κίνησις "kinesis", *movement* or *to move*

APPLIED REACTION KINETICS

EUROPEAN UNION
European Structural and Investing Funds
Operational Programme Research,
Development and Education

MINISTRY OF EDUCATION,
YOUTH AND SPORTS

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Resources and references

- **Notes from lectures**

- **Internet**
web.vscht.cz/bernauem/

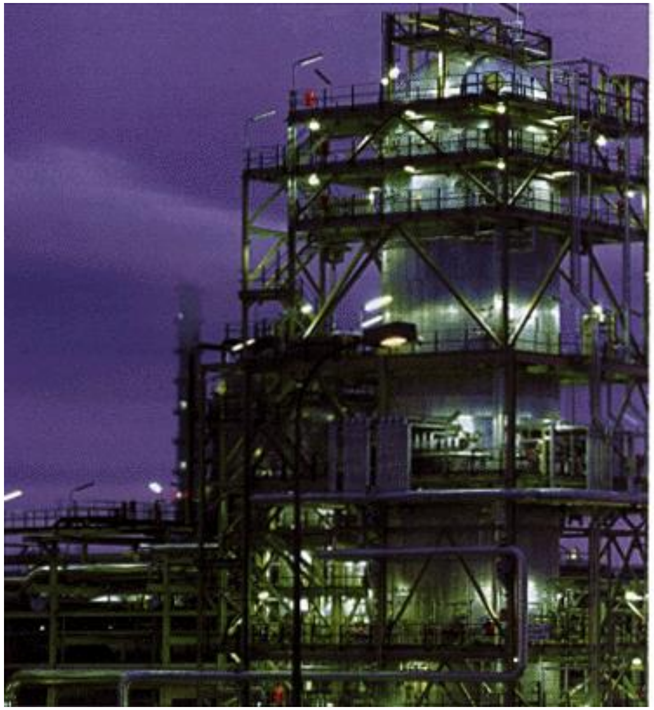
- **Textbooks**
Fogler Scott H.: Elements of Chemical Reaction Engineering, 4th Edition, Prentice Hall, 2006. (http://www.engin.umich.edu/~cre/)

Missen R.W., Mims C.A., Saville B.A., Introduction to Chemical Reaction Engineering and Kinetics, J. Wiley&Sons, N.Y. 1999.

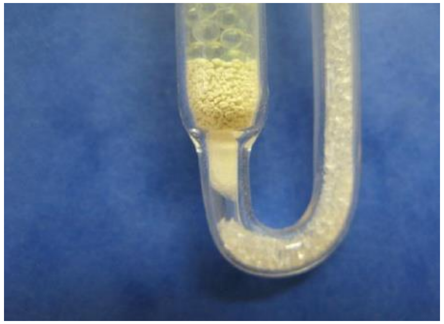
- **Journals (on-line)**

- **Software**
MS Excel, (**Matlab**, Octave, Athena Visual Studio, FORTRAN, Maple….)

Fischer-Tropsch (SASOL, RSA)



N_2O decomposition (IPC AS, CZ)



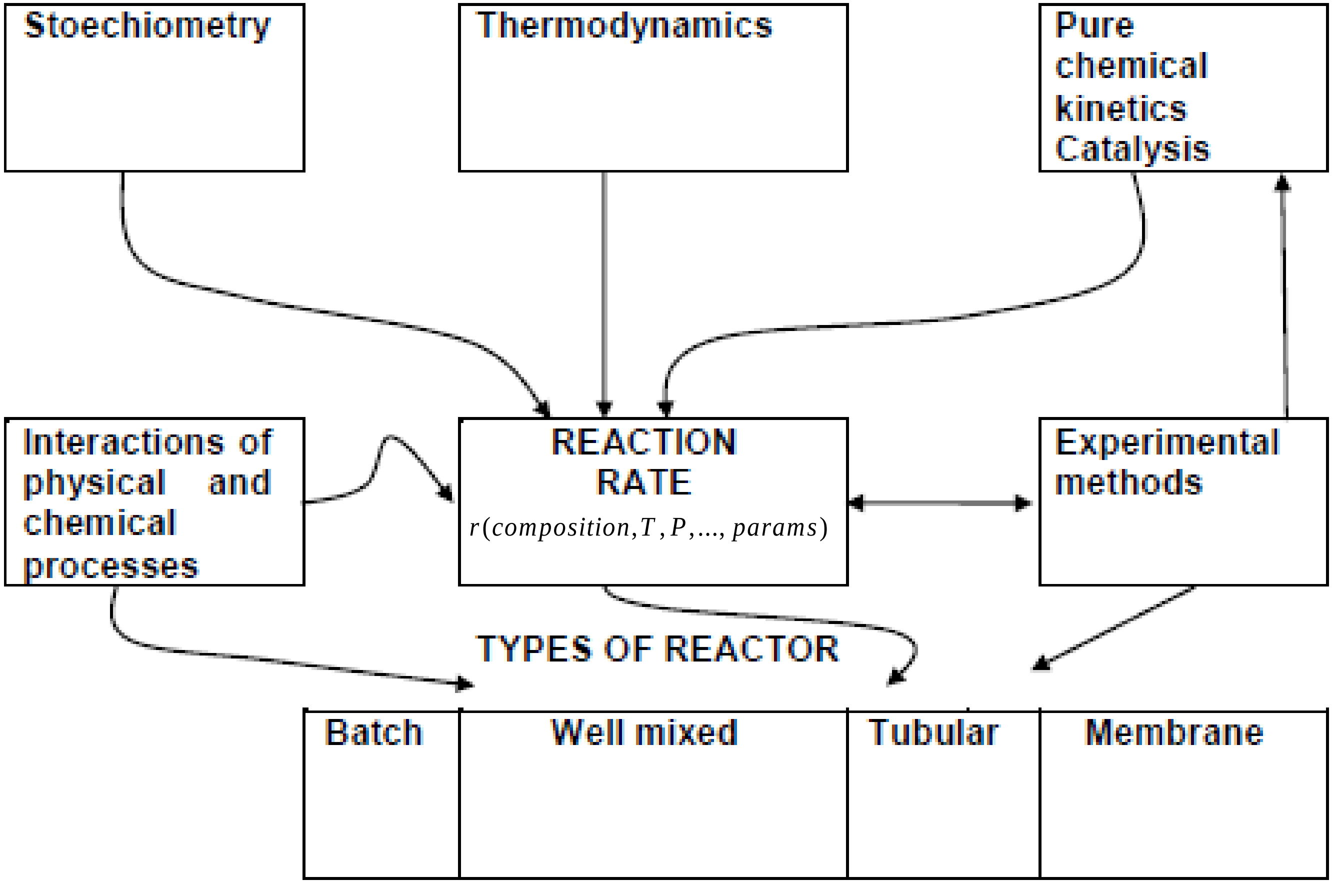
WGS (BASF, FRG)

