$ and $R(T)$ are

$$G(T) = X(T) = \frac{\tau\, k}{C_{A0}} \qquad \text{and} \qquad R(T) = X(T) = \frac{\left(T - T_0\right) + \kappa\left(T - T_c\right)}{J}$$

where $X(T)$ is the reaction conversion and k the specific reaction rate (mol m^{-3} s^{-1}). Sketch the shape of both functions with respect to temperature.

(b) Derive the expression for the critical value of the heat transfer area, i.e. the cooling area below which the reactor will run away and explode, and show that it is

$$A_c = \left[\frac{T - T_0 - \dfrac{R\,T^2}{E}}{\dfrac{R\,T^2}{E} - T + T_c}\right] \cdot \frac{v\,\rho\,c_p}{U}$$

where R is the universal gas constant (J mol^{-1} K^{-1}) and E the activation energy of the reaction (J mol^{-1}) .

(c) Calculate the critical value of the heat transfer area, A_c, when the input temperature to the reactor is 40° C, its temperature of operation is 95° C, and the temperature of the coolant is 20° C.
The volumetric feed rate to the reactor is 0.001 m3 s^{-1}, the density and specific heat of the reacting fluid are 1030 kg m^{-3} and 5000 J kg^{-1} K^{-1} respectively, and the heat transfer coefficient is 150 W m^{-2} K^{-1}.
Assume all the fluid properties are constant with respect to temperature. The value for E can be calculated from the following two experimental measurements: $k_{T1} = 0.02$ kmol m^{-3} s^{-1} at $T_1 = 20°$ C and $k_{T2} = 0.04$ kmol m-3 s^{-1} at $T_2 = 50°$ C.

4.3

Consider the reversible gas-phase reaction A $\Leftrightarrow$ B with $r = k_f\, P_A - k_b\, P_B$ with A and B behaving ideally in a CSTR at a constant pressure of 1 bar and $T_0 = 400\ K$. The feed is 20% component A and 80% inert with a flowrate $F_{T0} = 15$ mol/s. A conversion of 80% is desired.

The values for the pre-exponential factors are $A_f = 1.5$ x 10^3 and $A_b = 2.0$ x 10^6 mol m^{-3} s^{-1} bar^{-1}; and for the activation energies $E_f = 25000$ and $E_b = 70000$ J mol^{-1}, you can approximate $Cp_A = Cp_B = Cp_{inert} = 30$ J mol^{-1} K^{-1} as being constant.

(a) What is the minimum volume required for the reactor?
   [Hint: For a desired conversion calculate the temperature at which the reaction rate is a maximum and thus the reactor volume is minimum].

(b) What is the amount of heat to be supplied or removed to reach the operating condition found in part (a)?

(c) What would be the adiabatic reactor temperature, i.e. the one reached without external heat supply/removal?

Part 5: Design of catalytic reactors

5.1

The following apparent first order rate constants were measured on samples of crushed and 10 mm diameter spheres of catalyst:

	Crushed	10 mm spheres
Temp K	$k \ 10^{-2} \ s^{-1}$	$k \ 10^{-2} \ s^{-1}$
400	1.00	0.99
450	7.42	7.01
500	36.9	29.1
550	137.1	75.4

(a) Calculate the activation energy for the intrinsic (non diffusion limited) reaction rate.

(b) Given that the effectiveness factor η is expected to follow:

$$\eta = \frac{3}{\phi} \left[\frac{1}{\tanh \phi} - \frac{1}{\phi} \right]$$

where $\phi = \frac{d_p}{2} \sqrt{\frac{k}{D_e}}$

and d_p = catalyst pellet diameter
              D_e = effective diffusivity of reactant in the catalyst

Estimate the value for D_e at 550 K and calculate the value of η for 5mm diameter spheres of catalyst at 550 K.

5.2

(a) Show that the Langmuir adsorption theory applied to competitive adsorption between two gas molecules A and B predicts

$$\theta = \frac{K_A p_A + K_B p_B}{1 + K_A p_A + K_B p_B} \quad where \quad K_A = \frac{k_{aA}}{k_{dA}} \ ; K_B = \frac{k_{aB}}{k_{dB}} \ ; \theta = \theta_A + \theta_B$$

where θ = fraction of solid surface area covered by A and B, k_A, k_B are dependent only on temperature, and p_A, p_B are the gaseous phase partial pressures of A and B.

(b) The reaction between CO and NO:

$$CO + NO \rightarrow \frac{1}{2} N_2 + CO_2$$
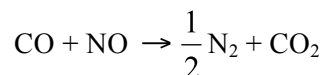
over a particular catalyst is first order with respect to the adsorbed concentration (kmol m^{-2}) of each reactant and, at atmospheric pressure, the surface reaction is the rate determining step in the reduction of NO with CO in vehicle exhaust gas passing over the catalyst.

