Applied reaction kinetics

Exercise book

The following text summarizes the basic relationships and computing techniques used to solve problems in chemical reactor design. The document is not exhaustive and contains only a brief introduction to the material and energy balance in chemical reactors. The main aim is to solve practical examples and to demonstrate a systematic approach to solve engineering problems. The source code (`Matlab, Octave, Excel or FORTRAN`) for many of the exercises presented here can be found on the website
https://web.vscht.cz/bernauem/ark/ark.html.

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MINISTRY OF EDUCATION,
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Contents

1 Introduction

1.1 Expressions of concentration of species in mixtures

Composition of a reaction mixture could be expressed in different ways:

- Molar fraction of component i

$$x_i = \frac{n_i}{\sum\limits_{j=1}^{N} n_j}, \tag{1}$$

  where n is the number of mols. Molar fraction is not dependent on temperature nor on pressure of a system.

- Weight fraction (or mass fraction) of compound i

$$w_i = \frac{m_i}{\sum\limits_{j=1}^{N} m_j}, \tag{2}$$

where m is the mass. Mass fraction, like molar fraction is invariant to temperature and pressure of the system.

- Molar concentration of compound i

$$C_i = \frac{n_i}{V} = x_i C \tag{3}$$

where V is system volume and C is overall concentration, or molar density. Molar concentration of ideal gaseous systems depend on temperature and pressure of the system

$$C = \frac{p}{\mathbf{R}T}, \tag{4}$$

where p is overall system pressure, $\mathbf{R}$ is universal gas constant and T is temperature.

Between above mentioned concentration expressions exists following relationships:

- Molar fraction => Mass fraction

$$w_i = \frac{M_i x_i}{\displaystyle\sum_{j=1}^{N}(M_j x_j)}, \tag{5}$$

where M is molar weight. The term $\overline{M} = \sum_{j=1}^{N}(M_j x_j)$ is called mean molar mass of the mixture.

- Mass fraction => Molar fraction

$$x_i = \frac{w_i/M_i}{\displaystyle\sum_{j=1}^{N}(w_j/M_j)} \tag{6}$$

1.2 Expressions for definition of flow

When calculating in continuous systems (i.e. plug flow reactors) we are often confronted to the problem how to express the flow, in other words the amount of a substance flowing through given element in defined time interval. The solution is not so obvious as can appear at the first approach. We have to take into account following considerations

- Steady-state ($\mathrm{d}n/\mathrm{d}t = 0$) ?
- Compressible or un-compressible flow?
- Number and behavior of different phases?
- Occurring chemical reaction?

- Plug flow or axial dispersion?

There is no unique and right answer where we should use a certain type of expression of flow. In following we present three basic flow expressions:

- Molar flow of component i [N T^{-1}]

$$\dot{n}_i \equiv F_i = x_i C v \mathbf{A} = x_i \vec{J} \mathbf{A} = x_i F, \tag{7}$$

  where v is mean stream velocity in [L T^{-1}], $\mathbf{A}$ is area perpendicular to the flow direction, $\vec{J}$ is the intensity of molar flow (in [N L^{-2} T^{-1}]), F is the overall molar flow. Molar flow in steady state is invariant to the temperature and pressure. In the case of reacting system, it is a function of reaction extent ξ where $\sum_{j=1}^{N} \nu_j \neq 0$. For further details see next sections dealing with definition of stoichiometry and reaction extent.

- Mass flow of compound i (mass per time unit [M T^{-1}])

$$\dot{m}_i \equiv G_i = w_i \rho v \mathbf{A} = w_i G, \tag{8}$$

  where ρ is mass density of streaming mixture. In steady state mass flow is independent on temperature, pressure and reaction extent.

- Volumetric flow rate (volume per time unit [L^3 T^{-1}])

$$\dot{V} = \frac{F}{C} = F \frac{\mathbf{R}T}{p}. \tag{9}$$

  Volumetic flow rate is dependent on temperature, pressure and reaction extent.

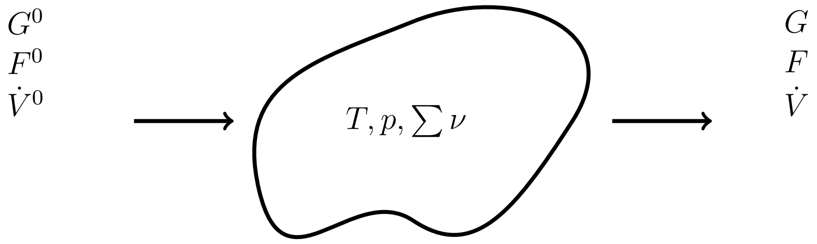

Table 1: Comparison of different expressions of flow (steady state) in terms of their dependence on temperature T, pressure p and change of number of mols $\sum \nu$. Values inside brackets [ ] are meant constants.

Total	$\sum \nu = 0$	$\sum \nu \neq 0$	$\sum \nu = 0$		$\sum \nu \neq 0$	
flow	$[T, p]$	$[T, p]$	$[p]$	$[T]$	$[p]$	$[T]$
G / $[\mathsf{M\ T}^{-1}]$	$G^0 = G$	$G^0 = G$	$G^0 = G$	$G^0 = G$	$G^0 = G$	$G^0 = G$
F / $[\mathsf{N\ T}^{-1}]$	$F^0 = F$	$F^0 \neq F$	$F^0 = F$	$F^0 = F$	$F^0 \neq F$	$F^0 \neq F$
$\dot{V}$ / $[\mathsf{L}^3\ \mathsf{T}^{-1}]$	$\dot{V}^0 = \dot{V}$	$\dot{V}^0 \neq \dot{V}$	$\dot{V}^0 \neq \dot{V}$	$\dot{V}^0 \neq \dot{V}$	$\dot{V}^0 \neq \dot{V}$	$\dot{V}^0 \neq \dot{V}$

1.3 Stoichiometry

Chemical substances undergoing a chemical reaction are combined in proportions according to the stoichiometry of the reaction involved. For single chemical reaction, such as ammonia synthesis, we wrote

$$\mathrm{N_2} + 3\,\mathrm{H_2} \longleftrightarrow 2\,\mathrm{NH_3}, \tag{10}$$

or in more general way, by switching chemical formulas of species to abstract mathematical variable "A_i" and stoichiometric coefficients to "ν" and rearranging equation 10 we obtain

$$\nu_1 A_1 + \nu_2 A_2 = \nu_3 A_3. \tag{11}$$

Obtained linear equation can be transformed into matrix (or vector in this case) notation

$$\sum_{i=1}^{N} \nu_i A_i = \boldsymbol{\nu}\mathbf{A}^T = \begin{bmatrix} -1 & -3 & 2 \end{bmatrix} \begin{bmatrix} \mathrm{N_2} \\ \mathrm{H_2} \\ \mathrm{NH_3} \end{bmatrix} = 0.$$

We can see, that products have in matrix $\boldsymbol{\nu}$ a positive sign and reactants negative.

Multiple reaction system, such as partial oxidation of methane, can be written as

$$\begin{aligned}
\mathrm{CH_4} + 2\,\mathrm{O_2} &\longleftrightarrow 2\,\mathrm{H_2O} + \mathrm{CO_2} \\
\mathrm{CH_4} + \frac{1}{2}\,\mathrm{O_2} &\longleftrightarrow \mathrm{H_2} + \mathrm{CO} \\
\mathrm{CO} + \frac{1}{2}\,\mathrm{O_2} &\longleftrightarrow \mathrm{CO_2} \\
\mathrm{H_2} + \frac{1}{2}\,\mathrm{O_2} &\longleftrightarrow \mathrm{H_2O} \\
\mathrm{CO_2} + \mathrm{C} &\longleftrightarrow 2\,\mathrm{CO} \\
\mathrm{CH_4} &\longleftrightarrow \mathrm{C} + 2\,\mathrm{H_2}
\end{aligned}$$

The stoichiometric matrix $\boldsymbol{\nu}$ of this system is as follows

$$\boldsymbol{\nu} = \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{array} \begin{array}{c} \begin{array}{ccccccc} CH_4 & H_2O & O_2 & H_2 & CO_2 & CO & C \end{array} \\ \left(\begin{array}{ccccccc} -1 & 2 & -2 & 0 & 1 & 0 & 0 \\ -1 & 0 & -1/2 & 1 & 0 & 1 & 0 \\ 0 & 0 & -1/2 & 0 & 1 & -1 & 0 \\ 0 & 1 & -1/2 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 2 & -1 \\ -1 & 0 & 0 & 2 & 0 & 0 & 1 \end{array}\right) \end{array}$$

1.3.1 Number of linearly independent reactions

In previous section we build a matrix of stoichiometric coefficients for a set of chemical reactions. Now we turn our attention to the question: Are certain reactions a linear combination of others reaction in studied set? This is useful and indispensable question in the case of large reaction system, where the possible reduction of reaction schema dimension is desirable. The solution can be found by evaluating the rank of matrix $\boldsymbol{\nu}$, in `Octave` or `Matlab` programming (or scripting) language

```
octave:1> NU =[\
> -1   2   -2   0   1   0   0;\
> -1   0 -1/2   1   0   1   0;\
>  0   0 -1/2   0   1  -1   0;\
>  0   1 -1/2  -1   0   0   0;\
>  0   0    0   0  -1   2  -1;\
> -1   0    0   2   0   0   1;]
octave:2> rank(NU)
ans =  5
```

1.4 Reaction extent

Lets begin with an example.

