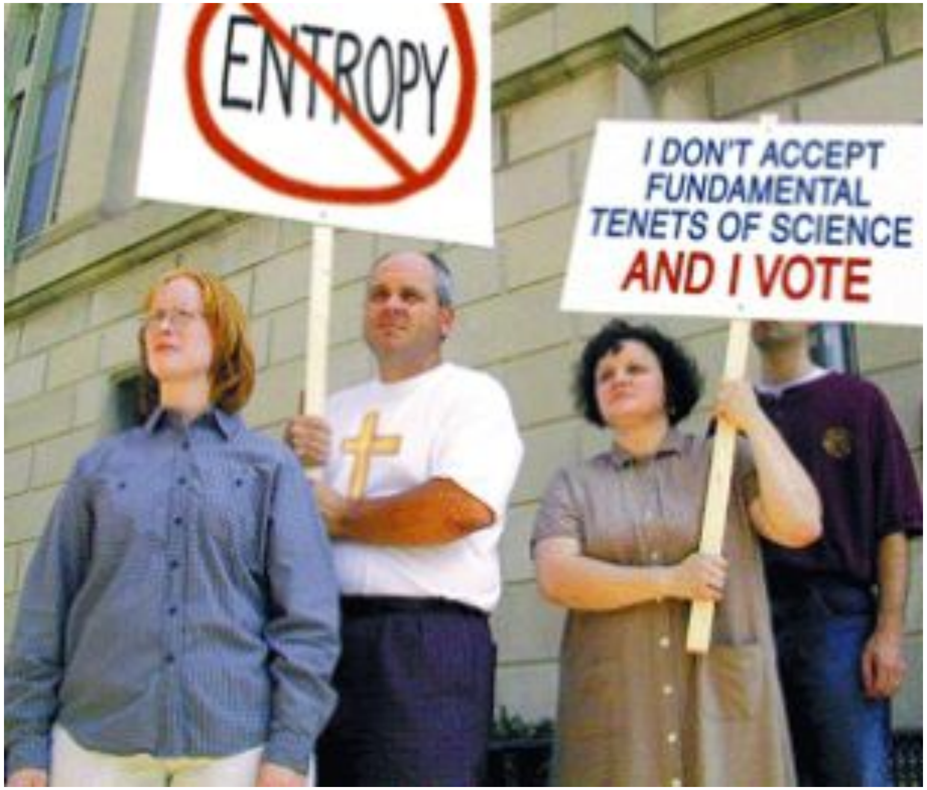
Thermodynamic Aspects of Heterogeneous Catalysis



Ways to cope with

Thermodynamics!

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Outline

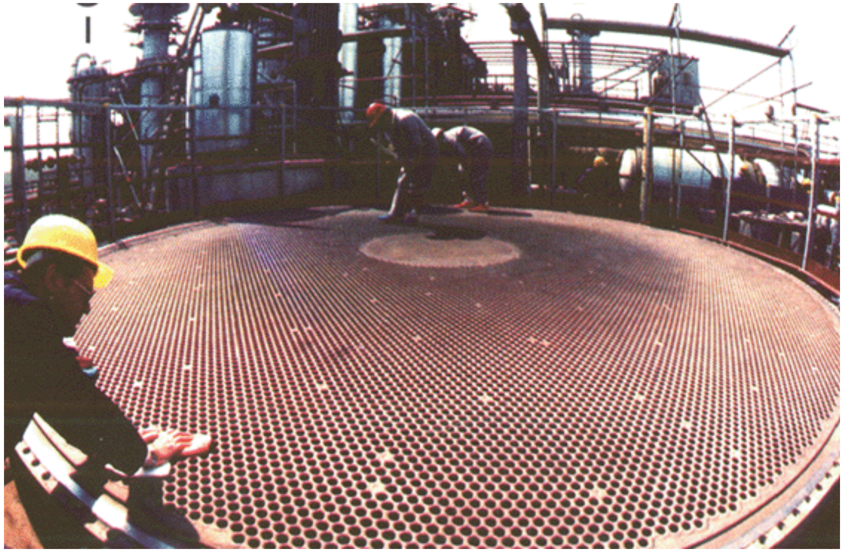
1. **Application of the First Law of Thermodynamics in Catalysis**
    a. Composition and Temperature Profiles in Catalytic Reactors

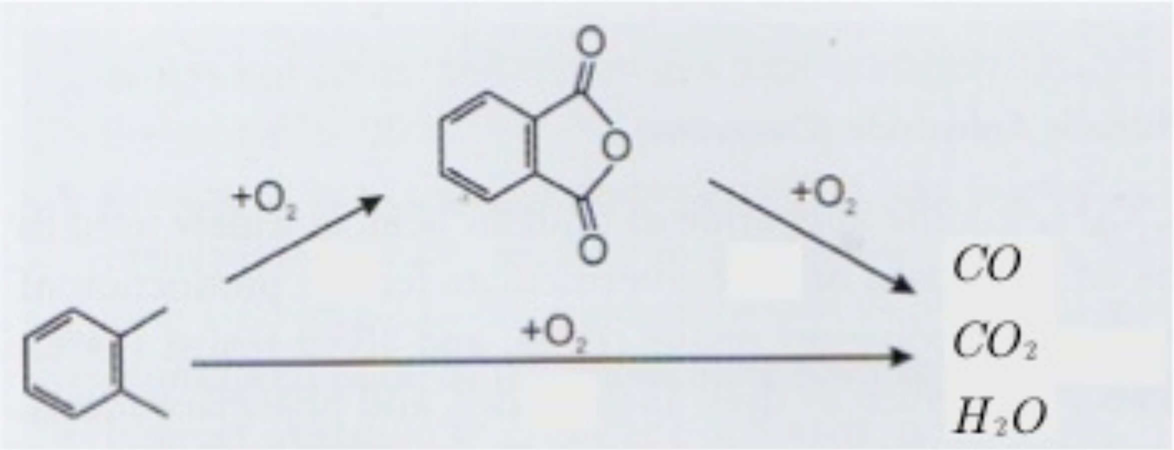
2. **Application of the Second Law of Thermodynamics in Catalysis**
    a. Calculating Thermodynamic Equilibrium for a Single Reaction
    b. Catalytic Reactors for Thermodynamically Limited Reactions
    c. Calculating Thermodynamic Equilibrium for Multiple Reactions

1.a. Composition and Temperature Profiles in Catalytic Reactors

Example 1: selective catalytic oxidation of o-xylene to phthalic anhydride

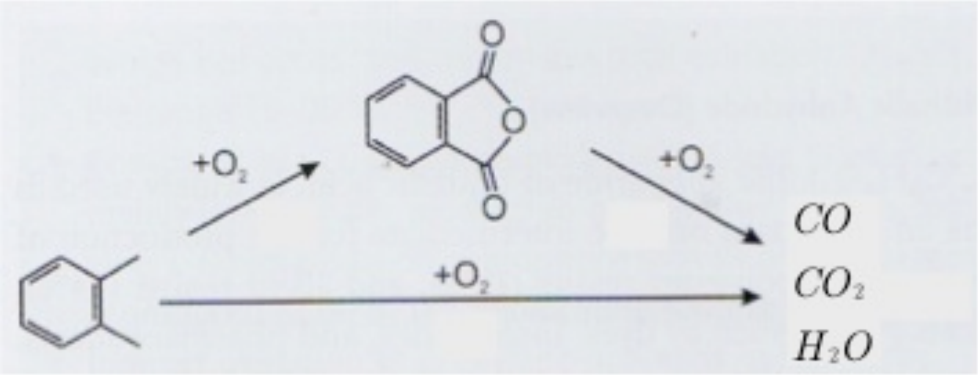
- esters are used as plasticizers
- 4.5 Mio t/a
- catalyst V_2O_5
- multi-tubular fixed bed reactor





1.a. Composition and Temperature Profiles in Catalytic Reactors

stoichiometry and kinetics



$$o-xylene + 3O_2 \xrightarrow{k_1} PSA + 3H_2O$$

$$PSA + 6.5O_2 \xrightarrow{k_2} 2CO + 6CO_2 + 2H_2O$$

$$o-xylene + 9.5O_2 \xrightarrow{k_3} 2CO + 6CO_2 + 5H_2O$$

$$[k_i] = \frac{kmol}{kg_{cat} \cdot h \cdot atm^2}$$

$$k_1 = \exp\left(-\frac{27000}{RT} + 19.84\right)$$

$$k_2 = \exp\left(-\frac{31400}{RT} + 20.86\right)$$

$$k_3 = \exp\left(-\frac{28600}{RT} + 18.97\right)$$

$$R = 1.98 \frac{cal}{mol \cdot K}$$

$$r_1 = k_1 \cdot p_{o-xylene} \cdot p_{O_2}$$

$$r_2 = k_2 \cdot p_{PSA} \cdot p_{O_2}$$

$$r_3 = k_3 \cdot p_{o-xylene} \cdot p_{O_2}$$

1.a. Composition and Temperature Profiles in Catalytic Reactors

thermodynamic data at reaction conditions (220°C):

species	o-xylene	PSA	CO_2	CO	H_2O	O_2
h_i / (kJ/mol)	-0.419	-425.4	-394.0	-110.1	-243.3	8.4

$$o-xylene+3O_2 \xrightarrow{k_1} PSA+3H_2O \quad \Delta_r H_1^\circ(T_{in}) = -1235\,kJ\cdot mol^{-1}$$