Surface adsorption experiments at the proposed operating temperature show that the catalyst surface is 50% covered by CO when the pressure of CO is 10^{-4} atma. Repeating the experiment with 10^{-4} atma of NO gives 20% surface coverage. Adsorption of other gases present in the exhaust is negligible.

It is desired to reduce 100ppm (v/v) of NO to N_2, and this is to be achieved by varying the initial concentration of CO. What CO concentration at the inlet to the catalyst will give the maximum rate of reaction?

5.3
A first order reaction A $\rightarrow$ B takes place in the catalyst-covered walls of a tube of diameter d. Species A is mixed with a fluid that flows through the tube with velocity u. The reaction rate is

$$r'' = k'' C_A$$

where r'' is the reaction rate in moles (m^{-2} of catalyst surface area) s^{-1} and k'' is the specific reaction rate in units of m s^{-1}.

(a) Show that the pseudohomogeneous reaction rate r in moles (m^{-3} of reactor volume) s^{-1} is

$$r = \frac{4}{d} r''$$

(b) Show that the concentration, C_A, of species A at the exit of the tube is

$$C_A = C_{A0} \exp\left[\frac{-4 k''}{u d}\right] z$$

where C_{A0} is the concentration at the entrance of the tube and z is the length of the tube. Assume that the concentration is uniform over the cross sectional area of the tube.

(c) A particular tube has $d = 1.0$ cm and $u = 2$ m s^{-1}. The value for k'' is 0.1 m s^{-1}.
   i.   Assuming that the conditions in part (b) are relevant to the particular fluid flowing through the tube, find the value of z to obtain 95% conversion.
   ii. A different fluid is used to transport species A through the reactor at $u = 2$ m s^{-1}.

In this case, the flow through the tube is laminar (and therefore Sh = 8/3). The diffusivity of species A in the fluid is $D_A = 1.5 \times 10^{-5}$ m^2 s^{-1}. Obtain a new estimate for the required length of the reactor for 95% conversion.

[*Hint*: The Sherwood number is defined as $\quad Sh = \dfrac{k_m d}{D_A} \quad$].

Part 6: Non-ideal reactors

6.1

Show that the residence time distribution function $E(t)$ for two continuous stirred tank reactors (CSTR) in series is

$$E(t) = \frac{v}{V_2 - V_1}\left[\exp\left(-\frac{v}{V_2}t\right) - \exp\left(-\frac{v}{V_1}t\right)\right]$$

where V_1, V_2 are the reactor volumes and v is the volumetric flow rate through the tanks.

6.2   *(problem 13.18 in Schmidt)*

We need to calculate the concentration of a pollutant A following a spill into a river which flows by our chemical plant at 400 m^3 h^{-1} at 8 km h^{-1}. There is a waterfall just upstream, so the water is saturated with air at $C_{O2} = 1.5 \times 10^{-3}$ moles litre^{-1}. The river bottom is rocky so that the flow is well mixed radially. This chemical is oxidized by dissolved O$_2$ with a rate

$$r = k\, C_A\, C_{O_2}$$

with $k = 2000$ litres mole^{-1} h^{-1} and r in moles litre^{-1} h^{-1}.

(a) Consider a steady leak of 40 litres h^{-1} at $C_A = 0.1$ moles litre^{-1}. What is C_{A0} in the river after mixing?
(b) If trout are killed at $C_A > 10^{-6}$ moles litre^{-1}, estimate the downstream distance at which the trout would be killed.
(c) Suppose that the leak is 400 litres h^{-1} of 10 molar A. What is C_{A0} in the river after mixing?
(d) If carp are not harmed by A but they die if $C_{O2} < 10^{-4}$ moles litre^{-1}, estimate the downstream distance at which the carp start being killed by the spill in part (c), assuming no replenishment of the O$_2$.

6.3   *(wetlands web module problem from Fogler)*

Design a model for a wetland of known dimensions through which waste water flows from left to right assuming that the system behaves as a PFR. Assume that the degradation of chemicals, such as atrazine, follows irreversible first-order homogeneous kinetics, and that part of the

waste water evaporates from the surface as it flows along the wetland. Obtain an equation that represents the molar flow of toxic substances (F_A) as a function of distance (z).

Consider that evaporation occurs on the wetland´s top surface area at a constant rate (Q in kmol water h^{-1} m^{-2}) and that none of the toxic chemicals are lost to the air by evaporation.