Example: 1.1
In a closed system the SO_2 is reacting with oxygen to form SO_3

$$SO_2 + \frac{1}{2}\,O_2 \rightleftharpoons SO_3. \tag{12}$$

Derive a material balance for all chemical compounds at time t^0 and $t > t^0$ and find the relationship between changes in number of mols for each compound.

Solution

In closed system the number of atoms is constant[1] and thus it is convenient to write down the balance equations in therms of number of atoms. The balance equations are summarized in following table: t^0 a t correspond to the reaction beginning and reaction end respectively.

	t^0	t
oxygen (O)	$2n^0_{SO_2} + 2n^0_{O_2} + 3n^0_{SO_3}$	$2n_{SO_2} + 2n_{O_2} + 3n_{SO_3}$
sulfur (S)	$n^0_{SO_2} + n^0_{SO_3}$	$n_{SO_2} + n_{SO_3}$

Balance equations for two involved atoms are, for oxygen

$$2n^0_{SO_2} + 2n^0_{O_2} + 3n^0_{SO_3} = 2n_{SO_2} + 2n_{O_2} + 3n_{SO_3}, \tag{13}$$

and sulfur

$$n^0_{SO_2} + n^0_{SO_3} = n_{SO_2} + n_{SO_3}. \tag{14}$$

By rearranging previous equation 13, in order to obtain differences $n_i - n_i^0$, we obtain

$$2(n^0_{SO_2} - n_{SO_2}) + 2(n^0_{O_2} - n_{O_2}) = 3(n_{SO_3} - n^0_{SO_3}), \tag{15}$$

and from equation 14

$$(n^0_{SO_2} - n_{SO_2}) = (n_{SO_3} - n^0_{SO_3}). \tag{16}$$

Then by combining previous relationships and after rearrangement we obtain

$$\frac{1}{2}(n_{SO_2} - n^0_{SO_2}) = (n_{O_2} - n^0_{O_2}) \tag{17}$$

$$\frac{1}{2}(n_{SO_2} - n^0_{SO_2}) = (n_{O_2} - n^0_{O_2}) = -\frac{1}{2}(n_{SO_3} - n^0_{SO_3}). \tag{18}$$

$$\frac{(n_{SO_2} - n^0_{SO_2})}{-1} = \frac{(n_{O_2} - n^0_{O_2})}{-1/2} = \frac{(n_{SO_3} - n^0_{SO_3})}{1}. \tag{19}$$

From previous example 1.1 and especially from equation 19 it is clear, that an extensive variable common to all species exists and is unique for given reaction (at time t). This variable is called **reaction extent** ξ and is defined by

$$\xi = \frac{n_i - n_i^0}{\nu_i}. \tag{20}$$

Reaction extent has a unit of mol and $\xi > 0$.

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[1] We expect that no nuclear reaction occurs.

1.5 Conversion

In order to describe the course of the chemical reaction in therms of a unit-less variable, the conversion is introduced as

$$X_k = \frac{\xi}{\xi_{\max,k}}, \tag{21}$$

where $\xi_{\max,k}$ is the maximal reaction extent

$$\xi_{max,k} = \frac{n_k^* - n_k^0}{\nu_k}, \tag{22}$$

where n_k^* is the limit value of number of mols of key component. If we combine equation 21, 20 and 22, we obtain for $n_k^* = 0$ following relationship for conversion of "i-th" component

$$X_i = \frac{\nu_k}{\nu_i} \frac{n_i^0 - n_i}{n_k^0}. \tag{23}$$

In the case of key component, previous equation become

$$X_k = \frac{n_k^0 - n_k}{n_k^0}. \tag{24}$$

The composition of reacting mixture could be expressed from 23

$$n_i = n_i^0 - \frac{\nu_i}{\nu_k} n_k^0 X_k. \tag{25}$$

If a we have a reaction system, where $NR > 1$ reaction occurs, it is necessary to express the conversion separately for each component in each reaction. For this reason it is more convenient to use instead of conversion the reaction extent ξ (see equation 20)

$$n_i = n_i^0 + \sum_{j=1}^{NR} \nu_{j,i} \xi_j \tag{26}$$

In matrix notation

$$\mathbf{n} = \mathbf{n}^0 + \boldsymbol{\nu}^T \boldsymbol{\xi}, \tag{27}$$

where $\mathbf{n}$ and $\mathbf{n}^0$ are column vectors and $\boldsymbol{\xi}$ is a column vector containing reaction extents of NR reactions.

Example: 1.2

Oxidation of ammonia by oxygen

NR	**Reaction**		
1	$4NH_3 + 5O_2$	=	$4NO + 6H_2O$
2	$2NH_3 + 2O_2$	=	$N_2O + 3H_2O$
3	$4NH_3 + 3O_2$	=	$2N_2 + 6H_2O$

a) Determine the stoichiometric matrix and evaluate the number of independent reactions.

b) Write balance equations for the system.

c) Evaluate the conversion of NH_3 if the molar fractions at the inlet and outlet are:

Compound	**Inlet mol.frac**	**Outlet mol.frac**
NH_3	0.5	0.087
O_2	0.5	0.028
NO	0	0.300
H_2O	0	0.550
N_2O	0	0.010
N_2	0	0.025

Example: 1.3

Consider the methane conversion

$$\mathrm{CH_4 + CO_2 = 2CO + 2H_2}$$

which occurs at temperature of 900 K and under atmospheric pressure. Feed composition is 3 mol of CO_2 and 2 mol of CH_4. Evaluate outlet composition for all components (in mol %) for methane conversion equal to 0.097.

Example: 1.4

Steam reforming of methane is accompanied by the reaction of CO_2 with steam to form CO and H_2.

$$\begin{aligned} \mathrm{CH_4 + H_2O} &= \mathrm{CO + 3\,H_2} \\ \mathrm{CO + H_2O} &= \mathrm{CO_2 + H_2} \end{aligned}$$

The feed contains methane and water in molar ratio 1:1. The outlet stream contains (mol. frac.) 0.14 CH_4, 0.09 H_2O, 0.12 CO, 0.59 H_2 and 0.06 CO_2. Calculate reaction extent of both reaction and overall methane conversion. Reaction temperature and pressure are constant.

Example: 1.5

Consider a reactor with measured flows rates given in following table

Compound	Feed flow rate mol s^{-1}	Outlet flow rate mol s^{-1}
Cl_2	1.60	0.04
HCl	0.00	1.50
CH_4	0.70	0.04
CH_3Cl	0.28	0.17
CH_2Cl_2	0.02	0.63
$CHCl_3$	0.01	0.12
CCl_4	0.00	0.01

Evaluate corrected flow rates which satisfy the element conservation equations. For further details see Murthy, A.; *Ind. Eng. Chem. Process Des. Develop.*, 12, 246-248, **1973**.

1.6 Chemical equilibrium

Example: 1.6

The reaction specified in example 1.3 take a place in the reactor under atmospheric pressure and temperature of 1200 K

$$\mathrm{CH_4 + CO_2 = 2CO + 2H_2}$$

Feed contains equimolar mixture of CO_2 and CH_4. Equilibrium constant of this reaction at temperature 1200 K is 4.10^{-6}. Answer following questions:

a) What will be the equilibrium conversion of CH_4 at the outlet?

b) Describe the effect of pressure on the outlet composition (up to 1 MPa).

Solution

Equilibrium constant of r-th reaction is defined by means of activity of (NC) compounds

$$K_{\mathrm{a},r} = \prod_{i=1}^{NC} a_i^{\nu_{i,r}}, \qquad r = 1, \ldots, NR. \tag{28}$$

In order to express equilibrium composition in conventional quantities we have to define the standard state which is, in our case, the fugacity of pure compound in ideal gas state f_i^0, at the system temperature and at standard pressure of $1\ \mathrm{atm}$.

$$K_{\mathrm{a},r} = \prod_{i=1}^{NC} \left(\frac{f_i}{f_i^0}\right)^{\nu_{i,r}} = \prod_{i=1}^{NC} \left[y_i \left(\frac{f}{p}\right)_i \frac{p}{f_i^0} \right]^{\nu_{i,r}} = \prod_{i=1}^{NC} \left(p_i \frac{\varphi_i}{f_i^0} \right)^{\nu_{i,r}}, \tag{29}$$

where p is total pressure (in the same units as standard pressure!), y is molar fraction and φ is fugacity coefficient, which in ideal systems equals unity and thus we can rewrite previous equation as (in following text we omit the standard fugacity $f_i^0 = 1$ atm)

$$K_{\mathrm{a},r} = \left(\frac{p}{n}\right)^{\boldsymbol{\nu}_r} \prod_{i=1}^{NC} {n_i}^{\nu_{i,r}}, \tag{30}$$

where $\boldsymbol{\nu}_r = \sum_{i=1}^{NC} \nu_{i,r}$ and $n = \sum_{i=1}^{NC} n_i$. If we substitute n_i in equation 30 by expression from equation 26 we obtain

$$K_{\mathrm{a},r} = \left(\frac{p}{\sum_{i=1}^{NC}\left[n_i^0 + \sum_{r=1}^{NR}(\nu_{i,r}\xi_r)\right]}\right)^{\boldsymbol{\nu}_r} \prod_{i=1}^{NC}\left(n_i^0 + \sum_{r=1}^{NR}(\nu_{i,r}\xi_r)\right)^{\nu_{i,r}}. \tag{31}$$

But we want to known the value of ξ_r for known $K_{\mathrm{a},r}$ and known initial (inlet) values of n^0. To obtain the result we have to solve a nonlinear equation in the following form

$$f(\xi_k) = 0, \tag{32}$$

where the function $f(\xi_k)$ is nonlinear with respect to the reaction extent ξ_k. The equation takes a form

$$f(\xi_k) = \left(\frac{p}{\sum_{i=1}^{NC}\left[n_i^0 + \sum_{r=1}^{NR}(\nu_{i,r}\xi_r)\right]}\right)^{\nu_r} \prod_{i=1}^{NC}\left(n_i^0 + \sum_{r=1}^{NR}(\nu_{i,r}\xi_r)\right)^{\nu_{i,r}} - K_{\mathrm{a},r} = 0. \tag{33}$$

How-to solve nonlinear equation(s) The goal of this section is not to provide a extensive description of problem of solving nonlinear equations, but only a brief summary ("cook-book") dedicated to our example 1.6.