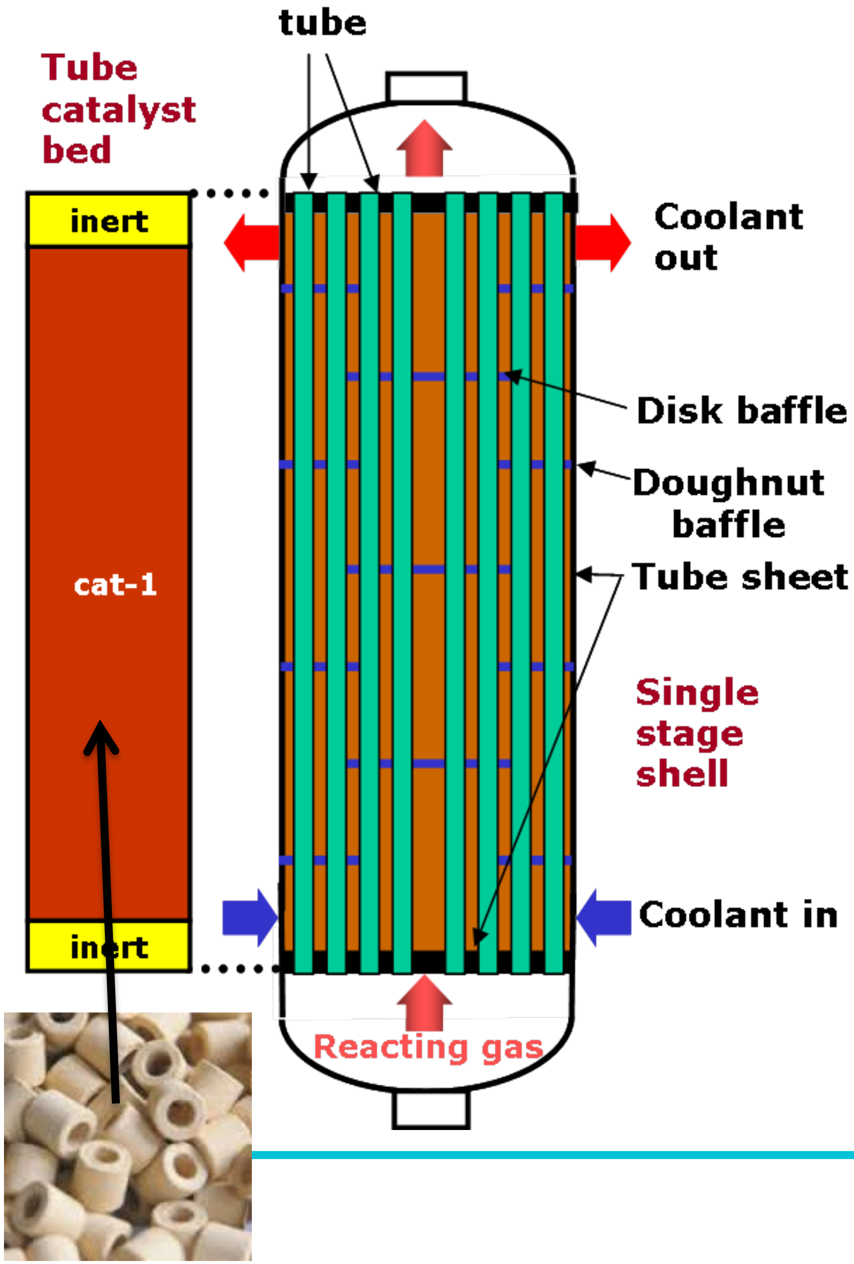
$$PSA+6.5O_2 \xrightarrow{k_2} 2CO+6CO_2+2H_2O \quad \Delta_r H_2^\circ(T_{in}) = -2700\,kJ\cdot mol^{-1}$$

$$o-xylene+9.5O_2 \xrightarrow{k_3} 2CO+6CO_2+5H_2O \quad \Delta_r H_3^\circ(T_{in}) = -3880\,kJ\cdot mol^{-1}$$

heat capacity of the reaction mixture (assumed constant)

$$c_p = 1.089\,\frac{kJ}{kg\cdot K}$$

1.a. Composition and Temperature Profiles in Catalytic Reactors



reactor data

$$8928\, tubes$$

$$d_{tube} = 2.5\, cm$$

$$p_{reactor} = 1.5 atm$$

$$\rho_{bed} = 1350\, kg\, cat \cdot (m^3\, reactor)^{-1}$$

$$T_{in} = 220°C$$

$$\dot{m}_{in}^{air} = 1.96 \cdot 10^4\, kg \cdot h^{-1}$$

$$b_{in}^{o-xylene} = 32.6\, g\, o-xylene \cdot (kg\, air)^{-1}$$

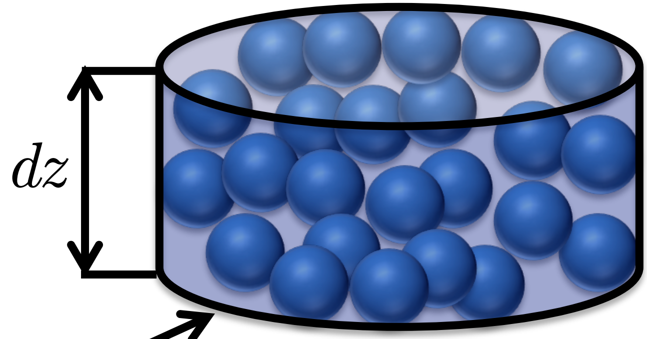
$$\bar{M}_{in} = 29.7\, g \cdot mol^{-1}$$

$$h_{cooling} = 116\, W \cdot m^{-2} \cdot K^{-1}$$

$$T_{cooling} = 343\, °C$$

1.a. Composition and Temperature Profiles in Catalytic Reactors

Conservations laws (species conservation, energy conservation, mass conservation, momentum conservation) are always formulated for a system. A system is a certain amount of matter with mass m.



control volume (CV)

$$d\dot{Q} = h_{cool} P dz (T_{cool} - T)$$

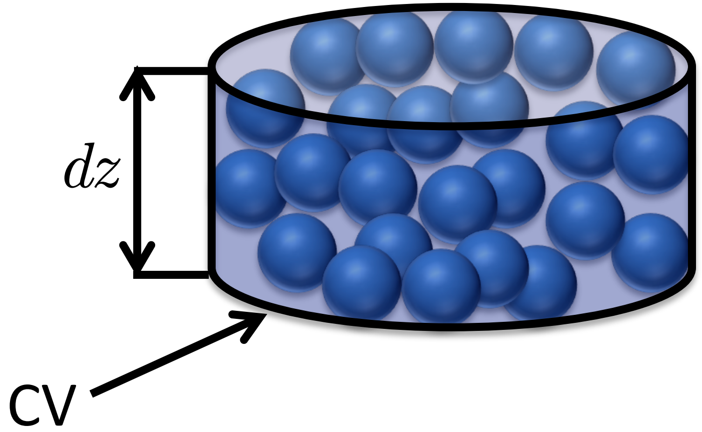
$$P = \pi d_{tube}$$

$$[h_{cool}] = \frac{J}{s \cdot m^2 \cdot K} = \frac{W}{m^2 \cdot K}$$

We define our system as the mass m that occupies the control volume at this very moment (time t_0)!

1.a. Composition and Temperature Profiles in Catalytic Reactors

Because temperature and concentrations will change along the tube we make the control volume small (dz) and assume plug flow (no radial gradients, no diffusive transport in flow direction).



species balance $\left(\frac{dm_i}{dt}\right)_{sys} = \int_{CV} \dot{\omega}_i M_i dV$

$$\dot{\omega}_i = \frac{consumption/production\ rate\ of\ species\ i}{reactor\ volume \cdot time} \qquad [\dot{\omega}_i] = \frac{mol}{m^3 s}$$

$$\begin{pmatrix} \dot{\omega}_1 \\ \vdots \\ \dot{\omega}_i \end{pmatrix} = \begin{bmatrix} \nu_{11} & \cdots & \nu_{1j} \\ \vdots & \ddots & \vdots \\ \nu_{i1} & \cdots & \nu_{ij} \end{bmatrix} \begin{pmatrix} r_1 \\ \vdots \\ r_j \end{pmatrix} \rho_{bed} \qquad [r_j] = \frac{mol}{kg_{cat} s} \qquad [\rho_{bed}] = \frac{kg_{cat}}{m^3}$$

1.a. Composition and Temperature Profiles in Catalytic Reactors

Exercise: Formulate the matrix of the stoichiometric coefficients for our reaction system!

$$o-xylene + 3O_2 \xrightarrow{k_1} PSA + 3H_2O$$

$$PSA + 6.5O_2 \xrightarrow{k_2} 2CO + 6CO_2 + 2H_2O$$

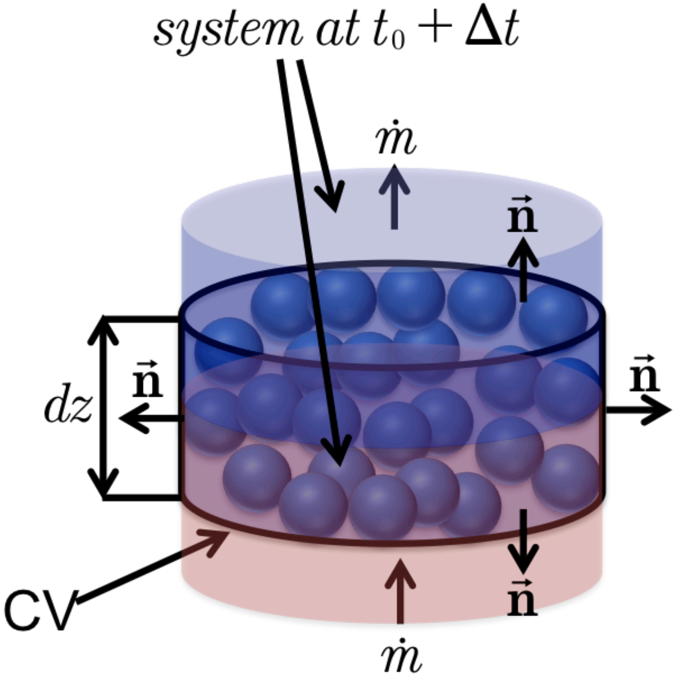
$$o-xylene + 9.5O_2 \xrightarrow{k_3} 2CO + 6CO_2 + 5H_2O$$

$$\begin{pmatrix} 1 = o-xylene \\ 2 = PSA \\ 3 = CO_2 \\ 4 = CO \\ 5 = H_2O \\ 6 = O_2 \end{pmatrix} \Rightarrow \boldsymbol{\nu} = \begin{pmatrix} -1 & 0 & -1 \\ 1 & -1 & 0 \\ 0 & 6 & 6 \\ 0 & 2 & 2 \\ 3 & 2 & 5 \\ -3 & -6.5 & -9.5 \end{pmatrix}$$

Remember: The stoichiometric coefficients of reactants are negative, those of products positive!