Chemical reactor(s) ➔ heart of chemical process

Methane aromatization (ICTP, CZ)

Raw material →separation → reaction → separation → product

Understanding the ostensible nature of chemical reaction systems



Stoechiometry

Thermodynamics

Pure chemical kinetics
Catalysis

Interactions of physical and chemical processes

REACTION RATE
$r(composition, T, P, \dots, params)$

Experimental methods

TYPES OF REACTOR

Batch

Well mixed

Tubular

Membrane

The reaction system in the environment of the reactor

Material and energy balances
Stability, transient behavior
Imperfections of models
Industrial chemical reactors, design, optimization, software

Summary of the 1st lecture

- Stoichiometry
- Extent of reaction
- Fractional conversion of key component
- Stoichiometric matrix
- Balance of chemical elements
- Selectivity, Yield
- Reaction rate definition

"*στοιχειον*" the material element (Plato)

"*μετρϖ*" the count, the quantity

Stoichiometry

$2NO \rightarrow N_2 + O_2$ closed (batch) system

	t =0	t > 0
Atoms of oxygen	$n^o_{NO} + 2n^o_{O_2} \ =$	$n_{NO} + 2n_{O_2}$
Atoms of nitrogen	$n^o_{NO} + 2n^o_{N_2} \ =$	$n_{NO} + 2n_{N_2}$

$$n^o_{NO} + 2n^o_{O_2} = n_{NO} + 2n_{O_2} \qquad n^o_{NO} + 2n^o_{N_2} = n_{NO} + 2n_{N_2}$$

$$n_{NO} - n^o_{NO} = -2(n_{O_2} - n^o_{O_2}) \qquad n_{NO} - n^o_{NO} = -2(n_{N_2} - n^o_{N_2})$$

$$\frac{n_{NO} - n^o_{NO}}{-2} = \frac{(n_{O_2} - n^o_{O_2})}{1} = \frac{(n_{N_2} - n^o_{N_2})}{1}$$

$-2NO + O_2 + N_2 = 0$

Symbols for species $NO = A_1$ $O_2 = A_2$ $N_2 = A_3$

Stoichiometric coefficients $\nu_1 = -2$ $\nu_2 = 1$ $\nu_3 = 1$

$$\sum_{i=1}^{3} \nu_i A_i = 0$$

$\nu_i > 0$ products

$\nu_i = 0$ inerts

$\nu_i < 0$ reactants

Molar extent of the reaction ξ [ksi:]

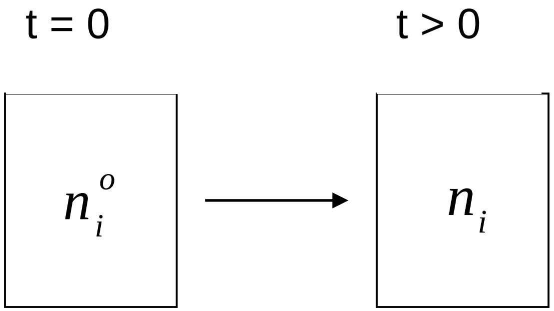
$$\xi = \frac{n_{NO} - n_{NO}^{o}}{-2} = \frac{(n_{O_2} - n_{O_2}^{o})}{1} = \frac{(n_{N_2} - n_{N_2}^{o})}{1}$$

$$\xi = \frac{n_i - n_i^{o}}{\nu_i}$$

From the definition of the reaction extent follows:

1. **The reaction extent has the dimension of moles (number of molecules)**
2. **The reaction extent value depends on stoichiometry of reaction**
3. **The reaction extent is an extensive variable**