In this example we solve one nonlinear equation 33 by Newton's method (Hamming, R. *Numerical methods for scientists and engineers*), McGraw-Hill New York 1973 [2]. This method finds the next iteration of unknown variable x_{l+1} using a recurrent formula

$$x_{l+1} = x_l - \frac{f(x_l)}{f'(x_l)}, \qquad l = 0, 1, \ldots, \tag{34}$$

where $f'(x_l)$ is the derivative of function $f(x)$ at x_l. The biggest difficulties arise from the estimation of initial value of x_0 and from the evaluation of the derivative $f'(x_l)$, which is mainly obtained by numerical procedure as follows

$$f'(x_l) \approx \frac{f(x_l + h) - f(x_l)}{h}, \qquad h \neq 0, \tag{35}$$

where h is "sufficiently" small number.

In our case $x = \xi$. A schematic picture of the solution is given below

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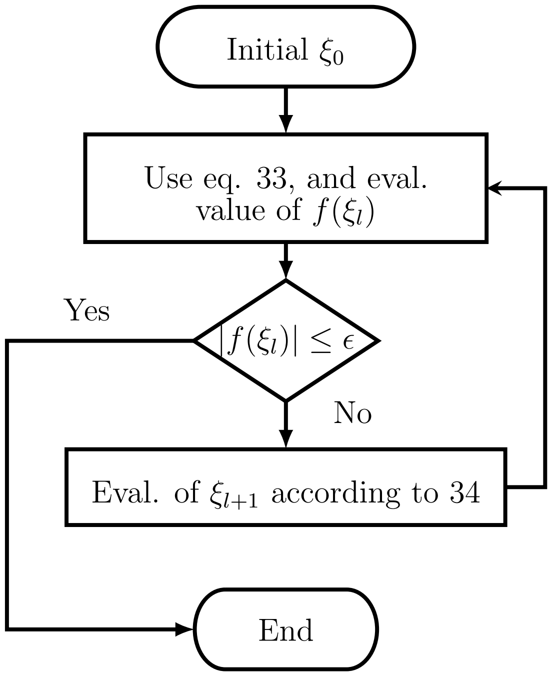
[2] see `http://books.google.com/books`.



In the case of multiple reactions, we have to solve a system of nonlinear equations

$$f_i(\xi_1, \xi_2, \ldots, \xi_N) = 0, \qquad i = 1, 2, \ldots, N. \tag{36}$$

For this purpose we use Newton-Raphson method which is based on Taylor expansion of the function 36

$$f_i(\boldsymbol{\xi} + \delta\boldsymbol{\xi}) = f_i(\boldsymbol{\xi}) + \sum_{j=1}^{N} \frac{\partial f_i}{\partial \xi_j} \delta\xi_j + O(\delta\boldsymbol{\xi}^2), \tag{37}$$

where $O(\delta\boldsymbol{\xi}^2)$ is higher derivative therm, which we can neglect. If we write equation 37 in matrix form, we obtain

$$\mathbf{f}(\boldsymbol{\xi} + \delta\boldsymbol{\xi}) = \mathbf{f}(\boldsymbol{\xi}) + \mathbf{J}\delta\boldsymbol{\xi}, \tag{38}$$

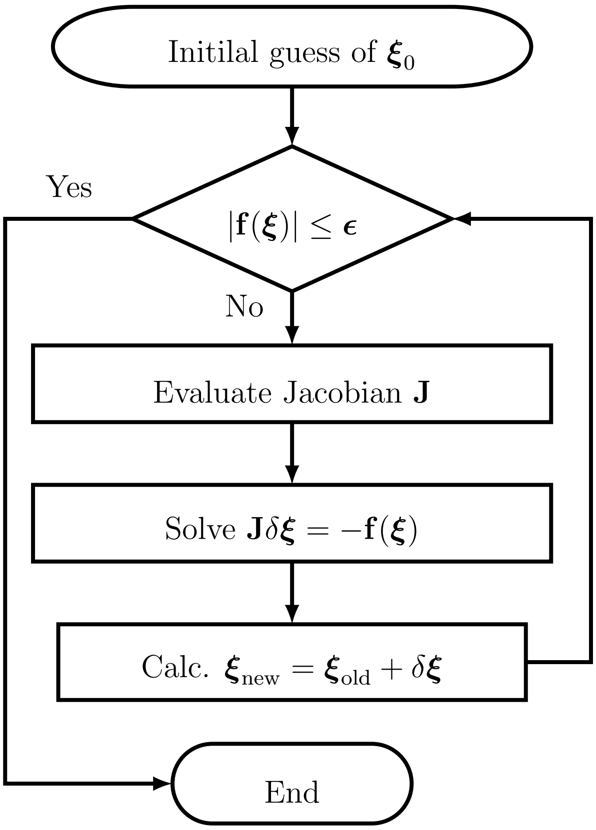
where $\mathbf{J}$ is a matrix of first derivations called Jacobian matrix. By setting $\mathbf{f}(\boldsymbol{\xi} + \delta\boldsymbol{\xi}) = 0$, we obtain a system of linear equations which provides a vector of corrections $\delta\boldsymbol{\xi}$. This vector will, in each step, lead the system (eq. 37) towards the solution (zero)

$$\mathbf{J}\delta\boldsymbol{\xi} = -\mathbf{f}(\boldsymbol{\xi}), \tag{39}$$

and then

$$\boldsymbol{\xi}_{\text{new}} = \boldsymbol{\xi}_{\text{old}} + \delta\boldsymbol{\xi}. \tag{40}$$

This system of linear equations eq 39 could be solved by tools of linear algebra (i.e. LU decomposition).



In most scientific programming languages a variety of tools is available to solve a system of nonlinear equation. Most of them are based on set of `FORTRAN` routines called `MINPACK`[3]. This routines are compiled in Matlab and Octave respectively and are accessible by the command `fsolve`.

Example: 1.7

A system of simultaneously occurring reactions is shown in following table

NR		**Reaction**		$\mathbf{K}_{eq}$ (900K)
1	A+B	=	C+D	1.00
2	B+C	=	X+Y	2.63
3	A+X	=	Z	5.00

Evaluate the equilibrium composition of reaction mixture at temperature of 900 K. Assume the ideal behavior of gas phase, pressure of 1 MPa and initial composition of the reaction mixture 2.5 mol A a 1.5 mol B.

Help

As initial guess for ξ use

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[3] see `http://www.netlib.org/minpack/`.

$\xi_1 = 0.7$
$\xi_2 = 0.6$
$\xi_3 = 0.5$

Solution

Equilibrium composition of reac. mixture 0.33 A, 0.02 B, 0.03 C, 0.23 D, 0.01 X, 0.19 Y, 0.18 Z.

Total conversion of A is 0.55.

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2 Reaction kinetics

2.1 Reaction rate

Definition of reaction rate is given by following equation

$$r = \frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{1}{\nu_i}\frac{\mathrm{d}n_i}{\mathrm{d}t}, \tag{41}$$

where ξ is reaction extent and n_i is a number of mols of i-th compound. Specific reaction rate is defined for following cases

- Reaction rate related to volume (volume of the system, the catalyst or the reaction mixture)
$$r_V = \frac{1}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{42}$$
- Related to the mass of catalyst
$$r_w = \frac{1}{W}\frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{43}$$
- Related to the inter-phase area
$$r_S = \frac{1}{S}\frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{44}$$

Example: 2.1
Consider a reaction

$$\mathrm{A} = 2\,\mathrm{R},$$

which occurs in closed vessel filled up with non-porous spherical particles. Specific area of the catalyst particles is 200 $\mathrm{m^2m^{-3}}$, its specific density 2500 $\mathrm{kg.m^{-3}}$ and the void fraction is $\epsilon = 0.4$. The rate of disappearing of compound A related to the mass of the catalyst is

$$r_{W,\mathrm{A}} = \frac{1}{W}\frac{\mathrm{d}n_\mathrm{A}}{\mathrm{d}t} = -0.1c_\mathrm{A}$$

a) What is the unit of k_W ?

b) Write the rate equation and the value of k_V for reaction rate related to the volume of the catalyst?

c) Write the rate equation and the value of k_S for reaction rate related to the surface of the catalyst?

Example: 2.2
In flow catalytic reactor the synthesis of methanol is carried out

$$\mathrm{CO} + 2\,\mathrm{H_2} = \mathrm{CH_3OH}$$

The inlet mass flow rate of CO is 1000 $\mathrm{kg\,h^{-1}}$ of CO and the inlet flow rate of hydrogen is supplied so that the inlet molar ratio H_2:CO is equal to 2:1. 1200 kg of the catalyst is placed in the reactor. The outlet mass flow of CO is 860 $\mathrm{kg\,h^{-1}}$.