1.a. Composition and Temperature Profiles in Catalytic Reactors

While conservation equations can only be formulated for systems, a certain amount of matter, a flowing system is hard to track as it leaves the control volume. While the catalyst stays in place, the fluid mass moves out and breaks apart.



The Reynolds transport theorem relates the time rate of change of an extensive property (e.g. m, m_i, **p**, E) in a flowing system to a fixed control volume that coincides with the system at an instant in time.

N (ext.)	η=N/m (int.)
m	1
m_i	y_i
p=mv	**v**
E	e

$$\left(\frac{dN}{dt}\right)_{system} = \int_{CV} \frac{\partial}{\partial t}(\eta\rho)dV + \int_{CS} \eta\rho\vec{\mathbf{v}}\cdot\vec{\mathbf{n}}dA$$

1.a. Composition and Temperature Profiles in Catalytic Reactors

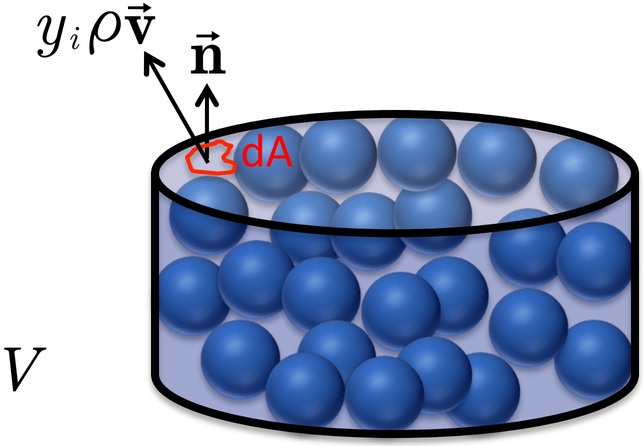
Applying the Reynolds transport theorem to our species balance yields:

$$\left(\frac{dm_i}{dt}\right)_{sys} = \underbrace{\int_{CV} \dot{\omega}_i M_i\, dV \qquad \left(\frac{d\overset{m_i}{N}}{dt}\right)_{system} = \int_{CV} \frac{\partial}{\partial t}(\overset{y_i}{\eta}\rho)\, dV}\; + \int_{CS} \overset{y_i}{\eta}\rho\vec{\mathbf{v}}\cdot\vec{\mathbf{n}}\, dA$$

$$\int_{CV} \omega_i M_i\, dV = \int_{CV} \frac{\partial}{\partial t}(y_i\rho)\, dV + \int_{CS} y_i\rho\vec{\mathbf{v}}\cdot\vec{\mathbf{n}}\, dA$$

Using the Gauss divergence theorem, the surface integral can be converted into a volume integral.

$$\int_{CS} y_i\rho\vec{\mathbf{v}}\cdot\vec{\mathbf{n}}\, dA = \int_{CV} (\nabla\cdot y_i\rho\vec{\mathbf{v}})\, dV$$



$$\Rightarrow \int_{CV} \omega_i M_i\, dV = \int_{CV} \left[\frac{\partial}{\partial t}(y_i\rho) + (\nabla\cdot y_i\rho\vec{\mathbf{v}})\right] dV$$

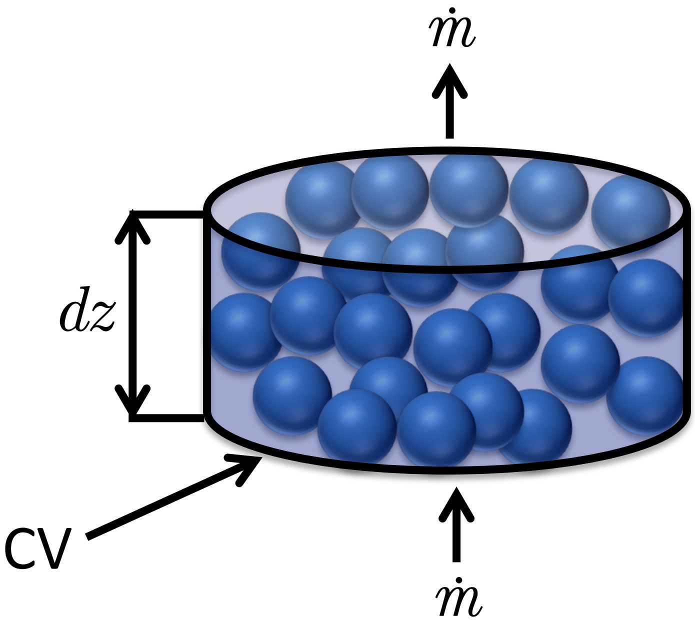
1.a. Composition and Temperature Profiles in Catalytic Reactors

Let‘s assume our PSA reactor operates at steady state:

$$\int_{CV} \omega_i M_i dV = \int_{CV} \left[\frac{\partial}{\partial t}(y_i \rho) + (\nabla \cdot y_i \rho \vec{\mathbf{v}}) \right] dV \Rightarrow \int_{CV} \omega_i M_i dV = \int_{CV} (\nabla \cdot y_i \rho \vec{\mathbf{v}}) dV$$

Because we assumed no radial gradients (plug flow) and a vanishingly small dz, the integrands in both volume integrals are constant.

$$\nabla \cdot y_i \rho \vec{\mathbf{v}} = \omega_i M_i$$



Writing the divergence operator in cylindrical coordinates yields.

$$\nabla \cdot y_i \rho \vec{\mathbf{v}} = \frac{\partial (y_i \rho v_z)}{\partial z} + \underbrace{\frac{1}{r} \frac{\partial (r y_i \rho v_r)}{\partial r}}_{0 \textit{ plug flow}} + \underbrace{\frac{1}{r} \frac{\partial (y_i \rho v_\theta)}{\partial \theta}}_{0 \textit{ plug flow}} \Rightarrow \frac{\partial (y_i \rho v_z)}{\partial z} = \omega_i M_i$$

1.a. Composition and Temperature Profiles in Catalytic Reactors

Because we assume steady state, mass conservation tells us (same analysis as before with m as extensive quantity):

$$\frac{\partial(\rho v_z)}{\partial z} = 0$$

Mass cannot be lost, so in steady state the mass flux must be the same at every axial coordinate z. With this we obtain for each species i a simple ODE which can be easily integrated (e.g. Runge Kutta).

$$\boxed{\rho v_z \frac{\partial y_i}{\partial z} = \omega_i M_i} \xrightarrow{\text{numerical integration}} y_i(z)$$

From the mass fractions, all other quantities can be calculated.

$$\bar{M} = \left(\sum_i \frac{y_i}{M_i}\right)^{-1} \qquad x_i = y_i \frac{\bar{M}}{M_i} \qquad \dot{n}_i = \frac{y_i \dot{m}}{M_i} \qquad X_{o-xylene} = \frac{\dot{n}^{in}_{o-xylene} - \dot{n}_{o-xylene}}{\dot{n}^{in}_{o-xylene}}$$

$$S_{PSA} = \frac{\dot{n}_{PSA}}{\dot{n}^{in}_{o-xylene} - \dot{n}_{o-xylene}} \qquad Y_{PSA} = X_{o-xylene} \cdot S_{PSA}$$

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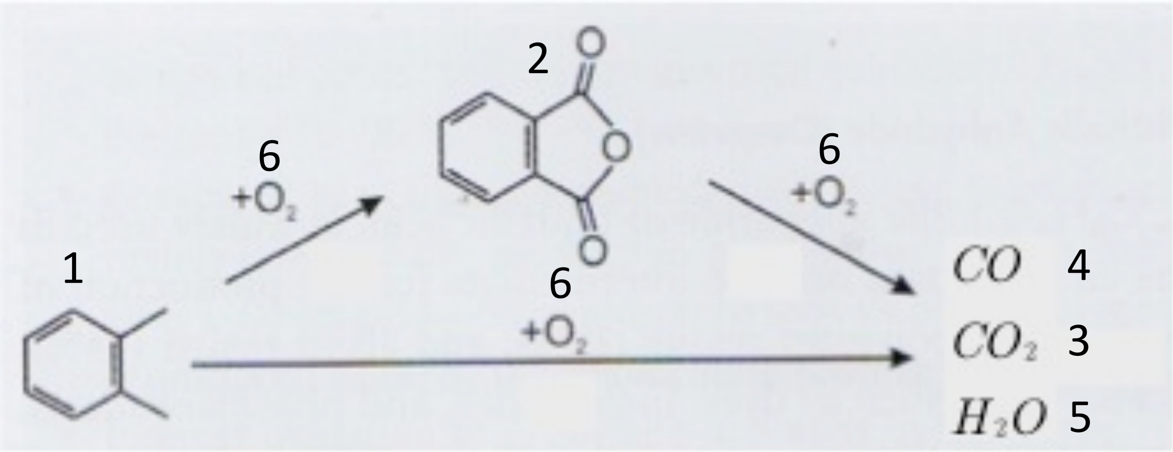
1.a. Composition and Temperature Profiles in Catalytic Reactors

Before we turn to the energy balance (first law of thermodynamics) we should ask ourselves for how many species do we have to solve the species balance.



