

1 Stoichiometry

1.1 Definitions

I.) BASICS:

N usually denotes the number of species/components in a reaction, whereas M denotes the number of reactions in a reaction system. We use the variables i and j as follows

$$i \in [1, \dots, N]$$

$$j \in [1, \dots, M]$$

II.) ELEMENT SPECIES MATRIX:

\underline{B} contains the number of atoms of an element per molecule of a species. You have to set it up as follows for the four species O_2 , CO_2 , H_2O and C_2H_5OH :

$$\underline{B} = \left(\begin{array}{c|cccc} & O_2 & CO_2 & H_2O & C_2H_5OH \\ \hline C & \beta_{C,O_2} & \beta_{C,CO_2} & \beta_{C,H_2O} & \beta_{C,C_2H_5OH} \\ O & \beta_{O,O_2} & \beta_{O,CO_2} & \beta_{O,H_2O} & \beta_{O,C_2H_5OH} \\ H & \beta_{H,O_2} & \beta_{H,CO_2} & \beta_{H,H_2O} & \beta_{H,C_2H_5OH} \end{array} \right) = \left(\begin{array}{c|cccc} & O_2 & CO_2 & H_2O & C_2H_5OH \\ \hline C & 0 & 1 & 0 & 2 \\ O & 2 & 2 & 1 & 1 \\ H & 0 & 0 & 2 & 6 \end{array} \right)$$

III.) AMOUNT OF SUBSTANCE:

$$\underline{\Delta n_i} = \begin{pmatrix} \Delta n_1 \\ \vdots \\ \Delta n_N \end{pmatrix} = \begin{pmatrix} \Delta n_{O_2} \\ \Delta n_{CO_2} \\ \Delta n_{H_2O} \\ \Delta n_{C_2H_5OH} \end{pmatrix}$$

IV.) REACTIONS NEED TO BE IN BALANCE:

The overall amount of elements is constant even though the amount of substance of particular species may change:

$$\underline{0} = \underline{B} \cdot \underline{\Delta n}$$
$$\rightsquigarrow \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} & O_2 & CO_2 & H_2O & C_2H_5OH \\ \hline C & \beta_{C,O_2} & \beta_{C,CO_2} & \beta_{C,H_2O} & \beta_{C,C_2H_5OH} \\ O & \beta_{O,O_2} & \beta_{O,CO_2} & \beta_{O,H_2O} & \beta_{O,C_2H_5OH} \\ H & \beta_{H,O_2} & \beta_{H,CO_2} & \beta_{H,H_2O} & \beta_{H,C_2H_5OH} \end{pmatrix} \cdot \begin{pmatrix} \Delta n_{O_2} \\ \Delta n_{CO_2} \\ \Delta n_{H_2O} \\ \Delta n_{C_2H_5OH} \end{pmatrix}$$

One will usually search for the Δn_i while \underline{B} is known. To do this: First one should apply the GAUSS elimination and then develop the linear equation system from it. The matrix form actually is already an equation system and it is possible to use it directly to get the needed values for the unknown Δn_i .

Please note, that the key components/species will be given (or in a laboratory measured).

V.) EXTENT OF REACTION (dt.: Reaktionslaufzahl):

The extent of reaction denotes the amount of substance which has already been consumed or produced. The used symbol is the small greek letter Xi (ξ ; the capital letter Xi looks like this: Ξ). The extent of reaction remains the same throughout one reaction!

$$\xi = \frac{n_i - n_{i0}}{\nu_i} = \frac{\Delta n_i}{\nu_i} = \frac{\Delta n_1}{\nu_1} = \dots = \frac{\Delta n_N}{\nu_N}$$

VI.) CONVERSION (dt.: Umsatzgrad):

The conversion denotes the percentage of amount of substance which has already reacted. It is specific to a single species but can be transferred to be meaningful for other species, too (see STOICHIOMETRIC TABLE).

$$X_i = \frac{n_{i0} - n_i}{n_{i0}}$$

1.2 Changes in amount of substance and key components

Basic equation: $\underline{B} \cdot \underline{\Delta n} = \underline{0}$

Approach:

- I.) Set up the element species matrix \underline{B} .
 - II.) Determine the rank of \underline{B} .
 \leadsto Number of key components: $N_{kc} = N - Rg(\underline{B})$
 - III.) Measure Δn of key components.
 \leadsto Δn of key components are known (or given).
 - IV.) Plug in Δn of key components into the basic equation.
 - V.) Solve the linear equation system (in form of a matrix) to get the Δn for non-key components.
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1.3 Extent of reaction and key reactions

Basic equation: $\underline{N} \cdot \underline{\xi} = \underline{\Delta n}$

Approach:

- I.) Set up the matrix of stoichiometric coefficients, \underline{N} .
- II.) Determine the rank of \underline{N} .
 \leadsto Number of key reactions: $N_{krc} = Rg(\underline{N})$
- III.) Linearly independent rows describe the key reactions stoichiometrically (i.e. form the key reactions by taking the ν 's from the rearranged matrix - rearranging was done using the GAUSS elimination).
- IV.) Delete ξ_j of the linearly dependent non-key reactions (i.e. cancel out the rows for the linearly dependent non-key reactions in the ξ -matrix/vector).
- V.) Delete ν_{ij} and Δn_i for the non-key reactions. (i.e. remove the respective rows from these matrices/vectors).
- VI.) Solve the equations for ξ_j of key reactions.