Calculate:

1. Mean reaction rate per mass of catalyst in $\mathrm{mol\,kg^{-1}s^{-1}}$
2. If specific internal surface of catalyst is 55 $\mathrm{m^2g^{-1}}$, calculate mean reaction rate per surface of catalyst in $\mathrm{mol\,m^2s^{-1}}$
3. If per 1 $\mathrm{m^2}$ of catalyst contains 10^{19} active sites, calculate mean reaction rate per active site in $\mathrm{s^{-1}}$.
4. Calculate inlet and outlet gas mixture composition in molar fractions

Data: M_{CO}= 28.010 $\mathrm{kg\,kmol^{-1}}$, NA=6.0221·10^{23} $\mathrm{mol^{-1}}$ (Avogadro number)

2.2 Temperature dependence of reaction rate

The reaction rate temperature dependence is usually expressed by Arrhenius relationship as temperature dependence of kinetic constant k

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{E}{\mathbf{R}T^2}, \tag{45}$$

where E is activation energy.

Example: 2.3
Estimate the reaction rate constant for following first order reaction

$$\mathrm{A} = \mathrm{B} + \mathrm{C},$$

for which the values of k were determined at different temperatures:

T / K	313.0	319.0	323.0	328.0	333.0
k / s^{-1}	0.00043	0.00103	0.00180	0.00355	0.00717

Solution: $E = 121.5$kJ mol^{-1}

Example: 2.4
Evaluate the relative uncertainty in reaction rate constant for a measurement where the uncertainty in temperature determination is about 1 K. The measurement is carried out at 50 °C and the activation energy is 25 kJ mol^{-1}.

Solution: $\sigma_r = 2.8\%$

2.3 Kinetics of elementary reactions

Consider a elementary irreversible reaction

$$\mathrm{A} \rightarrow \mathrm{B}. \tag{46}$$

From equation 41 we can derive a time profile of concentration of a compound involved in above chemical reaction

$$\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} = \nu_\mathrm{A} r_\mathrm{V}, \tag{47}$$

where r_V is reaction rate expressed in therms of power law kinetics

$$r_\mathrm{V} = k c_\mathrm{A}, \tag{48}$$

where k is the rate constant of reaction 51. Then to obtain concentration of a compound A as function of time ($c_\mathrm{A} = f(t)$), we have to solve following differential equation

$$\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} = \nu_\mathrm{A} k c_\mathrm{A}. \tag{49}$$

After elementary mathematical operations we obtain

$$c_\mathrm{A} = c_{\mathrm{A}^0}\, e^{(\nu_\mathrm{A} k t)}, \tag{50}$$

where c_{A^0} is initial concentration of compound A.

Example: 2.5
Draw a figure showing time profiles of simple reaction

$$\begin{array}{ccc} \mathrm{A} & \rightarrow & \mathrm{B} \\ \nu_\mathrm{A}\mathrm{A} & + & \nu_\mathrm{B}\mathrm{B} = 0 \end{array}$$

for compound A, B and the conversion of A. Consider following reaction rate expressions

1. $r_\mathrm{V} = kc_\mathrm{A}$, $k = 1\ \mathrm{s}^{-1}$ and $c_{\mathrm{A}^0} = 1\ \mathrm{mol\ m}^{-3}$
2. $r_\mathrm{V} = kc_\mathrm{A}^n$, $k = 1\ (\mathrm{mol}^{-1}\mathrm{m}^3)^{(n-1)}\mathrm{s}^{-1}$ where $n = -1 \ldots 5$ and $c_{\mathrm{A}^0} = 1\ \mathrm{mol\ m}^{-3}$
3. $r_\mathrm{V} = kc_\mathrm{A}$, and $c_{\mathrm{A}^0} = 1\ \mathrm{mol\ m}^{-3}$, $k = 1\ \mathrm{s}^{-1}$ for $\nu_\mathrm{A} = -2$

Compare analytic solution and numerical solution of the problem.

Example: 2.6

Consider a simple equilibrium reaction

$$\mathrm{A} \rightleftharpoons \mathrm{B}.$$

Evaluate concentration time profiles for different ratios of rate constants of forward and backward reactions.

Solution

The above reaction can be written as two parallel reactions

$$\begin{aligned} 1 &: \mathrm{A} \longrightarrow \mathrm{B} \qquad r_{\mathrm{V},1} = k_1 c_\mathrm{A} \\ 2 &: \mathrm{B} \longrightarrow \mathrm{A} \qquad r_{\mathrm{V},2} = k_2 c_\mathrm{B}, \end{aligned}$$

and for time evolution of compounds A and B the differential equations are as follows

$$\begin{aligned} \frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} &= \sum_{j=1}^{NR} \nu_{\mathrm{A},j} r_{\mathrm{V},j} \\ \frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} &= \sum_{j=1}^{NR} \nu_{\mathrm{B},j} r_{\mathrm{V},j}, \end{aligned}$$

or in matrix form

$$\frac{\mathrm{d}\mathbf{c}}{\mathrm{d}t} = \boldsymbol{\nu}^T \mathbf{r},$$

which gives for our simple reaction

$$\begin{aligned} \frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} &= k_2 c_\mathrm{B} - k_1 c_\mathrm{A} \\ \frac{\mathrm{d}c_\mathrm{B}}{\mathrm{d}t} &= k_1 c_\mathrm{A} - k_2 c_\mathrm{B}. \end{aligned}$$

Above differential equation can be solved analytically for c_A assuming $c_\mathrm{B} = c_{\mathrm{A}0} + c_{\mathrm{B}0} - c_\mathrm{A}$ by variation of constant or using integration factor

$$\begin{aligned} \frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} &= k_2(c_{\mathrm{A}0} + c_{\mathrm{B}0} - c_\mathrm{A}) - k_1 c_\mathrm{A} \\ c_\mathrm{A} &= c_{\mathrm{A}0} \exp\left(-(k_1 + k_2)t\right) + \frac{k_2(c_{\mathrm{A}0} + c_{\mathrm{B}0})}{k_1 + k_2} \left[1 - \exp\left(-(k_1 + k_2)t\right)\right]. \end{aligned}$$

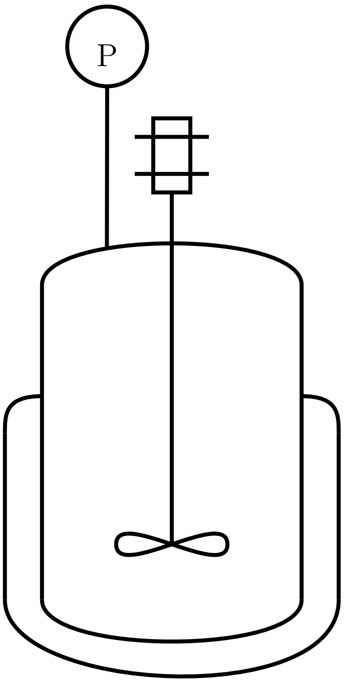
3 Ideal isothermal reactors

Equations describing behavior of the reacting mixture (in time and space) are formulated on the basis of the material balance of an extensive property B in space element for a time interval

$$\left(\begin{array}{l}\textbf{Amount of}\\ B \textbf{ entering}\\ \textbf{into element}\\ \textbf{per } \Delta t\end{array}\right) + \left(\begin{array}{l}\textbf{Source of}\\ B \textbf{ in the}\\ \textbf{element}\end{array}\right) = \left(\begin{array}{l}\textbf{Amount of}\\ B \textbf{ leaving}\\ \textbf{element per}\\ \Delta t\end{array}\right) + \left(\begin{array}{l}\textbf{Acc. of } B\\ \textbf{in the element}\end{array}\right) \tag{51}$$

The extensive property B could be for example the mass, number of moles, enthalpy or momentum.

3.1 Ideally stirred tank reactor (BATCH)



$$\underbrace{\dot{F}_i^0 - \dot{F}_i}_{0} + \sum_{k=1}^{NR} \nu_{k,i} \int_V r_{V,k} \mathrm{d}V = \frac{\partial n_i}{\partial t}, \tag{52}$$

where $\dot{F}_i$ is the molar flow of i, $\nu_{k,i}$ is stoichiometric coefficient of i in k-th reaction, r_V is the reaction rate of k-th reaction related to the volume of the reaction mixture and n_i is the number of moles of i. For constant volume of the reaction mixture V

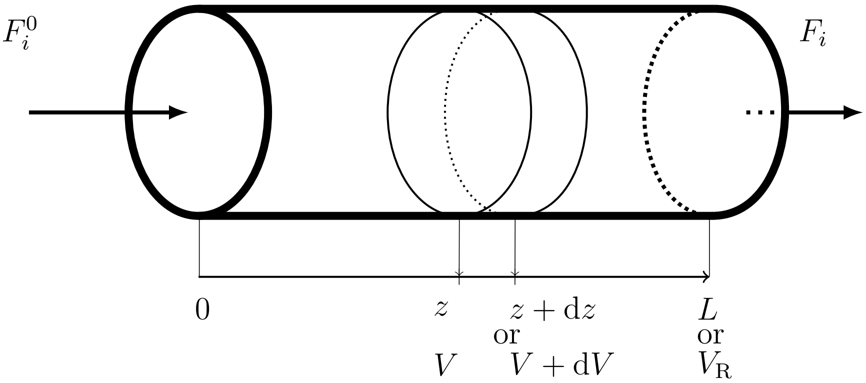
$$\frac{1}{V}\frac{\mathrm{d}n_i}{\mathrm{d}t} = \frac{\mathrm{d}(n_i/V)}{\mathrm{d}t} = \frac{\mathrm{d}c_i}{\mathrm{d}t} = \sum_{k=1}^{NR} \nu_{k,i} r_{V,k}. \tag{53}$$