Reaction extent for a single reaction in closed (batch) system



t = 0

t > 0

n_i^o

n_i

Closed system

$$\sum_{i=1}^{N} \nu_i A_i = 0$$

$\nu_i > 0$ products

$\nu_i = 0$ inerts

$\nu_i < 0$ reactants

$$\xi = \frac{n_i - n_i^o}{\nu_i}$$

$$n_i = n_i^o + \nu_i \xi$$

Example

$2NO \rightarrow N_2 + O_2$

$$A_1 = \mathrm{NO},\, A_2 = \mathrm{N}_2,\, A_3 = \mathrm{O}_2$$

$$\nu_1 = -2, \nu_2 = 1, \nu_1 = 1$$

$$\mathbf{v}^T = \begin{pmatrix} -2 & 1 & 1 \end{pmatrix}, \mathbf{A} = \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix}$$

Matrix notation

$$\mathbf{v}^T \mathbf{A} = \begin{pmatrix} -2 & 1 & 1 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix} = 0$$

Fractional conversion of key component, j X_j

$$X_j = \frac{\xi}{\xi_{\max}}$$

$$\xi_{\max} = \frac{\boxed{n_j^*} - n_j^o}{\nu_j}$$

Number of moles of key component in limits (chemical equilibrium or 0)

$$\boxed{n_j^* = 0}$$

$$X_j = \frac{\xi}{\xi_{\max}} = \frac{\dfrac{n_i - n_i^o}{\nu_i}}{\dfrac{-n_j^o}{\nu_j}} = \frac{\nu_j}{\nu_i}\,\frac{n_i^o - n_i}{n_j^o} \longrightarrow$$

$i = j$

$$X_j = \frac{n_j^o - n_j}{n_j^o} \qquad X_j \in (0,1)$$

$$X_j = 100\,\frac{n_j^o - n_j}{n_j^o} \qquad X_j \in (0,100)$$

$$\xi = X_j \xi_{\max} = -X_j \frac{n_j^o}{\nu_j} \longrightarrow \boxed{n_i = n_i^o - \frac{\nu_i}{\nu_j} n_j^o X_j}$$

Stoichiometric matrix in the case of several reactions

$$\sum_{i=1}^{N} \nu_{ki} A_i = 0 \qquad k = 1, NR$$

reaction component

Stoechimetric matrix has NR rows and N columns

$$\boldsymbol{\nu} = \begin{pmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1N} \\ \nu_{21} & \nu_{22} & \cdots & \nu_{2N} \\ . & & & \\ \nu_{NR,1} & \nu_{NR,2} & \cdots & \nu_{NR,N} \end{pmatrix}, \mathbf{A} = \begin{pmatrix} A_1 \\ A_2 \\ . \\ A_N \end{pmatrix}$$

$$\boldsymbol{\nu}\mathbf{A} = \mathbf{0}$$

Number of moles of i-th component consumed or created in k-th reaction : $n_{ki} - n_{ki}^{o}$

Molar extent of k-th reaction : $\xi_k = \dfrac{n_{ki} - n_{ki}^{o}}{\nu_{ki}}$

Number of moles of i-th components:

$$\boxed{n_i = n_i^{o} + \sum_{k=1}^{NR} \nu_{ki} \xi_k}$$

Matrix notation

$$\mathbf{n} = \mathbf{n}^{o} + \boldsymbol{\nu}^{T} \boldsymbol{\xi}$$

$$\mathbf{n} = \begin{pmatrix} n_1 \\ n_2 \\ .. \\ n_N \end{pmatrix}, \mathbf{n}^{o} = \begin{pmatrix} n_1^{o} \\ n_2^{o} \\ .. \\ n_N^{o} \end{pmatrix}, \boldsymbol{\xi} = \begin{pmatrix} \xi_1 \\ \xi_2 \\ .. \\ \xi_{NR} \end{pmatrix}$$

Problem 1.1

Oxidation of ammonia on Pt-Rh catalyst

$NH_3 + 1.25\,O_2 \rightarrow NO + 1.5H_2O$ (1)
$NH_3 + O_2 \rightarrow 0.5\,N_2O + 1.5H_2O$ (2)
$NH_3 + 0.75O_2 \rightarrow 0.5\,N_2 + 1.5H_2O$ (3)

Task: To write down the stoichiometric matrix.

	A_1	A_2	A_3	A_4	A_5	A_6
Reaction	NH_3	O_2	NO	N_2O	N_2	H_2O
(1)	-1	-1.25	1	0	0	1.5
(2)	-1	-1	0	0.5	0	1.5
(3)	-1	-0.75	0	0	0.5	1.5

Molar balance table of component in closed (batch) system

Component	t = 0	t > 0
NH_3	n_1^o	$n_1 = n_1^o - (\xi_1 + \xi_2 + \xi_3)$
O_2	n_2^o	$n_2 = n_2^o - 1.25\xi_1 - \xi_2 - 0.75\xi_3$
NO	n_3^o	$n_3 = n_3^o + \xi_1$
N_2O	n_4^o	$n_4 = n_4^o + 0.5\xi_2$
N_2	n_5^o	$n_5 = n_5^o + 0.5\xi_3$
H_2O	n_6^o	$n_6 = n_6^o + 1.5(\xi_1 + \xi_2 + \xi_3)$
Σ	$\sum_{i=1}^{6} n_i^o$	$\sum_{i=1}^{6} n_i^o + 0.25(\xi_1 + \xi_3)$

e.g. molar fraction of NH_3

$$y_1 = \frac{n_1^o - (\xi_1 + \xi_2 + \xi_3)}{\sum_{i=1}^{6} n_i^o + 0.25(\xi_1 + \xi_3)}$$