To answer this question we construct the Element Species Matrix (ESM).

$$ESM = \left[\begin{array}{c|ccc|ccc} & C_8H_{10} & C_8H_4O_3 & CO_2 & CO & H_2O & O_2 \\ C & 8 & 8 & 1 & 1 & 0 & 0 \\ H & 10 & 4 & 0 & 0 & 2 & 0 \\ O & 0 & 3 & 2 & 1 & 1 & 2 \end{array}\right]$$

$$rank(ESM) = 3$$

⬇

3 key species

⬇

3 non key species

Non key species must contain all elements!

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1.a. Composition and Temperature Profiles in Catalytic Reactors

Now we take advantage of stoichiometry. Regardless of the reactions taking place between the species, no atoms can appear or disappear!

$$\mathbf{ESM}\cdot\Delta\dot{\mathbf{n}}=\mathbf{0}\quad\Rightarrow\quad\left[\mathbf{ESM}_{kc}\,\mathbf{ESM}_{nck}\right]\begin{bmatrix}\Delta\dot{\mathbf{n}}_{kc}\\ \Delta\dot{\mathbf{n}}_{nkc}\end{bmatrix}=\mathbf{0}$$

$$\Rightarrow\quad\Delta\dot{\mathbf{n}}_{nkc}=-\mathbf{ESM}_{\mathbf{nkc}}{}^{-1}\,\mathbf{ESM}_{1}\,\Delta\dot{\mathbf{n}}_{kc}$$

$$\begin{pmatrix}\Delta\dot{n}_{CO}\\ \Delta\dot{n}_{H_2O}\\ \Delta\dot{n}_{O_2}\end{pmatrix}=-\begin{bmatrix}1 & 0 & 0\\ 0 & 0.5 & 0\\ -0.5 & -0.25 & 0.5\end{bmatrix}\cdot\begin{bmatrix}8 & 8 & 1\\ 10 & 4 & 0\\ 0 & 3 & 2\end{bmatrix}\cdot\begin{pmatrix}\Delta\dot{n}_{C_8H_{10}}\\ \Delta\dot{n}_{C_8H_4O_3}\\ \Delta\dot{n}_{CO_2}\end{pmatrix}$$

We only need to solve three species balances for the key components o-xylene, PSA and CO_2. The molar flow rates of all reacting species are then obtained from

$$\dot{n}_i=\dot{n}_i^{in}+\Delta\dot{n}_i$$

1.a. Temperature and Composition Profiles in Catalytic Reactors

$$\boxed{\rho v_z \frac{\partial y_i}{\partial z} = \omega_i M_i} \xrightarrow{\text{numerical integration}} y_i(z)$$

The species balances of the key components cannot be integrated yet because $\omega_i(T)$ and we don‘t know the temperature profile of the reactor. Now thermodynamics comes into play. Again, the 1st law of thermodynamics (conservation of energy) can only be formulated for a system, viz. a defined mass of matter.

The total energy of a system can only change if heat flows into or out of a system or if work is done on or by the system!

$$\boxed{\text{1st law of thermodynamics} \quad \frac{dE_t}{dt} = \frac{dQ}{dt} + \frac{dW}{dt}}$$

1.a. Temperature and Composition Profiles in Catalytic Reactors

The total energy of the system includes internal, kinetic and potential energy.

kinetic energy

- ➢ directed motion

$$\frac{E_t}{m} = e_t = \left(u + \frac{1}{2}(\mathbf{v}\cdot\mathbf{v}) - \mathbf{g}\cdot\mathbf{r}\right)$$

IMPORTANT

internal energy

- ➢ random motion
- ➢ vibrations
- ➢ rotations
- ➢ energy in bonds
- ➢ intermolecular forces

potential energy

- ➢ displacement of system relative to some reference plane

1.a. Temperature and Composition Profiles in Catalytic Reactors

If we neglect kinetic and potential energy and we assume again that our system occupies our control volume at this very moment in time we can rewrite the 1st law in the following way:

$$\frac{dE_t}{dt} = \frac{dQ}{dt} + \frac{dW}{dt}$$

$$\Big\uparrow \qquad \Big\uparrow \qquad \Big\uparrow$$

$$\int_{CS} \rho u \mathbf{v} \cdot \mathbf{n} dA = d\dot{Q} - \int_{CS} p \mathbf{v} \cdot \mathbf{n} dA$$

$$\Big\downarrow$$

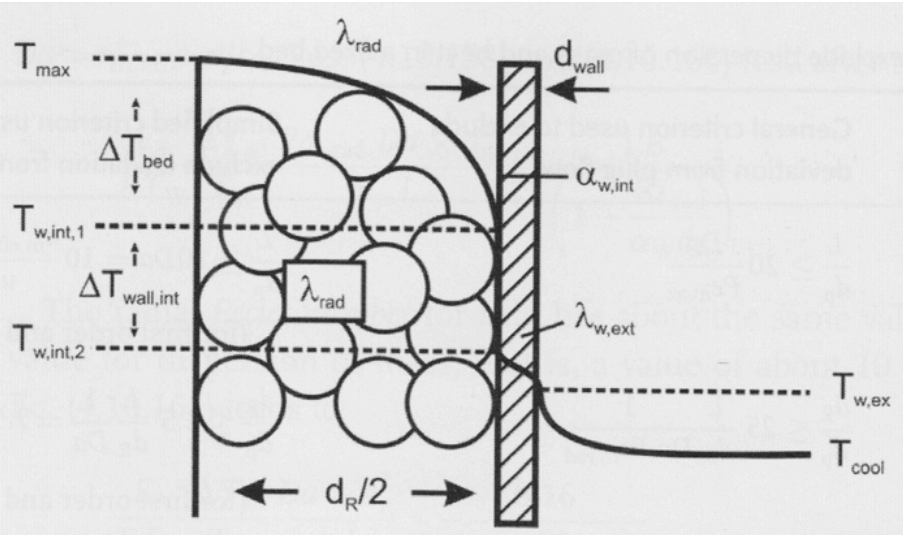
$$\int_{CS} \left(u + \frac{p}{\rho} \right) \rho \mathbf{v} \cdot \mathbf{n} dA = d\dot{Q}$$

$$\Big\downarrow \; u + \frac{p}{\rho} = h \, (enthalpy)$$

$$\int_{CS} h \rho \mathbf{v} \cdot \mathbf{n} dA = d\dot{Q}$$

1.a. Temperature and Composition Profiles in Catalytic Reactors

In catalytic reactors, heat is in most cases removed or added through the reactor wall. The processes of heat transfer from the bed through the wall and into a cooling (heating fluid) are rather complicated. The main resistance is on the bed side!



In our simple 1D plug flow model we lump these complex processes into a single heat transfer coefficient $h_{cooling}$. This overall heat transfer coefficient depends on the packing (Raschig rings, cylinders, spheres, split etc.), the flow conditions inside the tube (gas, liquid, flow velocity etc.) and the cooling mechanism (salt melt, boiling water etc.). It needs to be measured or calculated.

$$d\dot{Q} = h_{cooling}(Pdz)(T_{cooling} - T)$$

1.a. Temperature and Composition Profiles in Catalytic Reactors

➡ $$\int_{CS} h\rho\mathbf{v}\cdot\mathbf{n}dA = h_{cooling}(Pdz)(T_{cooling}-T)$$

Applying the Gauss divergence theorem we can convert the surface integral into a volume integral.

➡ $$\int_{CV} \nabla\cdot\rho h\mathbf{v}dV = h_{cooling}(Pdz)(T_{cooling}-T)$$

If we make our control volume differentially small, the integrand will be a constant and can be taken out of the integral.

➡ $$\nabla\cdot\rho h\mathbf{v}\int_{CV} dV = \nabla\cdot\rho h\mathbf{v}\delta V = h_{cooling}(Pdz)(T_{cooling}-T)$$

1.a. Temperature and Composition Profiles in Catalytic Reactors

$$\nabla\cdot\rho h\mathbf{v}\int_{CV} dV = \nabla\cdot\rho h\mathbf{v}\,\delta V = h_{cooling}(Pdz)(T_{cooling}-T)$$

Writing the divergence in cylindrical coordinates, dropping the radial and angular terms (plug flow) and considering that the total mass flux does not change in a catalytic reaction (ρv_z=const) we get:

$$\frac{\partial \rho h v_z}{\partial z} + \frac{1}{r}\overbrace{\frac{\partial r\rho h v_r}{\partial r}}^{0} + \frac{1}{r}\overbrace{\frac{\partial v_\theta}{\partial \theta}}^{0} = h_{cooling}\frac{\overbrace{\pi d_{tube}}^{P}dz}{\underbrace{\frac{\pi}{4}d_{tube}^{2}dz}_{\delta V}}(T_{cooling}-T)$$

$$\frac{d(\rho h v_z)}{dz} = h_{cooling}\frac{4}{d_{tube}}(T_{cooling}-T)$$

This equation shows that the enthalpy of the reactant mixture does only change by heat transfer through the tube wall. If the reactor was adiabatic ($h_{cooling}$=0), the enthalpy of the mixture would be constant.