For constant pressure we can write

$$\frac{1}{V}\frac{\mathrm{d}n_i}{\mathrm{d}t} = \frac{1}{V}\frac{\mathrm{d}(c_iV)}{\mathrm{d}t} = \frac{\mathrm{d}c_i}{\mathrm{d}t} + c_i\frac{\mathrm{d}\ln V}{\mathrm{d}t} = \sum_{k=1}^{NR} \nu_{k,i} r_{V,k}. \tag{54}$$

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = \sum_{k=1}^{NR} \nu_{k,i} r_{V,k} - c_i\frac{\mathrm{d}\ln V}{\mathrm{d}t} \tag{55}$$

3.2 Plug flow reactor (PFR)



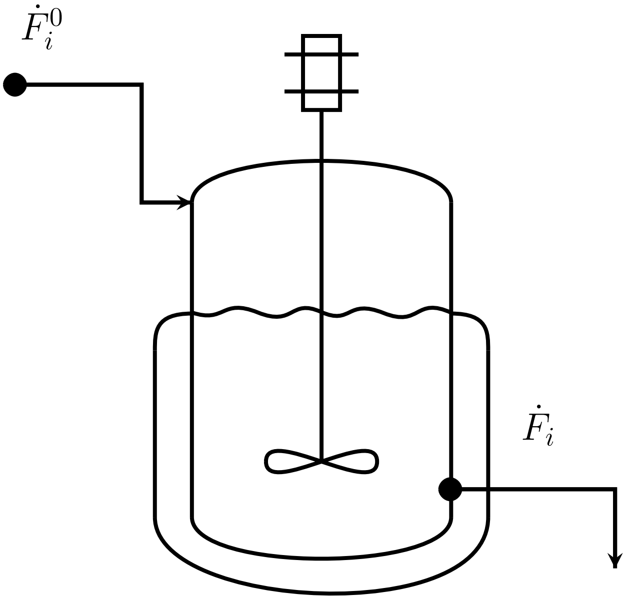
$$\underbrace{F_{(V+\mathrm{d}V)} - F_{(V)}}_{\text{in-out}} = \sum_{k=1}^{NR} \nu_{k,i} r_{V,k} \mathrm{d}V, \tag{56}$$

$$\frac{\mathrm{d}F_i}{\mathrm{d}V} = \sum_{k=1}^{NR} \nu_{k,i} r_{V,k} \tag{57}$$

$$\frac{\mathrm{d}J_i}{\mathrm{d}z} = \sum_{k=1}^{NR} \nu_{k,i} r_{V,k} \tag{58}$$

$$\frac{\mathrm{d}(vc_i)}{\mathrm{d}z} = \sum_{k=1}^{NR} \nu_{k,i} r_{V,k} \tag{59}$$

3.3 Continuous ideally stirred tank reactor (CSTR)



In steady state

$$\underbrace{F_i^0 - F_i}_{\text{in-out}} + \sum_{k=1}^{NR} \nu_{k,i} r_{V,k} V_R \quad = \quad 0. \tag{60}$$

Example: 3.1
Following reaction takes place in isothermal plug flow reactor

$$2\,\mathrm{A} \quad = \quad \mathrm{B}.$$

Reaction occurs in liquid phase with compound C as inert, the velocity of the reaction mixture is constant along the reactor and is 0.5 m.s^{-1}. Rate of generation of compound B is described by $r_\mathrm{B} = \nu_\mathrm{B} k c_\mathrm{A}^2$. Rate constant is 0.3 m^3.kmol^{-1}.s^{-1} and the reactor length is 2.4 m. At reactor inlet we consider $c_A(0) = 2\,\mathrm{kmol.m^{-3}}$, $c_B(0) = 0\,\mathrm{kmol.m^{-3}}$, $c_C(0) = 2\,\mathrm{kmol.m^{-3}}$. Derive equations describing concentrations profiles of all compounds and evaluate the conversion of compound A. Compare analytic and numeric solution of the problem.

Solution

Material balance:

Compound	$z = 0$	$z = L$
A	c_{A^0}	$c_\mathrm{A} = c_{\mathrm{A}^0} - \frac{\nu_\mathrm{A}}{\nu_\mathrm{A}} c_{\mathrm{A}^0} X_\mathrm{A}$

Material balance of PFR (eq. 59)

$$\frac{\mathrm{d}c_i}{\mathrm{d}z} = \frac{1}{v}\nu_i r_V. \tag{61}$$

For overall reaction rate r_V

$$r_\mathrm{V} = r_\mathrm{B}/\nu_\mathrm{B} = kc_\mathrm{A}^2. \tag{62}$$

Writing 61 for component A, we obtain a differential equation in therms of conversion of component A

$$\frac{\mathrm{d}X_\mathrm{A}}{\mathrm{d}z} = -\frac{\nu_\mathrm{A} r_V}{v c_{\mathrm{A}^0}}. \tag{63}$$

To obtain analytic solution we have to solve eq. 63, by separating variables and integrating obtained equation

$$-\frac{v c_{\mathrm{A}^0}}{\nu_\mathrm{A}} \int_0^f \frac{1}{r_\mathrm{V}} \mathrm{d}X_\mathrm{A} = \int_0^L \mathrm{d}z, \tag{64}$$

where f is the unknown conversion and L is reactor length. Substituting r_V from equation 62 and c_A from material balance we obtain

$$-\frac{v}{k c_{\mathrm{A}^0} \nu_\mathrm{A}} \int_0^f \frac{1}{(1-X_\mathrm{A})^2} \mathrm{d}X_\mathrm{A} = \int_0^L \mathrm{d}z, \tag{65}$$

and

$$-\frac{v}{k c_{\mathrm{A}^0} \nu_\mathrm{A}} \left(\frac{1}{1-f} - 1 \right) = L. \tag{66}$$

For f we obtain

$$f = 1 - \frac{v}{v - Lkc_{A^0}\nu_A}. \tag{67}$$

Example: 3.2

Ethyl acetate is produced by esterification of acetic acid with ethanol in BATCH isothermal reactor. Stoichiometry of the reaction is as follows

$$\mathrm{CH_3COOH(A) + CH_2CH_3OH(B) = CH_3COOC_2H_5(R) + H_2O(S)}$$

Reaction mixture contains 500 kg m^{-3} of ethanol and 250 kg m^{-3} of acetic acid. Remaining of the reaction mixture is water with traces of HCl as catalyst. Density of reaction mixture is 1040 kg m^{-3} and is assumed to be constant.

Reaction rate of the esterification reaction (equilibrium reaction) is described

$$r_1 = k_1 c_\mathrm{A} c_\mathrm{B}, \tag{68}$$

$$r_2 = k_2 c_\mathrm{R} c_\mathrm{S}, \tag{69}$$

$$r_\mathrm{V} = r_1 - r_2. \tag{70}$$

Values of rate constants are at 373 K

$$\begin{aligned} k_1 &= 8\times 10^{-9} \qquad \mathrm{m^3mol^{-1}s^{-1}}, \\ k_2 &= 2.55\times 10^{-9} \qquad \mathrm{m^3mol^{-1}s^{-1}}. \end{aligned}$$

Reaction is stopped ant conversion $X_\mathrm{A} = 0.3$. If we consider, that for reactor emptying, cleaning and filling we need 30 min. calculate the reactor volume for daily production 10 t of ethyl acetate.

Result: V = 7 m^3

Example: 3.3

In constant volume BATCH reactor take place at constant temperature the following reaction

$$a\mathrm{A} + b\mathrm{B} = s\mathrm{S}.$$

Reaction rate is described by $r_V = kc_\mathrm{A}^\alpha c_\mathrm{B}^\beta$, where $\alpha \neq 0$ and $\beta \neq 0$. Express a general (differential) form the time dependence of the conversion of compound A.

Solution:

$\frac{\mathrm{d}X_\mathrm{A}}{\mathrm{d}t} = -akc_\mathrm{A0}^{(\alpha-1)}\left((1-X_\mathrm{A})^\alpha(c_\mathrm{B0} - \frac{b}{a}c_\mathrm{A0}X_A)^\beta\right)$

Example: 3.4

A new catalyst is planned for use in the phosgene plant. It is assumed that the existing reactor will be used. Its dimensions are: Volume 4 L, maximal working pressure is 300 kPa and working temperature 150°C. Inlet total molar flow is: F^0=0.244 $\mathrm{mol\,s^{-1}}$, and its molar composition is $y^0_\mathrm{CO} = y^0_\mathrm{Cl_2} = 0.5$. Phosgene synthesis is described by following reaction

$$\mathrm{CO(A) + Cl_2(B) \rightarrow COCl_2(C)}. \tag{71}$$

Kinetic equation describing the reaction rate was derived on the basis of the steady state hypothesis (SSH),

$$r_\mathrm{V} = kc_\mathrm{A}c_\mathrm{B}^{3/2}. \tag{72}$$

Two sets of experimental data for two different catalysts were found in the literature.

In the first article catalyst α was studied in constant volume BATCH reactor at 423 K. Reactor contained an equimolar mixture of CO and Cl$_2$ at 600 kPa at the beginning of the experiment. Obtained experimental data are shown in table 2.

In second paper a PFR was used to examine the convesion dependence on residence time for catalys of type β. Volume of the catalys bed was 2 ml, rector temperature 423 K and reactor pressure 300 kPa. The feed was an stoichiometric mixture of CO and Cl$_2$. Experimental data are summarized in table 2.

Calculate the conversion of CO at the outlet of the industrial reactor for both catalysts (α a β).

Table 2: Experimental data for phosgene synthesis obtained on two different types of catalyst(α a β).