Independent reactions

Set of NR reactions in reaction network is *independent* if

Rank(ν)=NR

or

number of independent reactions = Rank(ν)

Problem 1.2

$NH_3 + 1.25\ O_2 \rightarrow NO + 1.5H_2O$ (1)
$NH_3 + O_2 \rightarrow 0.5\ N_2O + 1.5H_2O$ (2)
$NH_3 + 0.75O_2 \rightarrow 0.5\ N_2 + 1.5H_2O$ (3)
$2NO \rightarrow N_2 + O_2$ (4)

Task: To calculate the number of independent reactions.

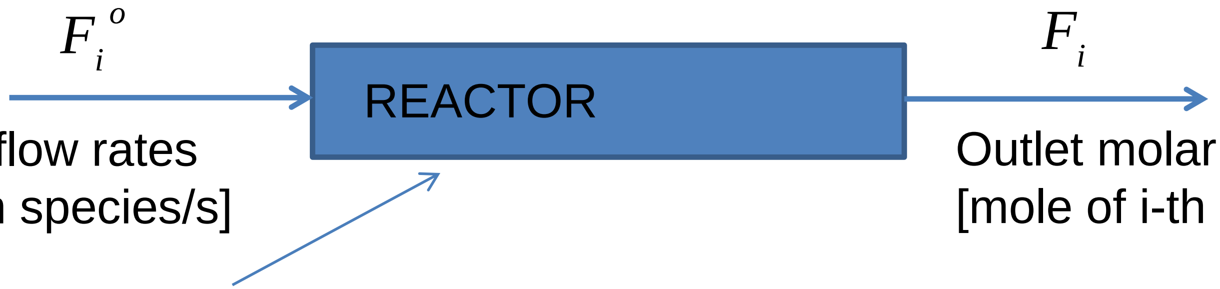
We determine the rank of stoichiometric matrix by Gaussian elimination:

$$\begin{pmatrix} -1 & -1.25 & 1 & 0 & 0 & 1.5 \\ -1 & -1 & 0 & 0.5 & 0 & 1.5 \\ -1 & -0.75 & 0 & 0 & 0.5 & 1.5 \\ 0 & 1 & -2 & 0 & 1 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} -1 & -1.25 & 1 & 0 & 0 & 1.5 \\ 0 & 0.25 & -1 & 0.5 & 0 & 0 \\ 0 & 0.5 & -1 & 0 & 0.5 & 0 \\ 0 & 1 & -2 & 0 & 1 & 0 \end{pmatrix} \rightarrow$$

$$\rightarrow \begin{pmatrix} -1 & -1.25 & 1 & 0 & 0 & 1.5 \\ 0 & 0.25 & -1 & 0.5 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0.5 & 0 \\ 0 & 0 & 2 & -2 & 1 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} -1 & -1.25 & 1 & 0 & 0 & 1.5 \\ 0 & 0.25 & -1 & 0.5 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0.5 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

Rank(ν)=3 → only 3 reactions are independent

Extent of the reaction in a flow system



F_i^o

REACTOR

F_i

Inlet molar flow rates
[mole of i-th species/s]

Outlet molar flow rates
[mole of i-th species/s]

$$\sum_{i=1}^{N} \nu_{ki} A_i = 0 \qquad k = 1, NR$$

Open (flow) system in a <u>steady state</u>

$$F_i = F_i^o + \sum_{k=1}^{NR} \nu_{ki} \dot{\xi}_k \qquad \dot{\xi}_k = \frac{\xi_k}{\bar{\tau}}$$

F_i, F_i^o -outlet, inlet molar flow rates of i-th species [mole/s]

$\dot{\xi}_k$ – extent of k-th reaction per unit of time [mole/s]

$\bar{\tau}$ – mean residence time [s]

$$\mathbf{F} = \mathbf{F}^{\mathbf{o}} + \boldsymbol{\nu}^T \dot{\boldsymbol{\xi}}$$

$$\mathbf{F} = \begin{pmatrix} F_1 \\ F_2 \\ .. \\ F_N \end{pmatrix}, \mathbf{F}^o = \begin{pmatrix} F_1^o \\ F_2^o \\ .. \\ F_N^o \end{pmatrix}, \dot{\boldsymbol{\xi}} = \begin{pmatrix} \dot{\xi}_1 \\ \dot{\xi}_2 \\ .. \\ \dot{\xi}_{NR} \end{pmatrix}$$

A reaction is at steady-state if the concentration of all species in each element of the reaction space (i.e. volume in the case of homogeneous reaction or surface of catalyst in the case of catalytic heterogeneous reaction) does not change in time.