2 Thermodynamics

2.1 Important definitions

- I.) Enthalpy change on reaction ΔH_R is the molar heat of formation of the products $\Delta H_{f,i}$ minus the molar heat of formation of educts.
 \leadsto The heat tonality can be exo- ($\Delta H_R < 0$; i.e. heat is produced by the reaction), endo- ($\Delta H_R > 0$; i.e. the reaction consumes energy) or diathermic (i.e. neutral).
- II.) HESS's law of heat summation: ΔH_R is independent of the reaction path. (This allows to calculate the heat of reaction for any reaction, although it might not be possible to realize it experimentally!)
- III.) LE CHATELIER's principle: A system in chemical equilibrium shifts in response to any imposed change of factors governing the equilibrium.
NOTE: Catalysts never have any influence on the equilibrium. They accelerate or inhibit a reaction, but they never shift the equilibrium!
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2.2 Important formulae

- I.) Enthalpy change on reaction / heat of reaction

$$\begin{aligned}\Delta H_R^0 &= \sum_{i=1}^N \nu_i \cdot \Delta H_{f,i}^0 \quad \text{this holds for STP} \\ \Delta H_R(T) &= \Delta H_R^0 + \int_{T^{(0)}}^T \Delta c_p(T) dT \\ \Delta c_p(T) &= \sum_{i=1}^N \nu_i \cdot c_{pi}(T)\end{aligned}$$

Often the formula to calculate Δc_{pi} appears similar to this

$$\Delta c_{pi}(T) = A + BT + CT^2 + DT^3,$$

where A, B, C and D are coefficients one can find in standard tables.

- II.) Gibbs free energy

$$\begin{aligned}\Delta G_R^0 &= \sum_{i=1}^N \nu_i \cdot \Delta G_{f,i}^0 \quad \text{this holds for STP} \\ &= -RT \cdot \ln K_p^0 \\ &= -RT \cdot \ln K_a^0 \\ \ln K_p(T) &= \ln K_p^0 + \int_{T^{(0)}}^T \frac{\Delta H_R^0}{RT^2} dT \\ \ln K_a(T) &= \ln K_a^0 + \int_{T^{(0)}}^T \frac{\Delta H_R^0}{RT^2} dT \\ K_a^0 &\sim K_p^0\end{aligned}$$

- III.) Equilibria

- 1.) K_c \longrightarrow concentration equilibrium
- 2.) K_a \longrightarrow activity equilibrium
- 3.) K_p \longrightarrow pressure equilibrium

4.) K_x → conversion equilibrium

$$K_c = \prod_{i=1}^N c_i^{\nu_i} = \prod_{i=1}^N \left(\frac{c_i}{c^{(0)}} \right)^{\nu_i} \quad (\text{"normalized form"})$$

$$K_a = \prod_{i=1}^N a_i^{\nu_i}$$

$$K_p = \prod_{i=1}^N p_i^{\nu_i} = K_c \cdot \left(\frac{c^{(0)} \cdot RT}{p^{(0)}} \right)^{\sum_{i=1}^N \nu_i} = \prod_{i=1}^N \left(\frac{p_i}{p^{(0)}} \right)^{\nu_i} \quad (\text{"normalized form"})$$

$$K_x = \prod_{i=1}^N x_i^{\nu_i} = K_p \cdot \left(\frac{p}{p^{(0)}} \right)^{-\sum_{i=1}^N \nu_i} \quad (\text{where } p \text{ is the overall pressure})$$

The equilibria values relate as follows:

$$K_a = \left(p^{(0)} \right)^{-\sum_{i=1}^N \nu_i} \cdot K_p = \left(\frac{p}{p^{(0)}} \right)^{\sum_{i=1}^N \nu_i} \cdot K_x = c^{-\sum_{i=1}^N \nu_i} \cdot K_c$$

2.3 Explanations

- I.) STP means: **S**tandard **T**emperature and **P**ressure
- II.) Standard temperature: $25^0C = 298K$
- III.) Standard pressure: $p^{(0)} = 1,013bar = 101,3kPa = 1,013 \cdot 10^5 Pa$
- IV.) Standard concentration: $c^{(0)} = 1 \frac{mol}{l}$
- V.) IMPORTANT: $\Delta G_{f,i}^0 = \Delta H_{f,i}^0 = 0$ for elements!