Cat. α, BATCH		Cat. β, PFR	
t / s	p / Pa	t_r / s	X_{A}
0	599554	45.9	0.997
2	434817	22.9	0.995
4	393038	9.2	0.992
6	373953	4.6	0.987
8	378726	2.3	0.979
10	357128	1.5	0.971
12	351020	1.1	0.965
14	336651	0.9	0.958
16	343442	0.8	0.952
18	337214	0.7	0.946
20	325668	0.5	0.928
22	333051	0.2	0.871
24	342957		
26	327858		
28	321577		
30	325457		
32	334276		
34	319888		
36	329878		
38	317612		

Solution:
$k_{\alpha,\mathrm{BATCH}} = 1.1 \times 10^{-3}\ (\mathrm{m^3mol^{-1}})^{3/2}\mathrm{s^{-1}}$, $X_{\mathrm{CO},\alpha} = 0.330$
$k_{\beta,\mathrm{PFR}} = 57.2 \times 10^{-3}\ (\mathrm{m^3mol^{-1}})^{3/2}\mathrm{s^{-1}}$, $X_{\mathrm{CO},\beta} = 0.965$
Help:
$\int_0^X ((2-X)/(1-X))^{5/2}\mathrm{d}X =$

$$2\left(\frac{\left(\frac{2-x}{1-x}\right)^{\frac{3}{2}} + 6\sqrt{\frac{2-x}{1-x}}}{3} - \frac{\sqrt{\frac{2-x}{1-x}}}{\frac{2\,(2-x)}{1-x} - 2} - \frac{5\,\ln\left(\sqrt{\frac{2-x}{1-x}} + 1\right)}{4} + \frac{5\,\ln\left(\sqrt{\frac{2-x}{1-x}} - 1\right)}{4}\right)$$

Example: 3.5

Compound B undergoes a dimerization

$$2\mathrm{B} = \mathrm{R}.$$

The reaction occurs at 600 K in gas phase and is performed in discountinous BATCH constant volume reactor. At the beginning the reactor is filled by pure compound B under pressure of 1.5 bar. Reaction rate is

$$r_\mathrm{V} = kp_\mathrm{B}^2,$$

where k is $2.5{\cdot}10^{-13}$ mol $\mathrm{m^{-3}Pa^{-2}s^{-1}}$. Calculate the composition of the reaction mixture and its pressure after one hour of the reaction.

Solution:
$x_\mathrm{B} = 0.60, p = 1.06\ \mathrm{bar}$

Example: 3.6

An irreversible first-order reaction gave 80% conversion in a batch reactor in 20 min

1. Calculate the total residence time for this conversion for CSTRs in series for 1,2,3, and 4 equal-volume reactors.
2. What residence time will be required for a very large number of equal-volume CSTRs?

Example: 3.7

(Taken from Hill, Introduction to Chemical Engineering Kinetics and Reactor Design) Walter [J. Chem. Eng. Data 5 (468), 1960] has studied the kinetics of ethylene chloride pyrolysis over a pumice catalyst.

$$\mathrm{ClCH_2{-}CH_2Cl} \longrightarrow \mathrm{HCl} + \mathrm{CH_2{=}CHCl}$$

The reactor consists of a cylindrical tube 59 cm long packed with pumice stone. The catalyst charge was constant in all of the runs below and equal to W. The reactor void volume was approximately 100 cm^3. The reaction is believed to be first-order in ethylene chloride under the conditions of this study and in all cases the feedstock was pure reactant. Both the reactants and the products are gases at the conditions involved. Ideal gases may be assumed. The following data were reported at 600°C and one atmosphere.

Input flow rate (moles/ksec)	Fractional conversion
0.550	0.86
0.544	0.85
0.344	0.94

Calculate:

a) What is the reaction rate constant at 600°C in s^{-1}?

b) If the reaction rate constant at 500°C is 0.141 s^{-1}, what is the activation energy for the reaction?

Example: 3.8

(Taken from Hill, Introduction to Chemical Engineering Kinetics and Reactor Design) Acetaldehyde is to be decomposed in a tubular reactor operating at 520°C and 101 kPa. The reaction stoichiometry is

$$\mathrm{CH_3CHO} \longrightarrow \mathrm{CH_4} + \mathrm{CO}$$

Under these conditions the reaction is known to be irreversible with a rate constant of 0.43 m^{3}kmol^{-1}s^{-1}. If 0.1 kg s^{-1} of acetaldehyde is fed to the reactor, determine the reactor volume necessary to achieve 35% decomposition.

Example: 3.9

(Taken from Hill, Introduction to Chemical Engineering Kinetics and Reactor Design) The following gas phase reaction takes place at 120°C in a tubular reactor.

$$\mathrm{A} + 2\,\mathrm{B} \longleftrightarrow \mathrm{C} + \mathrm{D}$$

The initial concentrations of A and B in the feedstream are each 10 mol m^{-3}. The remainder of the stream consists of inerts at a concentration of 30 mol m^{-3}. The reaction is reversible and substantial amounts of all species exist at equilibrium under the pressure and temperature conditions employed. The forward reaction is first-order with respect to A and first- order with respect to B. At 120°C the rate constant for the forward reaction is 1.4 m^{3}mol^{-1}ksec^{-1}. The reverse reaction is first-order in C, first-order in D, and inverse first-order in B. The rate constant for the reverse reaction is 0.6 ksec^{-1}. Determine the reactor volume necessary to convert 60% of the limiting reagent at a total input flow rate of 100 liters hr^{-1}.

4 Ideal non-isothermal reactors

Energy (E) balance could be formulated as follows

$$\begin{aligned}\begin{pmatrix}\textbf{Acumulation}\\ \textbf{of } E \textbf{ in the}\\ \textbf{system}\end{pmatrix} &= \begin{pmatrix}\textbf{Exchange of}\\ E \textbf{ through}\\ \textbf{systems}\\ \textbf{boundaries}\end{pmatrix} - \begin{pmatrix}\textbf{Amount of}\\ \textbf{work done by}\\ \textbf{the system}\end{pmatrix}\\ &+ \begin{pmatrix}\textbf{Amount of}\\ E \textbf{ provided}\\ \textbf{by the feed}\\ \textbf{stream}\end{pmatrix} - \begin{pmatrix}\textbf{Amount of}\\ E \textbf{ removed}\\ \textbf{by the outlet}\\ \textbf{stream}\end{pmatrix}\end{aligned} \tag{73}$$

Enthalpy (partial molar enthalpy) is usually used as the energy unit.

4.1 Energy balance for CSTR

$$\frac{\mathrm{d}T}{\mathrm{d}t}\sum_{i=1}^{N} n_i C_{p,i} = \kappa A_m (T_m - T) - \sum_{i=1}^{N} F_i^o C_{p,i}\,(T - T_0) + (-\Delta H_R) r_V V_R. \tag{74}$$

4.2 Energy balance for BATCH

$$\frac{\mathrm{d}T}{\mathrm{d}t}\sum_{i=1}^{N} n_i C_{p,i} = \kappa A_m (T_m - T) + (-\Delta H_R) r_V V_R. \tag{75}$$

4.3 Energy balance for PFR (steady state)

$$\frac{\mathrm{d}T}{\mathrm{d}z}\sum_{i=1}^{N} F_i C_{p,i} = \pi d_R \kappa (T_m - T) + (-\Delta H_R) r_V \pi d_R^2/4, \tag{76}$$

Example: 4.1
Sulfur dioxide SO_2 is oxidized in a micro-structured device according to

$$\mathrm{SO_2} + \frac{1}{2}\mathrm{O_2} = \mathrm{SO_3}. \tag{77}$$

We assume no external mass transfer effects and the reaction rate (r_V in $\mathrm{mol\,s^{-1}\,m^{-3}}$) is described by

$$r_V = k\left(y_{\mathrm{SO_2}} y_{\mathrm{O_2}}^{0.5} - \frac{y_{\mathrm{SO_3}}}{K}\right), \tag{78}$$

where y_i are molar fractions, k is the rate constant and K is the equilibrium constant. The rate constant is dependent on temperature

$$k = 1.05 \cdot 10^7 \exp\left(\frac{-60000}{\mathrm{R}T}\right), \tag{79}$$

where k has units $(\mathrm{mol\,s^{-1}\,m^{-3}})$. Equilibrium constant is described by following equation

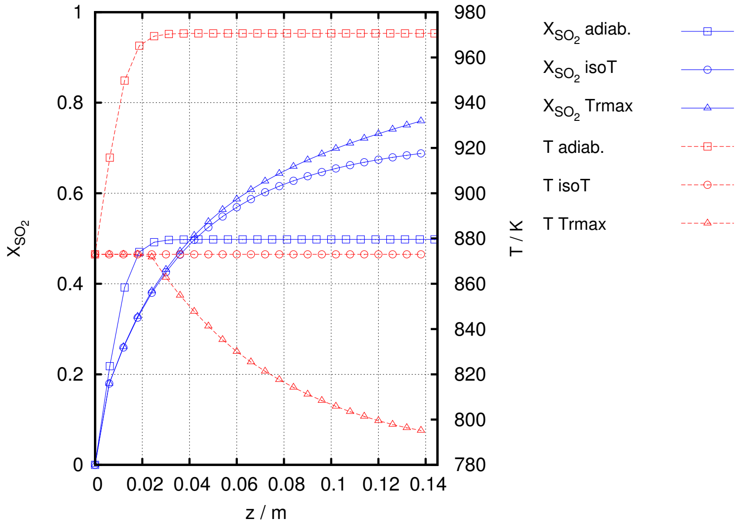
$$\ln K = -11.12 + 11750/T. \tag{80}$$

The enthalpy of reaction is assumed to be constant $\Delta H_R = -98\ \mathrm{kJ\,mol^{-1}}$ ans well as the molar heat capacity of the reaction mixture $C_p = 30\ \mathrm{J\,mol^{-1}\,K^{-1}}$. Feed composition in molar fraction is 0.06 SO_2, 0.15 O_2, 0.0 SO_3 and 0.79 N_2. Feed rate is $1.50{\cdot}10^{-6}\ \mathrm{mol\,s^{-1}}$ and its temperature is 873 K. The reactor is considered as isobaric and is keep at 101 kPa. Reactor length is 0.15 m and its diameter d_R is 250 $\cdot 10^{-6}$ m.