Balance of chemical elements

$$\sum_{i=1}^{N} \nu_{ki} A_i = 0 \qquad k = 1, NR$$

Open (flow) system at steady state

$$\Phi_j = \Phi_j^o$$

Φ_j, Φ_j^o -outlet, inlet molar flows

of j-th chemical element [mole/s]

$$\mathbf{\Phi} = \mathbf{\Phi^o}$$

$$\mathbf{\Phi} = \begin{pmatrix} \Phi_1 \\ \Phi_2 \\ .. \\ \Phi_{NEL} \end{pmatrix}, \mathbf{\Phi^o} = \begin{pmatrix} \Phi_1^o \\ \Phi_2^o \\ .. \\ \Phi_{NEL}^o \end{pmatrix}$$

NEL - Number of chemical elements

Formula matrix E

NEL elements → NEL=3

N components ↓ **N=6**	**N**	**H**	**O**
NH_3	**1**	**3**	**0**
O_2	**0**	**0**	**2**
NO	**1**	**0**	**1**
N_2O	**2**	**0**	**1**
N_2	**2**	**0**	**0**
H_2O	**0**	**2**	**1**

Formula vector of NH_3

There are no creation or annihilation of chemical elements in chemical reactions:

$$\mathbf{vE} = \mathbf{0} \Rightarrow \begin{pmatrix} \nu_{11} & \nu_{12} & \cdots & \nu_{1N} \\ \nu_{21} & \nu_{22} & \cdots & \nu_{2N} \\ . & & & \\ \nu_{NR,1} & \nu_{NR,2} & \cdots & \nu_{NR,N} \end{pmatrix} \begin{pmatrix} E_{11} & E_{12} & \cdots & E_{1,NEL} \\ E_{21} & \cdots & \cdots & E_{2,NEL} \\ . & & & \\ E_{N,1} & E_{N,2} & \cdots & E_{N,NEL} \end{pmatrix} = \left. \underbrace{\begin{pmatrix} 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ . & & & \\ 0 & 0 & \cdots & 0 \end{pmatrix}}_{\text{NEL}} \right\} \text{NR}$$

Molar* weight (relative molecular mass) of i-th species:

$$M_i = \sum_{j=1}^{NEL} E_{ij} m_j$$

$$\mathbf{M} = \mathbf{E}\mathbf{m}$$

Atomic weights (relative atomic mass) of j-th element

$$\mathbf{M} = \begin{pmatrix} M_1 \\ M_2 \\ .. \\ M_N \end{pmatrix}, \mathbf{m} = \begin{pmatrix} m_1 \\ m_2 \\ .. \\ m_{NEL} \end{pmatrix}$$

and we have for molar weights of species

$$\boldsymbol{\nu}\mathbf{M} = \boldsymbol{\nu}\mathbf{E}\mathbf{m} = 0$$

$$\text{because } \boldsymbol{\nu}\mathbf{E} = 0$$

The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 *kilogram of carbon* 12.

Avogadro constant = 6.022 141 29(27) × 10^{23} mol^{-1} (http://www.nist.gov)

Balances of atoms in batch and flow systems

Closed (batch) system:

$$\mathbf{n} = \mathbf{n}^{\mathbf{o}} + \boldsymbol{\nu}^T \boldsymbol{\xi}$$

$$\mathbf{E}^T\mathbf{n} = \mathbf{E}^T\mathbf{n}^{\mathbf{o}} + \mathbf{E}^T\boldsymbol{\nu}^T\boldsymbol{\xi} = \mathbf{E}^T\mathbf{n}^{\mathbf{o}} + \left(\boldsymbol{\nu}\mathbf{E}\right)^T \boldsymbol{\xi} = \mathbf{E}^T\mathbf{n}^{\mathbf{o}}$$

Open (flow) system at steady state:

$$\mathbf{F} = \mathbf{F}^{\mathbf{o}} + \boldsymbol{\nu}^T \dot{\boldsymbol{\xi}}$$

$$\mathbf{E}^T\mathbf{F} = \mathbf{E}^T\mathbf{F}^{\mathbf{o}} + \mathbf{E}^T\boldsymbol{\nu}^T\dot{\boldsymbol{\xi}} = \mathbf{E}^T\mathbf{F}^{\mathbf{o}} + \left(\boldsymbol{\nu}\mathbf{E}\right)^T \dot{\boldsymbol{\xi}} = \mathbf{E}^T\mathbf{F}^{\mathbf{o}}$$

because $\boldsymbol{\nu}\mathbf{E} = \mathbf{0}$

Finally

$$\left.\begin{aligned}\mathbf{E}^T\left(\mathbf{n} - \mathbf{n}^{\mathbf{o}}\right) = \mathbf{E}^T\left(\mathbf{n}^{\mathbf{o}} - \mathbf{n}\right) = \mathbf{0} \\ \mathbf{E}^T\left(\mathbf{F} - \mathbf{F}^{\mathbf{o}}\right) = \mathbf{E}^T\left(\mathbf{F}^{\mathbf{o}} - \mathbf{F}\right) = \mathbf{0}\end{aligned}\right\}$$

These equations are used in data reconciliation tasks around chemical reactors.

The last equation (flow system) is valid only at steady state.