3 Microkinetics (Reaction kinetics)

3.1 Description of kinetics

I.) Reaction rate (N being the number of species, M being the number of reactions and $i=1,\dots,N$; $M=1,\dots,M$):

$$r_j = \frac{1}{\nu_{i,j}} \cdot \frac{1}{V} \cdot \frac{dn_i}{dt} = \frac{1}{\nu_{i,j}} \cdot \frac{dc_i}{dt} \quad (\text{because } V = \text{const. and } c = \frac{n}{V})$$

II.) Power law:

$$r_j = k_j \cdot \prod_{i=1}^N c_i^{\kappa_{i,j}} \quad \text{with } \kappa_{i,j} = \begin{cases} |\nu_{i,j}| & \text{for educts} \\ 0 & \text{for educts} \\ 0 & \text{for products} \\ |\nu_{i,j}| & \text{for products} \end{cases} \quad \text{or} \quad \begin{cases} 0 & \text{for educts} \\ |\nu_{i,j}| & \text{for products} \end{cases}$$

for elementary reactions only!

III.) ARRHENIUS' law (dependency on temperature):

$$k_j(T) = k_{\infty,j} \cdot e^{-\frac{E_{a,j}}{RT}}$$

IV.) Net rate of changes in amount of substance:

$$R_i = \frac{dc_i}{dt} = \sum_{j=1}^M \nu_{i,j} r_j$$

For ideal gases we have $c_i = \frac{p_i}{R \cdot T}$, hence:

$$R_i = \frac{dc_i}{dt} = \frac{1}{RT} \cdot \frac{dp_i}{dt}$$

3.2 Determination of kinetics

Measure the values for concentration at different points in time: $c(t); c(t + \Delta t)$

I.) Differential method

1.) Calculate approximation values for r:

$$r = \frac{1}{\nu_i} \cdot \frac{c_i}{dt} \approx \frac{1}{\nu_i} \cdot \underbrace{\frac{c_i(t + \Delta t) - c_i(t)}{\Delta t}}_{\text{similar to the definition of the differential}}$$

2.) Use the power law ($r = k \cdot \prod_{i=1}^N c_i^{\kappa_i}$)

3.) Find the logarithms:

$$\log r = \log k + \sum_{i=1}^N (\kappa_i \log c_i)$$

⇒ You get a linear set of equations, κ_i can be estimated by solving it.

⇒ Plot $\log r$ versus $\log c_i$ to determine k .

II.) Integral method

Example: $A_1 \longrightarrow A_2$

1.) Use the power law and set it equal to the differential form:

$$r = k \cdot \prod_{i=1}^N c_i^{\kappa_i} = k \cdot c_1^{\kappa_1} \quad \iff \quad r = \frac{1}{\nu_i} \cdot \frac{dc_i}{dt} = \frac{1}{-1} \cdot \frac{dc_1}{dt} = -\frac{dc_1}{dt} \quad \rightsquigarrow \quad k \cdot c_1^{\kappa_1} = -\frac{dc_1}{dt}$$

2.) Solve the differential equation by separating the variables

$$\frac{dc_1}{c_1^{\kappa_1}} = -k dt \quad \leadsto \quad c_1 = c_{10} \cdot e^{-kt}$$

3.) Find the logarithms

$$\ln c_1 = \ln c_{10} - kt$$

⇒ Plot $\ln c_1$ versus t to determine k .

IN GENERAL FOR $\kappa_1 \neq 1$ IT HOLDS $\left(\frac{1}{c_1}\right)^{\kappa_1-1} - \left(\frac{1}{c_{10}}\right)^{\kappa_1-1} = (\kappa_1 - 1)k_{\kappa_1} \cdot t$

3.3 Special reactions

General approach:

I.) Get the number of species and of reactions.

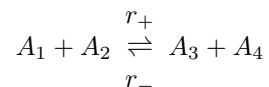
II.) Set up the differential equations $R_i = \frac{dc_i}{dt} = \sum_{j=1}^M \nu_{i,j} \cdot r_j$

III.) Substitute r_j by the power law.

IV.) Make any necessary assumptions.

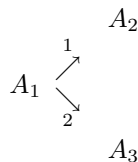
V.) Solve the system of differential equations.