Calculate SO_2 conversion and temperature profile if:

1. The reactor is isothermal
2. The reactor behaves adiabatically
3. The reactor has an optimal temperature profile

Solution

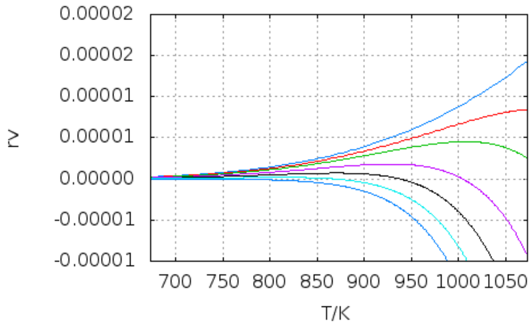


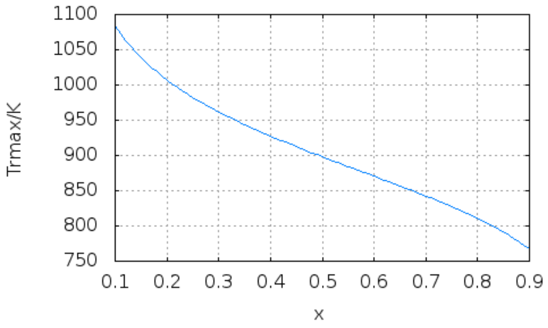
To evaluate optimal temperature profile we need to solve

$$\frac{\mathrm{d}r_V}{\mathrm{d}T} = 0 \tag{81}$$

after rearrangement

$$
\begin{aligned}
0 &= \frac{E_a \exp\left(-\frac{E_a}{\mathbf{R}T}\right)\left(y_{\mathrm{SO}_2}\sqrt{y_{\mathrm{O}_2}} - y_{\mathrm{SO}_3}\exp\left(-\frac{A_2}{T} - A_1\right)\right)}{\mathbf{R}} - \\
&- A_2 y_{\mathrm{SO}_3} \exp\left(-\frac{E_a}{\mathbf{R}T} - \frac{A_2}{T} - A_1\right)
\end{aligned}
$$





Example: 4.2

In PFR following reaction take place in liquid phase

$$\mathrm{A} \rightleftharpoons \mathrm{B}. \tag{82}$$

Feed is composed by compound A and an inert I. Inlet molar ratio is A:I=0.5. Reaction rate is described by

$$r_V = k\left(c_{\mathrm{A}} - \frac{c_{\mathrm{B}}}{K}\right), \tag{83}$$

where K is an equilibrium constant. Following table contains all needed add itional data

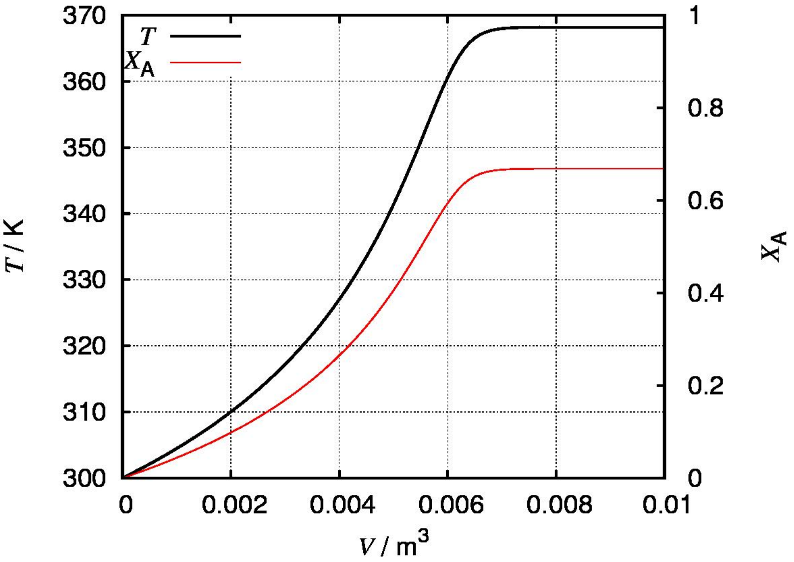
c_{A}^0	2000	mol m^{-3}	Ea	41.8	kJ mol^{-1}
F_{A}^0	0.083	mol s^{-1}	ΔH_R	-83.6	kJ mol^{-1}
F_{B}^0	0	mol s^{-1}	K	1000	(300 K)
F_{I}^0	0.167	mol s^{-1}	k_1	0.0017s^{-1}	(300 K)
$C_{\mathrm{p,A}}$	668	J mol^{-1} K^{-1}	V_R	0.01	m^3
$C_{\mathrm{p,B}}$	668	J mol^{-1} K^{-1}			
$C_{\mathrm{p,I}}$	75	J mol^{-1} K^{-1}			

Calculate conversion of compound A if the PFR behaves adiabatically. Consider the density of the reacting mixture to be constant.

Solution & help

Equilibrium constant is a function of temperature

$$\left(\frac{\partial \ln K_a}{\partial T}\right)_p = \frac{\Delta H_R}{\mathbf{R}T^2}$$



Example: 4.3

Compound B is produced in constant volume BATCH equipped by an external cooling. The reaction is highly exothermic

$$\mathrm{A} \longrightarrow \mathrm{B}, \qquad (\Delta H_R = -200\ \mathrm{kJ\ mol^{-1}}) \tag{84}$$

Reaction rate is described by following equation

$$r_V = k c_\mathrm{A}, \tag{85}$$

where reaction rate constant is

$$k = 2.5 \cdot 10^{-5} \exp\left(\frac{68 \cdot 10^3 (T - T_0)}{\mathrm{R} T T_0}\right), \tag{86}$$

The k is in s^{-1} and T_0 is the reference temperature equal to $273\ \mathrm{K}$.

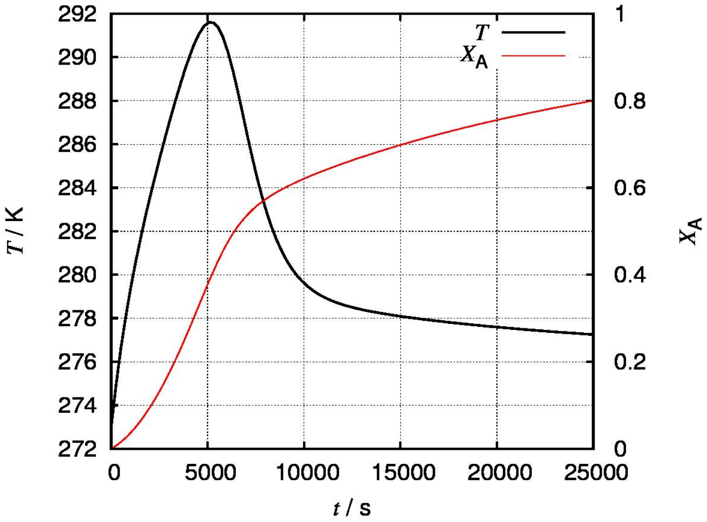
A BATCH reactor of volume 0.5 m^3 is used. Heat transfer coefficient is 6.25 $\mathrm{kW\ m^{-2}\ K^{-1}}$ ant the area is 0.42 m^2. Reaction mixture properties are:

Specific heat capacity c_p	4200	$\mathrm{J\ kg^{-1}\ K^{-1}}$
Density ρ	1000	$\mathrm{kg\ m^{-3}}$
c_{A^0}	4000	mol m^{-3}

Calculate the temperature of cooling media in order to obtain the conversion $X_{\mathrm{A}} \approx 0.8$ in shortest reaction time possible and keep the reaction mixture temperature under 410 K (temperature of decomposition of product B). The accuracy of the cooling media temperature control is 2 K.

Solution

$T_m = 276$ K, $\qquad t_{reac} \approx 7$ hr



Example: 4.4

A reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow 2\,\mathrm{C} \qquad (\Delta H_{\mathrm{R}} = -83.74\ \mathrm{kJ\,mol^{-1}})$$

is carried out in a CSTR. The reaction rate is described by

$$r_V = k c_{\mathrm{A}} c_{\mathrm{B}}, \tag{87}$$

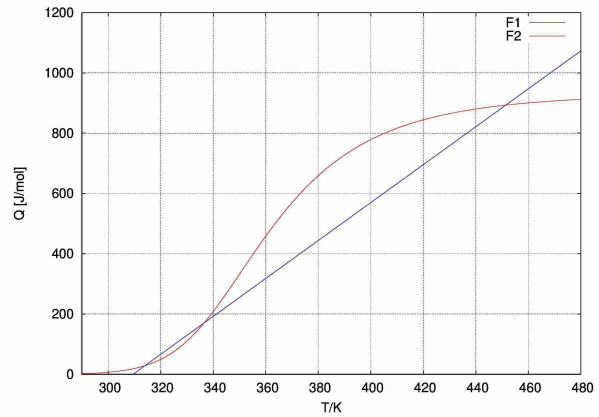
where the rate constant is a function of temperature according to

$$k = 0.55 \cdot 10^6 \exp\left(-\frac{1 \cdot 10^4}{T}\right), \qquad k[\mathrm{s^{-1}\ mol^{-1}\ m^3}] \tag{88}$$

The heat exchange area is 0.025 m^2 and the heat transfer coefficient is 70 $\mathrm{W\,m^{-2}\,K^{-1}}$. Heat capacity of the reaction mixture $c_{\mathrm{p}} = 2720\mathrm{kJ\,m^{-3}\,K^{-1}}$. The feed is a equimolar mixture of A and B, C_{A}^0=6.67·$10^3\mathrm{mol\,m^{-3}}$. The feed rate is 1.67·$10^{-6}\mathrm{m^3\,s^{-1}}$. Define and analyze steady states of the CSTR for feed temperature 290 K and temperature of the cooling media of 360 K.