Problem 1.3
Selective reduction of NO_x by C_3H_8

Steady state, unknown stoichiometry of reactions

	NO	NO_2	CO	C_3H_8	CO_2	H_2O	O_2	N_2
$F_i^o\,[\mu mole/\min]$	**4.563**	**0.1845**	**0**	**2.943**	**0**	**0**	**90**	**0**
$F_i\,[\mu mole/\min]$	**2.2905**	**2.3355**	**0**	**2.898**	**x**	**x**	**x**	**x**

Calculate the missing outlet molar flow rates

$$\mathbf{E}^T\left(\mathbf{F}^o - \mathbf{F}\right) = \mathbf{E}^T\Delta\mathbf{F} = \mathbf{0}$$

	1-NO	2-NO_2	3-CO	4-C_3H_8	5-CO_2	6-H_2O	7-O_2	8-N_2
N	1	1	0	0	0	0	0	2
O	1	2	1	0	2	1	2	0
C	0	0	1	3	1	0	0	0
H	0	0	0	8	0	2	0	0

$$\underbrace{\text{1-NO} \;\ldots\; \text{4-}C_3H_8}_{\mathbf{E}_1^T} \qquad \underbrace{\text{5-}CO_2 \;\ldots\; \text{8-}N_2}_{\mathbf{E}_2^T}$$

$$\begin{pmatrix} \Delta F_1 \\ \Delta F_2 \\ \Delta F_3 \\ \Delta F_4 \\ \Delta F_5 \\ \Delta F_6 \\ \Delta F_7 \\ \Delta F_8 \end{pmatrix} \begin{matrix} \left.\begin{matrix} \\ \\ \\ \\ \end{matrix}\right\} \text{known } \Delta F_i \\ \left.\begin{matrix} \\ \\ \\ \\ \end{matrix}\right\} \text{unknown } \Delta F_i \end{matrix}$$

$$\mathbf{E}_1^T\Delta\mathbf{F}_{KNOWN} + \mathbf{E}_2^T\Delta\mathbf{F}_{UNKNOWN} = \mathbf{0}$$

$$\mathbf{E}_2^T\Delta\mathbf{F}_{UNKNOWN} = -\mathbf{E}_1^T\Delta\mathbf{F}_{KNOWN}$$

$$\Delta\mathbf{F}_{UNKNOWN} = -\left(\mathbf{E}_2^T\right)^{-1}\mathbf{E}_1^T\Delta\mathbf{F}_{KNOWN} = \mathbf{Q}\Delta\mathbf{F}_{KNOWN}$$

$$\mathbf{Q} = -\left(\mathbf{E}_2^T\right)^{-1}\mathbf{E}_1^T$$

We obtain using Excel (homework 1)

$$\mathbf{Q} = \begin{pmatrix} 0 & 0 & -1 & -3 \\ 0 & 0 & 0 & -4 \\ -0.5 & -1 & 0.5 & 5 \\ -0.5 & -0.5 & 0 & 0 \end{pmatrix}$$

and taking $\Delta \mathbf{F}_2 = -\left(\mathbf{E}_2^T\right)^{-1} \mathbf{E}_1^T \Delta \mathbf{F}_1 = \mathbf{Q} \Delta \mathbf{F}_1$ we have

	NO	NO_2	CO	C_3H_8	CO_2	H_2O	O_2	N_2
$F_i^o [\mu mole / \min]$	**4.563**	**0.1845**	**0**	**2.943**	**0**	**0**	**90**	**0**
$F_i \ [\mu mole / \min]$	**2.2905**	**2.3355**	**0**	**2.898**	**0.135**	**0.18**	**88.76**	**0.061**

Selectivity

Moles of a particular product generated per mole of key reactant consumed

Yield

Moles of a particular product generated per one initial mole of key reactant

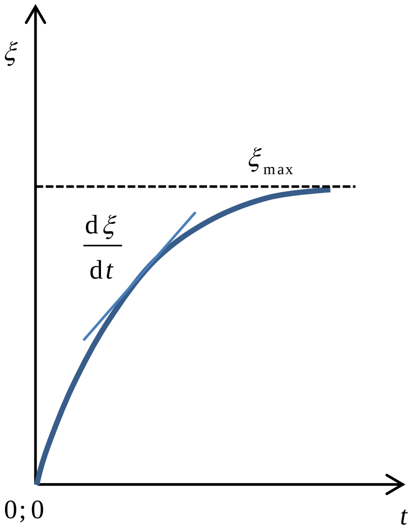
Ammonia oxidation

Component	t = 0	t > 0
NH_3	n_1^o	$n_1 = n_1^o - (\xi_1 + \xi_2 + \xi_3)$
O_2	n_2^o	$n_2 = n_2^o - 1.25\xi_1 - \xi_2 - 0.75\xi_3$
NO	n_3^o	$n_3 = n_3^o + \xi_1$
N_2O	n_4^o	$n_4 = n_4^o + 0.5\xi_2$
N_2	n_5^o	$n_5 = n_5^o + 0.5\xi_3$
H_2O	n_6^o	$n_6 = n_6^o + 1.5(\xi_1 + \xi_2 + \xi_3)$

$$S_{NO-NH_3} = \frac{n_3^o + \xi_1}{(\xi_1 + \xi_2 + \xi_3)} = \frac{\xi_1}{(\xi_1 + \xi_2 + \xi_3)}$$

$$Y_{NO-NH_3} = \frac{n_3^o + \xi_1}{n_1^o} \overset{(n_3^o = 0)}{=} \frac{\xi_1}{n_1^o}$$

Reaction rate



(IUPAC Gold Book = rate of conversion)

$$r = \frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{dn_i}{dt} \qquad \text{mole.s}^{-1}$$

$$r_k = \frac{d\xi_k}{dt}$$

Closed system of uniform pressure, temperature and composition.