1.a. Temperature and Composition Profiles in Catalytic Reactors

$$\rho v_z \frac{dh}{dz} = h_{cooling}\frac{4}{d_{tube}}\left(T_{cooling} - T\right)$$

The ODE derived above looks already much more useful than the 1st law of thermodynamics. However we need to manipulate it a little further to get an ODE that involves temperature as dependent variable.

Let‘s assume that our reaction mixture behaves like an ideal gas (good assumption for catalytic gas phase reactions in many cases). The mass-averaged mean properties of the reaction mixture are then given by:

$$h = \sum_i y_i h_i \qquad c_p = \sum_i y_i c_{p,i}$$

$$\rho v_z \frac{dh}{dz} = \rho v_z \frac{d}{dz}\Big(\sum_i y_i h_i\Big) = \rho v_z \sum_i y_i \frac{\overbrace{dh_i}^{c_{p,i}dT}}{dz} + \rho v_z \sum_i h_i \frac{\overbrace{dy_i}^{mole\,balance}}{dz}$$

1.a. Temperature and Composition Profiles in Catalytic Reactors

mole balance

$$\boxed{\rho v_z \frac{\partial y_i}{\partial z} = \omega_i M_i}$$

$$\rho v_z \frac{dh}{dz} = \rho v_z \sum_i y_i \overbrace{\frac{dh_i}{dz}}^{c_{p,i}dT} + \rho v_z \sum_i h_i \overbrace{\frac{dy_i}{dz}}^{mole\ balance}$$

$$\rho v_z \frac{dh}{dz} = \rho v_z \frac{dT}{dz} \overbrace{\sum_i y_i c_{p,i}}^{c_p} + \sum_i h_i \omega_i M_i$$

$$\Downarrow$$

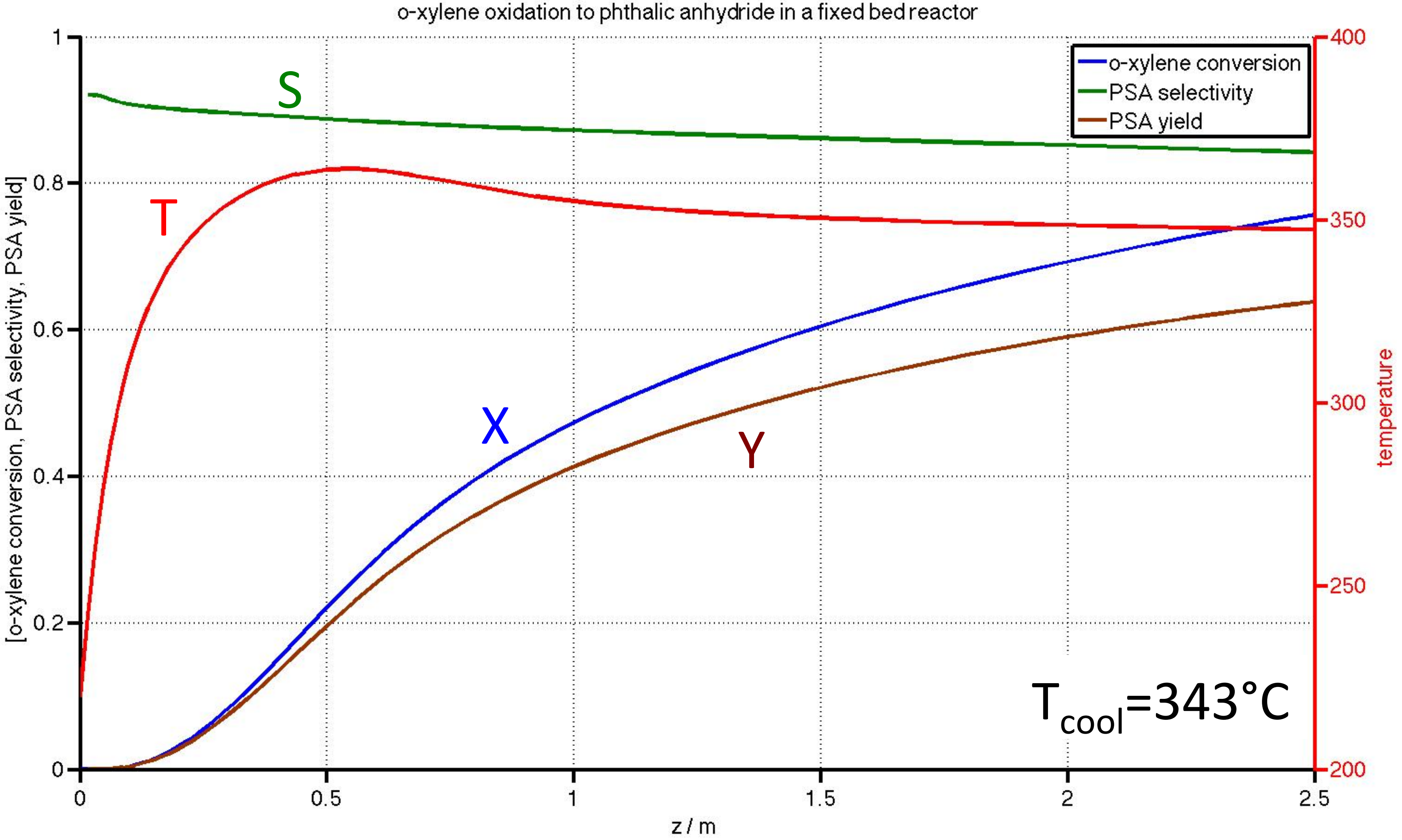
$$\rho v_z \frac{dh}{dz} = h_{cooling} \frac{4}{d_{tube}} (T_{cooling} - T)$$

$$\boxed{\frac{dT}{dz} = \frac{1}{\rho v_z c_p} \left[h_{cooling} \frac{4}{d_{tube}} (T_{cooling} - T) - \sum_i h_i \omega_i M_i \right]}$$

heat balance

Starting from the 1st law we derived an ODE that allows calculating the temperature profile of the reactor. It must be solved numerically together with the mole balance (e.g. Runge Kutta).