Solution

$T_{1,s} = 314$ K, $T_{2,s} = 451$ K, $T_{3,s} = 336$ K



Example: 4.5

A first order reaction is carried out in an adiabatic CSTR[4]

$$\mathrm{A} \rightarrow prod.$$

The feed is compound A only and the feed rate is 300 l min^{-1}. Inlet Concentration of A is 4 mol l^{-1}. Data:

Parameter	Value	Units
c_A^0	2	kmol m^{-3}
k_ref	$1{\cdot}10^{-3}$	min^{-1}
ρ	1000	$\mathrm{kg\ m}^{-3}$
T_0	298	K
T_ref	298	K
ΔH_R	$-30{\cdot}10^4$	$\mathrm{kJ\ kmol}^{-1}$
$\hat{C}_\mathrm{p}$	4	$\mathrm{kJ\ kg}^{-1}\ \mathrm{K}^{-1}$
E	$8{\cdot}10^3$	K

Temperature dependence of the reaction constant is

$$k = k_\mathrm{ref} \exp\left(-E(1/T - 1/T_\mathrm{ref})\right)$$

Calculate the conversion as function of the residence time interval ($\tau = V_\mathrm{R}/\dot{V}$) 0 - 40 min.

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[4] For details see: Rawlings and Ekerdt: *Chemical Reactor Analysis and Design Fundamentals*, **Nob Hill Publishing**, Madison 2002, Fig. 6.8, http://jbrwww.che.wisc.edu/home/jbraw/chemreacfun/

Example: 4.6

During hydrogen production process (partial oxidation or steam reforming) the WGS[5] reaction is used to convert carbon mono-oxide

$$\mathrm{CO} + \mathrm{H_2O} \rightleftharpoons \mathrm{CO_2} + \mathrm{H_2}, \qquad (\Delta H_\mathrm{R} = -39.4\ \mathrm{kJmol^{-1}})$$

in tubular reactor (PFR) at atmospheric pressure. Feed consists of 19% (mol) of CO and feed temperature is 653 K. Molar heat capacity of the reaction mixture is constant c_p=33.9 J mol^{-1} K^{-1}. Calculate:

a) CO conversion if the temperature at the outlet is 773 K

b) Maximal adiabatic temperature rise in the reactor (theoretical)

c) Maximal temperature rise when taking into account the thermodynamic equilibrium of the WGS reaction

Solution

X_A=0.55, ΔT$_\mathrm{ad}$=220 K

Example: 4.7

In adiabatic CSTR following reaction takes place

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}, \qquad (\Delta H_R = -1396\ \mathrm{kJ\ mol^{-1}}) \tag{89}$$

The feed temperature is 298 K. Molar heat capacities and feed composition are summarized below:

Compound	$c_\mathrm{p}/\mathrm{kJ\ mol^{-1}\ K^{-1}}$	x_i^0
A	29.3	0.5
B	20.9	0.5
C	20.9	0
D	29.3	0

Calculate:

a) Outlet (reactor) temperature if the conversion of A is 70%

b) The change in outlet temperature if the feed composition changes from the initial one to 30% of A, 30% of B and 40% of en inert, which molar heat capacity is 41.9 $\mathrm{kJ\ mol^{-1}\ K^{-1}}$. The conversion of A remains the same as in previous case.

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[5] WGS - water gas shift

Solution

a)T=317 K, b)T=307 K

Example: 4.8

Consider following a reaction in adiabatic BATCH reactor

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C}, \qquad (\Delta H_R = -20\ \mathrm{kJ\ mol^{-1}})$$

At the beginning of the temperature in the reactor is 298 K. Compositions and molar heat capacities are as follows:

Složka	$c_\mathrm{p}/\mathrm{J\ mol^{-1}\ K^{-1}}$	c_i^0/mol m^{-3}
A	56	5000
B	56	7500
C	56	0

Calculate conversion of A if the reactor temperature increases after a laps of time to 393 K.

Solution

X_A=0.58

Example: 4.9

Irreversible, gas phase, first order reaction is performed in CSTR up to 20% conversion of A under constant pressure. Stoichiometrics of the reaction is je

$$\mathrm{A} \rightarrow \mathrm{B}.$$

Reaction rate is

$$r_V = k c_\mathrm{A},$$

where reaction rate constant k (s^{-1}) is

$$k(T) = k^\infty \exp\left(-\frac{E_a}{\mathbf{R}T}\right) = 1.55 \cdot 10^{13} \exp\left(-\frac{29441}{T}\right)$$

Consider the reaction enthalpy ΔH_R as well as the molar heat capacity independent on temperature and composition

$$\Delta H_R\ (T_0) = -243\ \mathrm{kJ\ mol^{-1}} \qquad \mathrm{a} \qquad c_\mathrm{p} = 190\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

Calculate the volume of an adiabatic CSTR and the outle temperature. Consider the ideal gas behavior and the steady state. Data

$$\begin{aligned}\text{Feed temperature, } T_0 &= 600\ \mathrm{K}\\ \text{Volumetric feed rate (at } T_0 \text{ and compound A only), } \dot{V}^0 &= 2.78 \cdot 10^{-3}\ \mathrm{m^3\ s^{-1}}\\ \text{Feed concentration of A (at } T_0\text{), } c_{A^0} &= 1000\ \mathrm{mol\ m^{-3}}\end{aligned}$$

Solution

V_R=40.4·10^{-3} m^3, T=856 K

Example: 4.10

Irreversible reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}, \qquad (\Delta H_R = -168 \text{ kJ mol}^{-1}) \tag{90}$$

is carried out in BATCH reactor. Temperature of the reaction mixture at the $\tau = 0$ s is 313 K and the concentration of A is 2.4 kmol m^{-3}. Mean molar heat capacity of the reaction mixture is constant (2.09 kJ kg^{-1} K^{-1}). The density of the reaction mixture could be also considered as constant (960 kg m^{-3}). Check if the reactor could be operated in adiabatic regime for a conversion of A of 40%, without exceeding a temperature of compound B decomposition (373 K).

Solution

No, because T=393 K

Example: 4.11

The hydrolysis of ethylenoxide(A) to ethylen glycol(C) is performed in continuous reactor (CSTR) of a volume 10 m^3

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}. \tag{91}$$

Required production of ethylene glycol is 8000 tons/year (8000 hrs). Feed concentration of ethylene oxide is 1.7 kmol m^{-3} and the reaction rate of the hydrolysis is

$$r = 1.19 \cdot 10^{-5} \exp\left(-\frac{8083.7}{T}\right) \, c_\mathrm{A} [\text{kmol m}^{-3} \text{ s}^{-1}].$$

Calculate the reaction temperature if the conversion of A is 90%,

Solution

T=459 K

Example: 4.12

In CSTR a first order irreversible reaction occurs

$$\mathrm{A} \rightarrow \mathrm{R} + \mathrm{S}. \tag{92}$$

Rate constant for this reaction at 298 K is $1.7{\cdot}10^{-4}$ s^{-1} and its activation energy is $41.87{\cdot}10^3$ J mol^{-1}. Needed data (independent on temperature):

$$\begin{aligned}
\Delta H_{\mathrm{reac.}} &= -167.5 \cdot 10^3\ \mathrm{J\ mol^{-1}} \\
\dot{V}^0 &= 8.5 \cdot 10^{-4}\ \mathrm{m^3\ s^{-1}} \\
T^0 &= 298\ \mathrm{K} \\
c_{\mathrm{A}}^0 &= 2000\ \mathrm{mol\ m^{-3}} \\
c_{\mathrm{R}}^0, c_{\mathrm{S}}^0 &= 0\ \mathrm{mol\ m^{-3}} \\
V_{\mathrm{REAC}} &= 0.5\ \mathrm{m^{-3}} \\
\rho_{\mathrm{mix}} &= 1050\ \mathrm{kg\ m^{-3}} \\
c_{\mathrm{p,mix}} &= 4.19 \cdot 10^3\ \mathrm{J\ kg^{-1}K^{-1}}
\end{aligned}$$

Assume the steady state and calculate:

a) The amount of heat we need to remove to keep the reaction temperature at 298 K? How will be the conversion of A at this temperature?

b) The conversion if the reactor is operated adiabatically?

c) The temperature of the feed in order to obtain the outlet temperature for an adiabatic CSTR of 363 K? What will be the conversion of A for this case?

Solution

a)X_{A}=0.09, b) $T_{\mathrm{adiab.}} = 301$ $X_{\mathrm{A},adiab.} = 0.11$, c) $T^0(363) = 311$ K, $X_{\mathrm{A},363} = 0.67$