Rate of generation (consumption) of component A_i

$$R_{A_i} = \frac{dn_i}{dt} = \nu_i . \frac{d\xi}{dt} = \nu_i . r \quad \overset{\text{one reaction}}{\Rightarrow} \quad \mathbf{R} = \boldsymbol{\nu} r$$

$$R_{A_i} = \sum_{k=1}^{NR} \nu_{ki} . \frac{d\xi_k}{dt} = \sum_{k=1}^{NR} \nu_{ki} . r_k \quad \overset{\text{several reactions}}{\Rightarrow} \quad \mathbf{R} = \boldsymbol{\nu}^T \mathbf{r}$$

We measure usually the rates of generation (consumption) of components *R* and we want to calculate *r*

$$\mathbf{R}^{\exp} \cong \mathbf{v}^{T}\mathbf{r} \qquad \Rightarrow \quad \text{Objective function} \quad \Omega\left(\mathbf{r}\right) = \left(\mathbf{R}^{\exp} - \mathbf{v}^{T}\mathbf{r}\right)^{T}\left(\mathbf{R}^{\exp} - \mathbf{v}^{T}\mathbf{r}\right)$$

$$\text{minimization of } \Omega\left(\mathbf{r}\right) = \text{least squares solution of overdefined system (N>NR)}$$

$$\boxed{\mathbf{r} = \left(\mathbf{v}\mathbf{v}^{T}\right)^{-1}\mathbf{v}\mathbf{R}^{\exp}}$$

Problem 1.4

Steam reforming of methane (5 species, N=5, 2 reactions, NR=2)

1 2 3 4

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ **(1)**

5

$CO + H_2O \leftrightarrow CO_2 + H_2$ **(2)**

Measured R : (-0.97572, -2.88778, -1.02127, 4.832804, 2.078537)^T (mol/s)

$$\mathbf{v} = \begin{pmatrix} -1 & -1 & 1 & 3 & 0 \\ 0 & -1 & -1 & 1 & 1 \end{pmatrix} \qquad \mathbf{v}\mathbf{v}^{T} = \begin{pmatrix} 12 & 3 \\ 3 & 4 \end{pmatrix} \qquad \left(\mathbf{v}\mathbf{v}^{T}\right)^{-1}\mathbf{v} = \begin{matrix} -0.10256 & -0.02564 & 0.179487 & 0.230769 & -0.07692 \\ 0.076923 & -0.23077 & -0.38462 & 0.076923 & 0.307692 \end{matrix}$$

$$\begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = \begin{pmatrix} 0.94619 \\ 1.99546 \end{pmatrix}$$

Specific reaction rate

The reaction rate $\frac{\mathrm{d}\xi}{\mathrm{d}t}$ is, like ξ , an extensive property of the system, a specific rate (intensive property) is obtained by dividing $\frac{\mathrm{d}\xi}{\mathrm{d}t}$ by the total volume, mass, surface of the system:

Reaction rate per volume

$$r_V = \frac{1}{V} r = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{V}\frac{1}{\nu_i}\frac{dn_i}{dt} \qquad \mathrm{mole.m}^{-3}.s^{-1}$$

$$r_{V,k} = \frac{1}{V} r_k = \frac{1}{V}\frac{d\xi_k}{dt}$$

Reaction rate per mass

$$r_M = \frac{1}{m} r = \frac{1}{m}\frac{d\xi}{dt} = \frac{1}{m}\frac{1}{\nu_i}\frac{dn_i}{dt} \qquad \mathrm{mole.kg}^{-1}.s^{-1}$$

$$r_{M,k} = \frac{1}{m} r_k = \frac{1}{m}\frac{d\xi_k}{dt}$$

Reaction rate per surface

$$r_S = \frac{1}{S} r = \frac{1}{S} \frac{d\xi}{dt} = \frac{1}{S} \frac{1}{\nu_i} \frac{dn_i}{dt} \qquad \text{mole.m}^{-2}.s^{-1}$$

$$r_{S,k} = \frac{1}{S} r_k = \frac{1}{S} \frac{d\xi_k}{dt}$$

Reaction rate per active center (turnover number)

$$r_{RS} = \frac{1}{n_{RS}} r = \frac{1}{n_{RS}} \frac{d\xi}{dt} = \frac{1}{n_{RS}} \frac{1}{\nu_i} \frac{dn_i}{dt} \qquad \text{s}^{-1}$$

$$r_{RS,k} = \frac{1}{n_{RS}} r_k = \frac{1}{n_{RS}} \frac{d\xi_k}{dt}$$

Central problem of APPLIED CHEMICAL KINETICS

$$r = function\left(T, c_1, c_2, \ldots c_N, P, \text{catalytic activity, transport parameters,....}\right)$$

Rule 1: The rate function r at constant temperature generally decreases in monotonic fashion with time (or extent or conversion).