1.a. Temperature and Composition Profiles in Catalytic Reactors



T_{cool}=343°C

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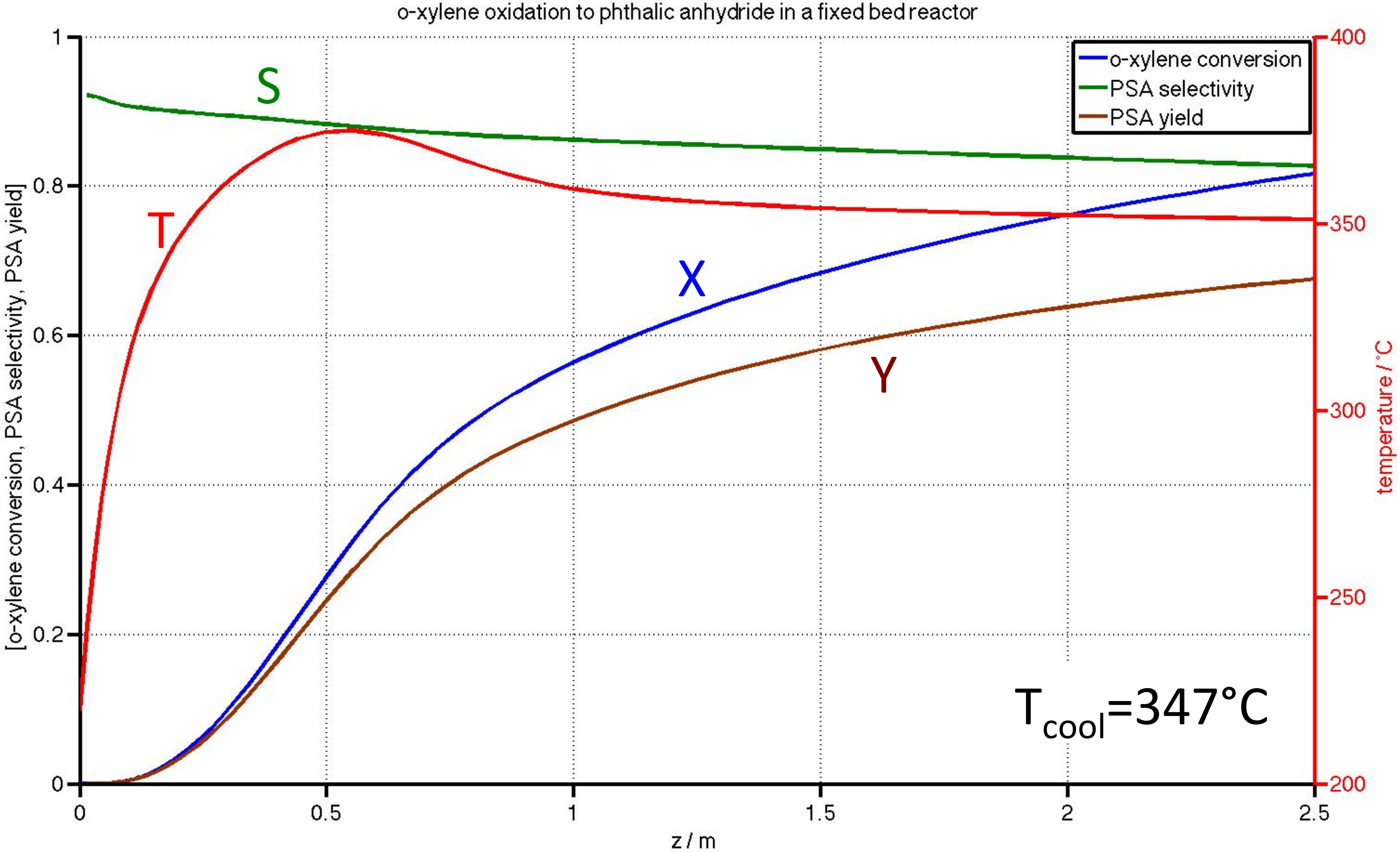
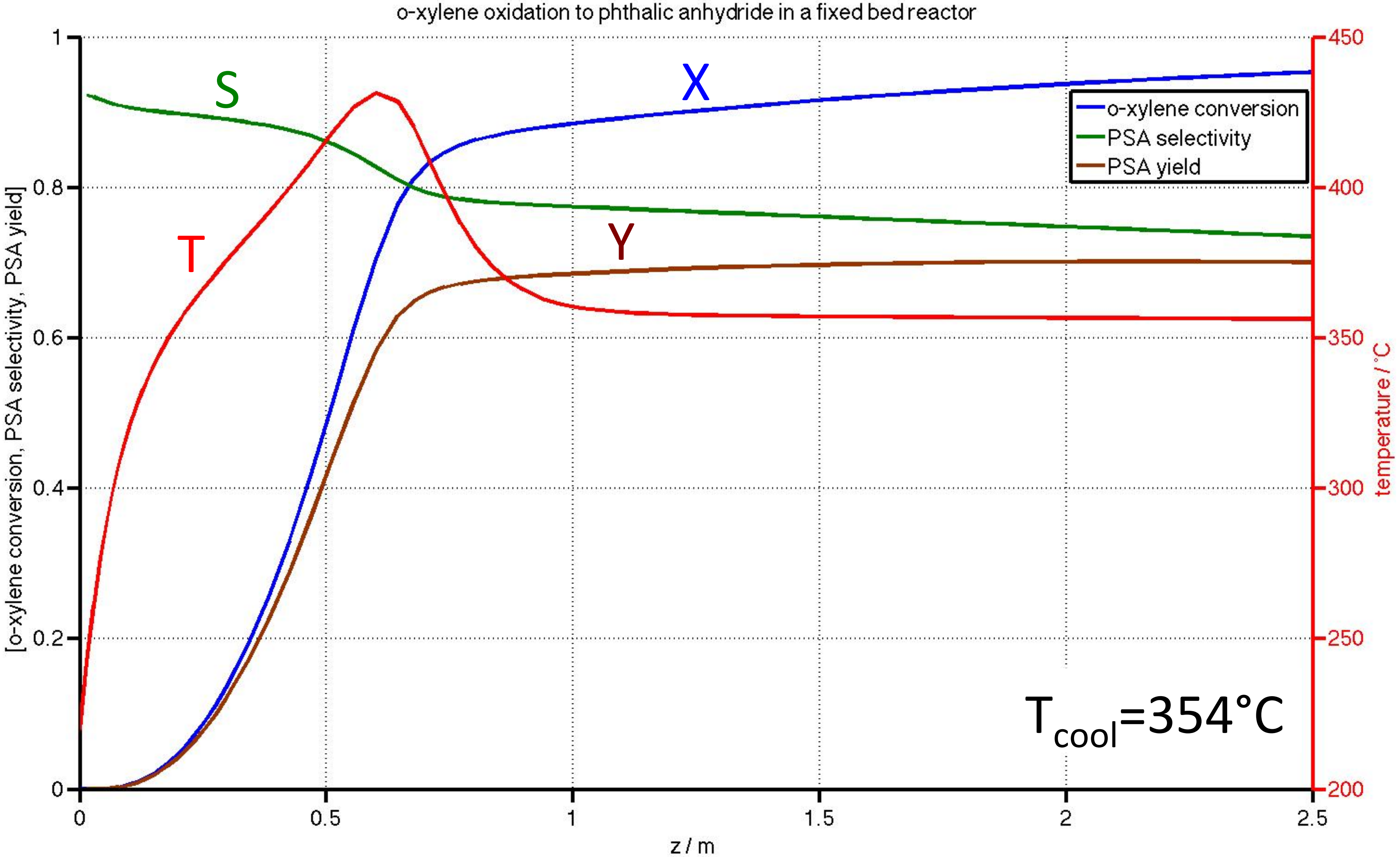
1.a. Temperature and Composition Profiles in Catalytic Reactors



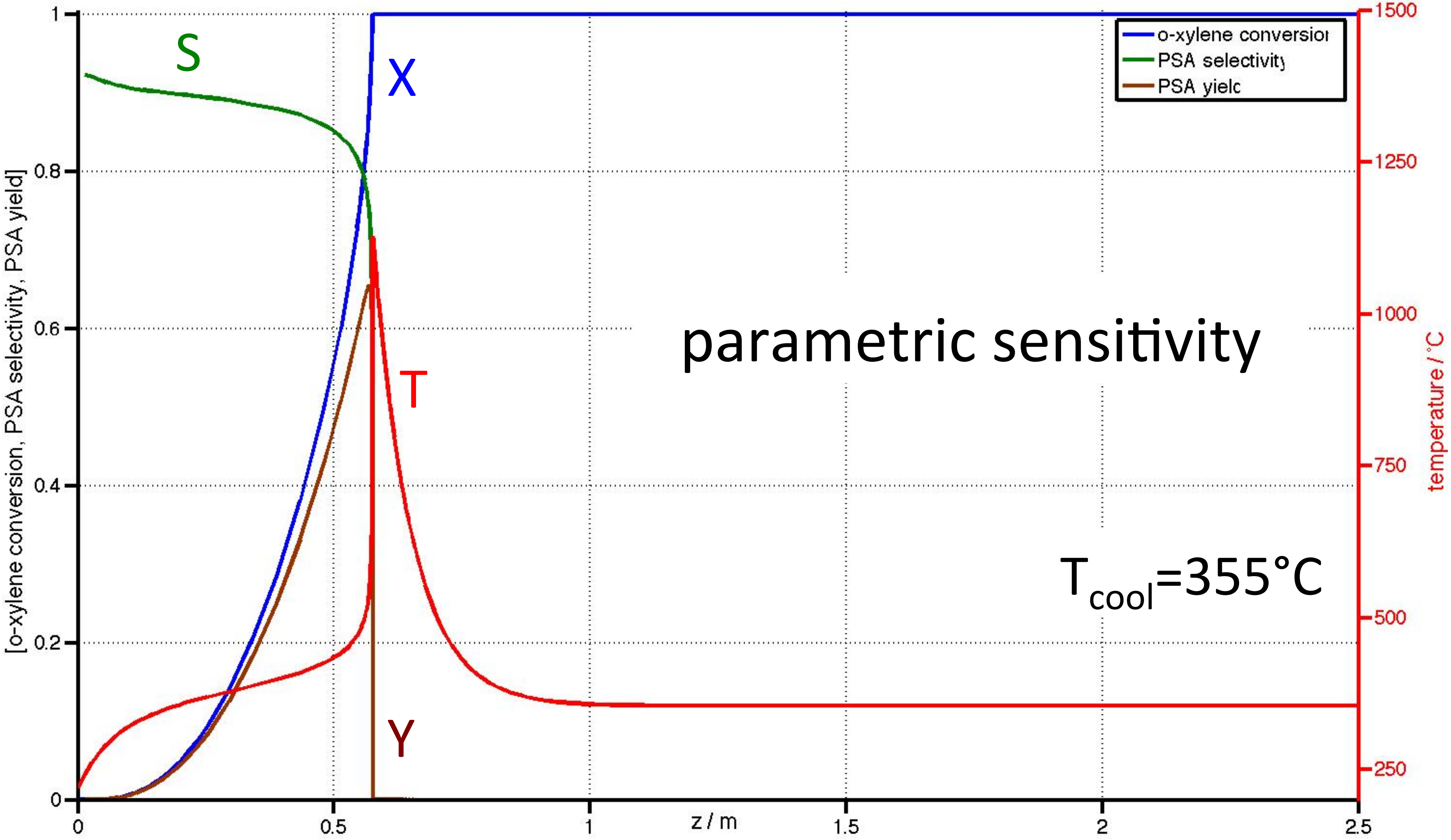
1.a. Temperature and Composition Profiles in Catalytic Reactors



T_{cool}=354°C

1.a. Temperature and Composition Profiles in Catalytic Reactors

o-xylene oxidation to phthalic anhydride in a fixed bed reactor



parametric sensitivity

T_{cool}=355°C

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

Example 2: Calculate the maximum NH_3 yield of the Haber-Bosch-Process for 25°C ≤ ϑ ≤ 600°C and 1bar ≤ p ≤ 500bar! Assume a stoichiometric feed and ideal gases for simplicity (standard state pure ideal gas at 1bar)!