1.) Reversible reactions

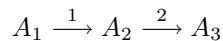


Considering equilibrium: $r_+ = r_-$

2.) Multiple concurrent reactions / parallel reactions (multiple reaction pathes)

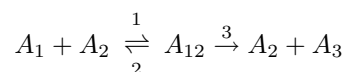


3.) Consecutive reactions



4.) Homogeneous catalyzed reactions

i. General reaction equation:



Where A_2 is the catalyst and A_{12} is the activated complex.

ii. Set up the differential equations for R_i using the power law for r_j .

iii. Assumptions:

* The total amount of catalyst is constant: $c_2 + c_{12} = c_{20}$

* Reaction (3) is the rate determination step $\leadsto r_1 = r_2$ or $\frac{dc_{12}}{dt} = 0$

4 Reactor design

4.1 Stoichiometric table for batch systems

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0 \quad \text{with } k=1$$

Species	n_{i0}	$\Delta n_i = -\frac{\nu_i}{\nu_k} n_{k0} X_k$	$n_i = n_{i0} + \Delta n_i$
A_1	n_{10}	$-n_{10} X_1$	$n_1 = n_{10} - n_{10} X_1$
A_2	n_{20}	$-\frac{\nu_2}{\nu_1} n_{10} X_1$	$n_2 = n_{20} - \frac{\nu_2}{\nu_1} n_{10} X_1$
A_3	n_{30}	$-\frac{\nu_3}{\nu_1} n_{10} X_1$	$n_3 = n_{30} - \frac{\nu_3}{\nu_1} n_{10} X_1$
A_4	n_{40}	$-\frac{\nu_4}{\nu_1} n_{10} X_1$	$n_4 = n_{40} - \frac{\nu_4}{\nu_1} n_{10} X_1$
Inert	n_{I0}	—	$n_I = n_{I0}$
Sum	$n_{\text{sum}0}$	—	$n_{\text{sum}} = n_{\text{sum}0} - (1 + \frac{\nu_2}{\nu_1} + \frac{\nu_3}{\nu_1} + \frac{\nu_4}{\nu_1}) n_{10} X_1$

4.2 Stoichiometric table for flow systems

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \nu_4 A_4 = 0 \quad \text{with } k=1$$

Species	F_{i0}	$\Delta F_i = -\frac{\nu_i}{\nu_k} F_{k0} X_k$	$F_i = F_{i0} + \Delta F_i$
A_1	F_{10}	$-F_{10} X_1$	$F_1 = F_{10} - F_{10} X_1$
A_2	F_{20}	$-\frac{\nu_2}{\nu_1} F_{10} X_1$	$F_2 = F_{20} - \frac{\nu_2}{\nu_1} F_{10} X_1$
A_3	F_{30}	$-\frac{\nu_3}{\nu_1} F_{10} X_1$	$F_3 = F_{30} - \frac{\nu_3}{\nu_1} F_{10} X_1$
A_4	F_{40}	$-\frac{\nu_4}{\nu_1} F_{10} X_1$	$F_4 = F_{40} - \frac{\nu_4}{\nu_1} F_{10} X_1$
Inert	F_{I0}	—	$F_I = F_{I0}$
Sum	$F_{\text{sum}0}$	—	$F_{\text{sum}} = F_{\text{sum}0} - (1 + \frac{\nu_2}{\nu_1} + \frac{\nu_3}{\nu_1} + \frac{\nu_4}{\nu_1}) F_{10} X_1$

4.3 Design equations

I.) BATCH REACTOR:

$$\overset{=0}{\text{input}} = \overset{=0}{\text{output}} + \text{disappearance} + \text{accumulation}$$

II.) CONTINUOUS STIRRED TANK REACTOR:

$$\text{input} = \text{output} + \text{disappearance} + \overset{=0}{\text{accumulation}}$$

III.) PLUG FLOW REACTOR:

$$\text{input} = \text{output} + \text{disappearance} + \overset{=0}{\text{accumulation}}$$

Batch Reactor (BR)	$n_{10} \cdot dX_1 = r \cdot V \cdot dt$	$t = n_{10} \cdot \int_0^{X_1} \frac{dX_1}{rV}$
Continuous Stirred Tank Reactor (CSTR)	$F_{10} \cdot X_1 = r \cdot V$	$\tau = n_{10} \cdot \frac{dX_1}{r}$
Plug Flow Reactor (PFR)	$F_{10} \cdot dX_1 = r \cdot dV$	$\tau = c_{10} \cdot \int_0^{X_1} \frac{dX_1}{r}$

Where t is the time that the mixture is in the batch reactor, τ is the space time. A space time of $5min$ denotes that every five minutes one reactor volume of feed is being treated by the reactor. $\tau = \frac{1}{s}$, where s is the space velocity (in min^{-1}) and denotes how many reactor volumes of feed are being treated during a given time.

NOTE: Volume of feed (V) is not necessarily the same as volume of reactor (V_R). But we only consider volume of feed and how much time is needed to treat one reactor volume of feed. $\leadsto V = \epsilon_R \cdot V_R$ (with ϵ_R being the ratio of filling volume by reactor volume).

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