Rule 2: The rate of irreversible reaction can be written as

$$r = k(T)\, g\left(c_1, c_2, \ldots c_N\right)$$

Rule 3: The rate constant k depends on temperature (Svante Arrhenius, 1889):

$$k(T) = A e^{-\frac{E}{\mathrm{R}T}}$$

Rule 4: The function g is independent of temperature:

$$g\left(c_1, c_2, \ldots c_N\right) = c_1^{\alpha_1} c_2^{\alpha_2} \ldots c_N^{\alpha_N} = \prod_{i=1}^{N} c_i^{\alpha_i}$$

Rule 5: When a reaction is reversible:

$$r = r_f - r_b = k_f(T)\, g_f\left(c_1, c_2, \ldots c_N\right) - k_b(T)\, g_b\left(c_1, c_2, \ldots c_N\right)$$

Problem 1.5 (homework 2)

In flow catalytic reactor the synthesis of methanol is carried out

$$CO_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(g)}$$

The inlet mass flow rate of CO is 1000 $kg.h^{-1}$ 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 $kg.h^{-1}$.

To determine:

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

Data:
M_{CO}= 28.010 $kg.kmol^{-1}$
N_A=6.0221413x10^{23} mol^{-1} (Avogadro number)

$$CO = A_1, H_2 = A_2, CH_3OH = A_3$$

$$\mathbf{v} = \begin{pmatrix} -1 \\ -2 \\ 1 \end{pmatrix}, \mathbf{R} = \begin{pmatrix} -1 \\ -2 \\ 1 \end{pmatrix} r$$

$$F_i = F_i^o + \sum_{k=1}^{NR} v_{ki}\dot{\xi}_k \Rightarrow F_i = F_i^o + v_i\dot{\xi} \Rightarrow$$

$$\overline{r}_M = \frac{\dot{\xi}}{m_{CAT}} = \frac{F_i - F_i^o}{v_i m_{CAT}}, \overline{r}_S = \frac{\dot{\xi}}{S} = \frac{F_i - F_i^o}{v_i S}, \overline{r}_{RS} = \frac{\dot{\xi}}{n_{RS}} = \frac{F_i - F_i^o}{v_i n_{RS}}$$

Fractional conversion of key component

$1 =$ key component

$$X_1 = \frac{\dot{\xi}}{\dot{\xi}_{MAX}} = \left(\frac{F_i - F_i^o}{\nu_i}\right) / \left(\frac{-F_1^o}{\nu_1}\right) \Rightarrow F_i = F_i^o - \frac{\nu_i}{\nu_1} F_1^o X_1$$

	inlet	y_i^o	**outlet**	y_i	
1-CO	F_1^o	$y_1^o = \frac{F_1^o}{3F_1^o} = \frac{1}{3}$	$F_1 = F_1^o + (-1)\dot{\xi}$	$y_1 = \frac{F_1^o + (-1)\dot{\xi}}{3F_1^o + (-2)\dot{\xi}}$	$F_1 = F_1^o(1 - X_1)$
2-H2	$2F_1^o$	$y_2^o = \frac{2F_1^o}{3F_1^o} = \frac{2}{3}$	$F_2 = F_2^o + (-2)\dot{\xi}$	$y_2 = \frac{2F_1^o + (-2)\dot{\xi}}{3F_1^o + (-2)\dot{\xi}}$	$F_2 = 2F_1^o - 2F_1^o X_1$
3-CH3OH	0	0	$F_3 = \cancel{F_3^o} + (+1)\dot{\xi}$	$y_3 = \frac{\dot{\xi}}{3F_1^o + (-2)\dot{\xi}}$	$F_3 = F_1^o X_1$
Σ	$F^o = 3F_1^o$	1	$F = F^o + (-2)\dot{\xi}$	1	$F = 3F_1^o - 2F_1^o X_1$

$$i = 1, \dot{\xi} = \frac{(860 - 1000)/0.02801/3600}{-1} = 1.38839 \text{ mol.s}^{-1}$$

$$\overline{r}_M = \frac{1.38839}{1200} = 1.157 \times 10^{-3} \text{ mol.kg}^{-1}.s^{-1}, \quad \overline{r}_S = \frac{1.38839}{55 \times 10^3 \times 1200} = 2.104 \times 10^{-8} \text{mol.m}^{-2}.s^{-1}$$

$$\overline{r}_{RS} = \frac{1.38839 \times 6.0221413 \times 10^{23}}{55 \times 10^3 \times 1200 \times 10^{19}} = 1.267 \times 10^{-3} \text{ s}^{-1}$$

$$X_1 = \frac{(1000 - 860)}{1000} = 0.14$$

	inlet y_i^o	outlet y_i
1-CO	$y_1^o = \frac{F_1^o}{3F_1^o} = \frac{1}{3}$	$y_1 = \frac{F_1^o(1 - X_1)}{3F_1^o - 2F_1^o X_1} = \frac{1 - X_1}{3 - 2X_1} = 0.3162$
2-H2	$y_2^o = \frac{2F_1^o}{3F_1^o} = \frac{2}{3}$	$y_2 = \frac{2F_1^o - 2F_1^o X_1}{3F_1^o - 2F_1^o X_1} = \frac{2(1 - X_1)}{3 - 2X_1} = 0.6324$
3-CH3OH	0	$y_3 = \frac{F_1^o X_1}{3F_1^o - 2F_1^o X_1} = \frac{X_1}{3 - 2X_1} = 0.05147$
Σ	1	1