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightleftarrows NH_3(g)$$

Thermodynamic Data (CRC Handbook, NIST Chemistry Webbook etc.):

Species	**ΔH_f° (298K) / $kJ \cdot mol^{-1}$**	**S° (298K) / $J \cdot mol^{-1} \cdot K^{-1}$**	**C_p° (298K) / $J \cdot mol^{-1} \cdot K^{-1}$**		
			A	**B / 10^{-3} K^{-1}**	**C / 10^{-6} K^{-2}**
N_2	0	191.6	24.98	5.912	-0.3376
H_2	0	130.7	29.07	-0.8368	2.012
NH_3	-45.9	192.8	25.93	32.58	-3.046

$$\frac{c_p^\circ}{J \cdot K^{-1} \cdot mol^{-1}} = A + B \cdot T + C \cdot T^2$$

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightleftarrows NH_3(g) \qquad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad -\frac{\Delta G^\circ}{RT} = \ln K$$

Species	ΔH_f° (298K) / kJ·mol^{-1}	S° (298K) / J·mol^{-1}·K^{-1}	C_p° (298K) / J·mol^{-1}·K^{-1}		
			A	B / 10^{-3} K^{-1}	C / 10^{-6} K^{-2}
N_2	0	191.6	24.98	5.912	-0.3376
H_2	0	130.7	29.07	-0.8368	2.012
NH_3	-45.9	192.8	25.93	32.58	-3.046

$$\Delta H^\circ = \left[-1/2\cdot 0 + (-3/2)\cdot 0 + 1\cdot(-45.9)\right]\frac{kJ}{mol} = -45.9\,\frac{kJ}{mol}$$

$$\Delta S^\circ = \left[-1/2\cdot 191.6 + (-3/2)\cdot 130.7 + 1\cdot 192.8\right]\frac{J}{mol\cdot K} = -99.05\,\frac{J}{mol\cdot K}$$

$$\Delta G^\circ = -45.9\,\frac{kJ}{mol} - 298.15\,K\cdot\left(-99.05\cdot 10^{-3}\right)\frac{kJ}{mol\cdot K} = -16.37\,\frac{kJ}{mol}$$

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(\frac{16.37\cdot 10^{3}\,J\cdot mol\cdot K}{mol\cdot 8.314\,J\cdot 298.15\,K}\right) = 738$$

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

Stoichiometry: $$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\rightleftarrows NH_3(g)$$

$$\xi\ extent\ of\ reaction\ [\xi]=mol$$

$$d\xi=\frac{1}{\nu_i}dn_i \quad \Rightarrow \quad \int_{n_{i,0}}^{n_i} dn_i=\nu_i\int_0^{\xi} d\xi \quad \Rightarrow \quad n_i=n_{i,0}+\nu_i\xi$$

Species	ν_i	n_{i0}/mol	n_i/mol	x_i
N_2	-1/2	1/2	1/2-1/2ξ	(1/2-1/2ξ)/(2-ξ)
H_2	-3/2	3/2	3/2-3/2ξ	(3/2-3/2ξ)/(2-ξ)
NH_3	1	0	ξ	ξ/(2-ξ)
Σ		2	2-ξ	1

$$X=\frac{n_{N_2,0}-n_{N_2}}{n_{N_2,0}}=\frac{-\nu_{N_2}\xi}{n_{N_2,0}}=\frac{-(-1/2)\xi}{1/2}=\xi \qquad Y=X\cdot\overbrace{S}^{1}=X=\xi$$

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightleftarrows NH_3(g)$$

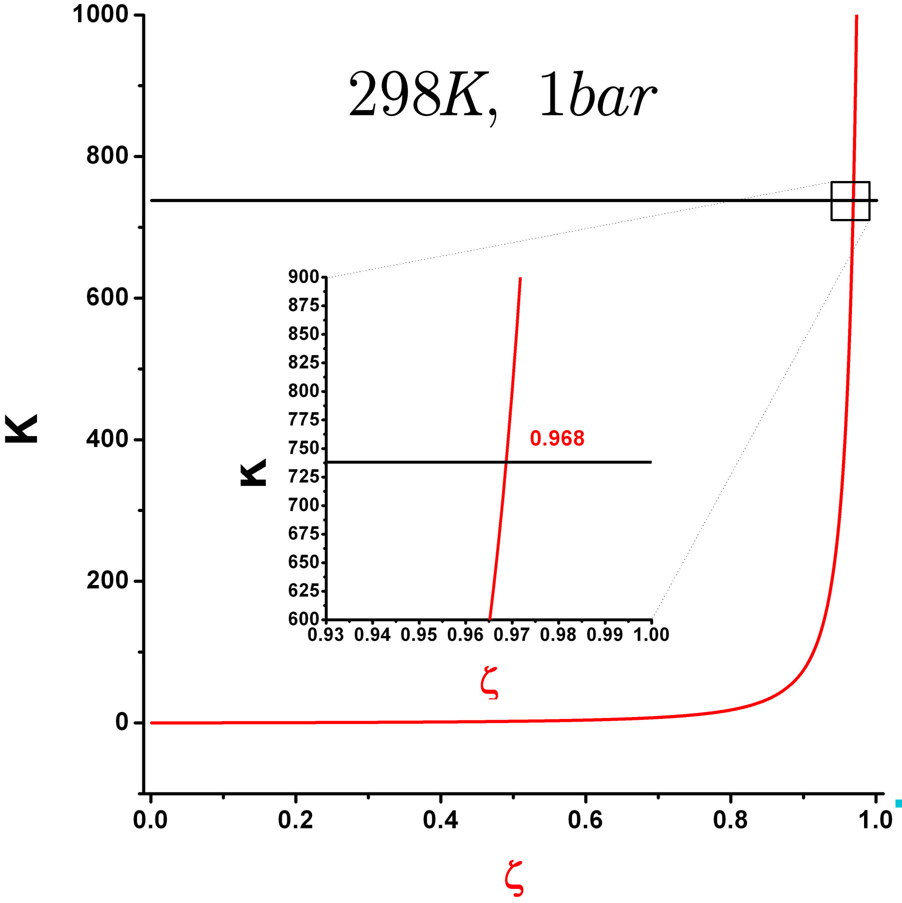
Species	ν_i	n_{i0}/mol	n_i/mol	x_i
N_2	-1/2	1/2	1/2-1/2ξ	(1/2-1/2ξ)/(2-ξ)
H_2	-3/2	3/2	3/2-3/2ξ	(3/2-3/2ξ)/(2-ξ)
NH_3	1	0	ξ	ξ/(2-ξ)
Σ		2	2-ξ	1

$$K(T)=\prod_i a_i^{\nu_i}=\frac{\left(\frac{p_{NH_3}}{p^\circ}\right)^1}{\left(\frac{p_{N_2}}{p^\circ}\right)^{1/2}\left(\frac{p_{H_2}}{p^\circ}\right)^{3/2}}=\frac{\left(\frac{\xi}{(2-\xi)}\frac{p}{p^\circ}\right)^1}{\left(\frac{(1/2-1/2\xi)}{(2-\xi)}\frac{p}{p^\circ}\right)^{1/2}\left(\frac{(3/2-3/2\xi)}{(2-\xi)}\frac{p}{p^\circ}\right)^{3/2}}$$

Standard state of a gas is the ideal gas at 1bar pressure! $p^\circ = 1bar$

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

$$K(298K) = 738 = \frac{\left(\frac{\xi}{(2-\xi)}\frac{1bar}{1bar}\right)^{1}}{\left(\frac{(1/2-1/2\xi)}{(2-\xi)}\frac{1bar}{1bar}\right)^{1/2}\left(\frac{(3/2-3/2\xi)}{(2-\xi)}\frac{1bar}{1bar}\right)^{3/2}}$$



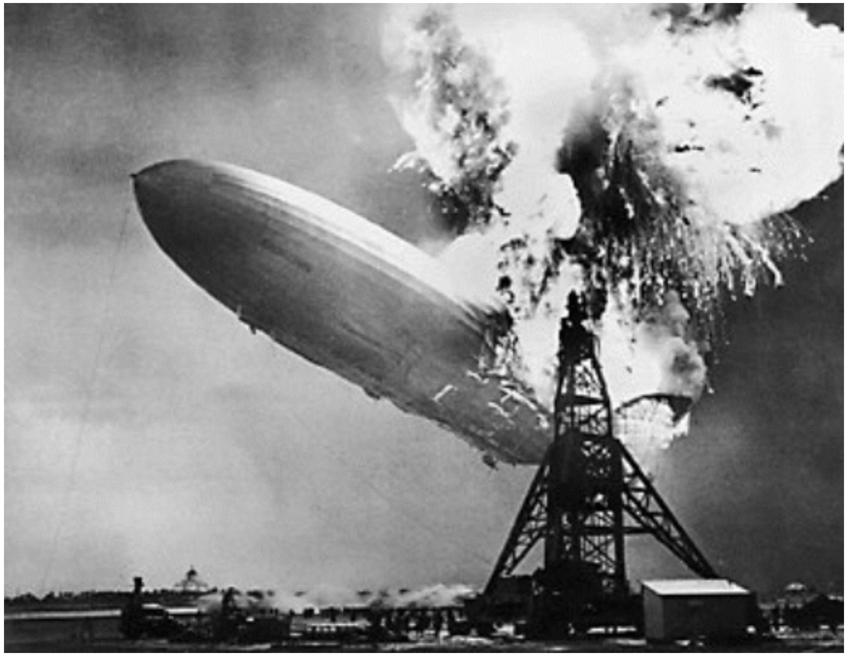
One way of solving this equation is by plotting LHS(ξ) vs. RHS(ξ) and see where the two are equal (Matlab, Origin, Excel etc.)

$$\xi_{\max}(298K, 1bar) =$$
$$Y_{NH3,\max}(298K, 1bar) = 0.968$$

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

$$\boxed{Y_{NH_3,\max}(298K, 1bar) = 0.968}$$

If we could do ammonia synthesis at room temperature, we could reach nearly 97% yield of ammonia (next Nobel prize is certain!). Unfortunately thermodynamics says nothing about the rate at which a reaction occurs. Ammonia synthesis is immeasurably slow at 298K!



2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \quad \Rightarrow \quad \ln K(T) = \ln K(T_{ref}) + \int_{T_{ref}}^{T} \frac{\Delta H^\circ(T)}{RT^2}\,dT$$

$$\Delta H^\circ(T) = \Delta H^\circ(T_{ref}) + \int_{T_{ref}}^{T} \Delta c_p^\circ(T)\,dT$$

Species	ΔH_f° (298K) / kJ·mol^{-1}	S° (298K) / J·mol^{-1}·K^{-1}	C_p° (298K) / J·mol^{-1}·K^{-1}		
			A	B / 10^{-3} K^{-1}	C / 10^{-6} K^{-2}
N_2	0	191.6	24.98	5.912	-0.3376
H_2	0	130.7	29.07	-0.8368	2.012
NH_3	-45.9	192.8	25.93	32.58	-3.046

$$\Delta c_p^\circ(T) = \Delta A + \Delta B \cdot T + \Delta C \cdot T^2 \qquad \Delta A = \sum_i \nu_i A_i \qquad etc.$$

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

$$\Delta H^{\circ}(T) = \Delta H^{\circ}(T_{ref}) + \int_{T_{ref}}^{T} (\Delta A + \Delta B \cdot T + \Delta C \cdot T^{2})\, dT$$

$$\Downarrow$$

$$\Delta H^{\circ}(T) = \overbrace{\Delta H^{\circ}(T_{ref}) - \Delta A \cdot T_{ref} - \frac{\Delta B}{2} \cdot T_{ref}^{2} - \frac{\Delta C}{3} \cdot T_{ref}^{3}}^{const.} + \Delta A \cdot T + \frac{\Delta B}{2} \cdot T^{2} + \frac{\Delta C}{3} \cdot T^{3}$$

$$\Downarrow$$

$$\frac{\Delta H^{\circ}(T)}{RT^{2}} = \frac{const.}{RT^{2}} + \frac{\Delta A}{RT} + \frac{\Delta B}{2R} + \frac{\Delta C}{3R} \cdot T$$

$$\ln K(T) = \ln K(T_{ref}) + \int_{T_{ref}}^{T} \frac{\Delta H^{\circ}(T)}{RT^{2}}\, dT$$

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

$$\ln K(T) = \ln K(T_{ref}) + \int_{T_{ref}}^{T} \left[\frac{const.}{RT^2} + \frac{\Delta A}{RT} + \frac{\Delta B}{2R} + \frac{\Delta C}{3R} \cdot T \right] dT$$

⬇

$$\ln K(T) = \ln K(T_{ref}) + \frac{const.}{R}\left[\frac{1}{T_{ref}} - \frac{1}{T} \right] + \frac{\Delta A}{R} \ln \frac{T}{T_{ref}} + \frac{\Delta B}{2R}(T - T_{ref}) + \frac{\Delta C}{6R}(T^2 - T_{ref}^2)$$

We know that $K(T_{ref} = 298K) = 738$

and that

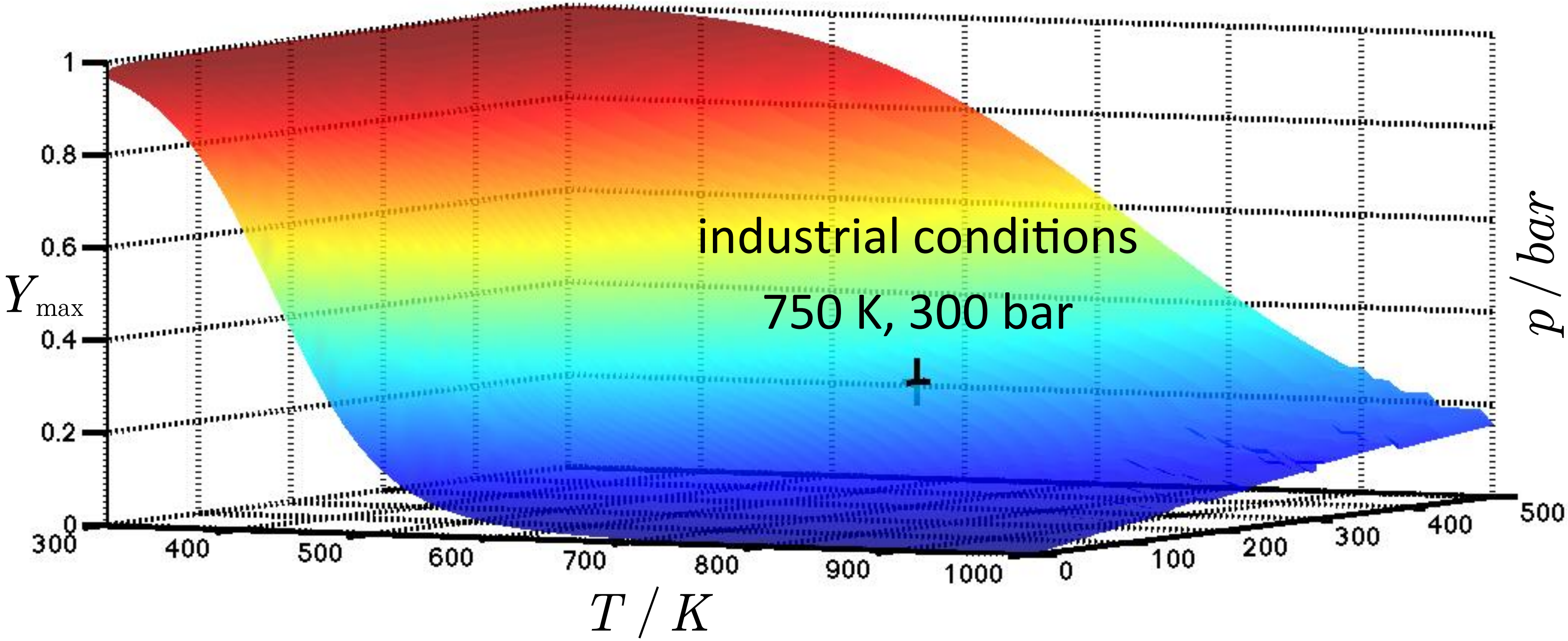
$$K(T) = \frac{\left(\frac{\xi}{(2-\xi)} \frac{p}{p^\circ} \right)^1}{\left(\frac{(1/2 - 1/2\xi)}{(2-\xi)} \frac{p}{p^\circ} \right)^{1/2} \left(\frac{(3/2 - 3/2\xi)}{(2-\xi)} \frac{p}{p^\circ} \right)^{3/2}}$$

so we can calculate $\xi = Y_{max}$ for the temperature and pressure range we are interested in (see Matlab file on class homepage).

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

Maximum ammonia yield as function of temperature and pressure.

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g)\overset{K}{\rightleftarrows}NH_3(g)$$



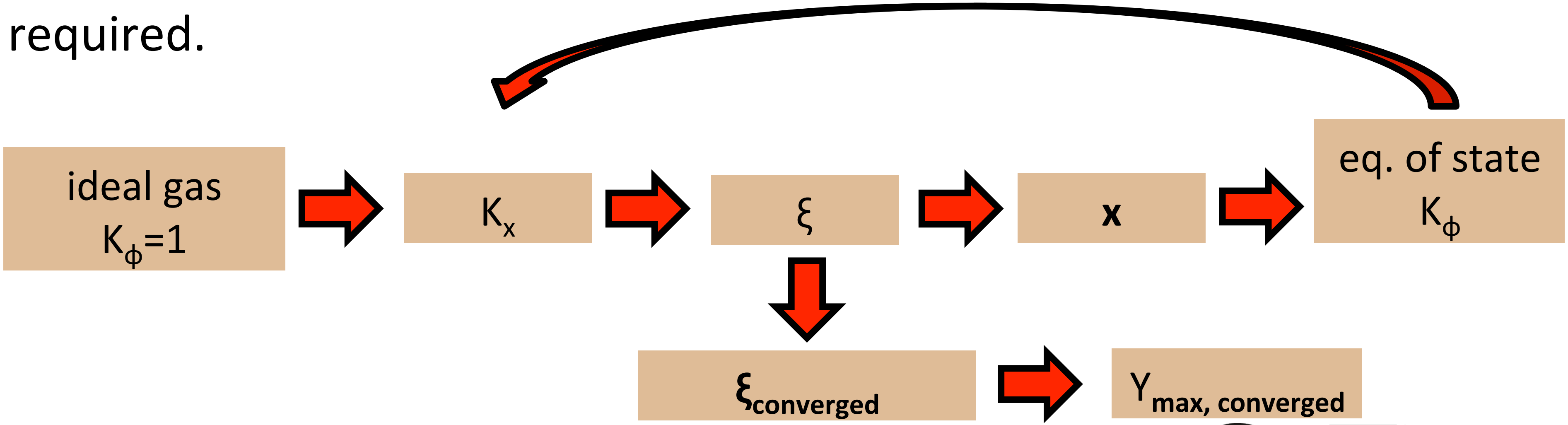
industrial conditions

750 K, 300 bar

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

$$K = \prod_i a_i^{\nu_i} = \underbrace{\prod_i x_i^{\nu_i}}_{K_x} \underbrace{\prod_i \bar{\varphi}_i^{\nu_i}}_{K_\varphi} \cdot \left(\frac{p}{1bar}\right)^{\sum_i \nu_i}$$

At high pressures gases are not ideal anymore. K(T) is only a function of T, but K_ϕ is not longer unity. This changes K_x and hence $\xi = X_{max} = Y_{max}$. Because fugacity coefficients need to be calculated from an equation of state requiring in turn mole fractions, an iterative computation is required.



ideal gas
$K_\phi = 1$

K_x

ξ

x

eq. of state
K_ϕ

$\xi_{\textbf{converged}}$

$Y_{\textbf{max, converged}}$

2.a. Calculating Thermodynamic Equilibrium for a Single Reaction

$$K = \prod_i a_i^{\nu_i} = \underbrace{\prod_i x_i^{\nu_i}}_{K_x} \underbrace{\prod_i \bar{\varphi}_i^{\nu_i}}_{K_\varphi} \cdot \left(\frac{p}{1bar}\right)^{\sum_i \nu_i}$$

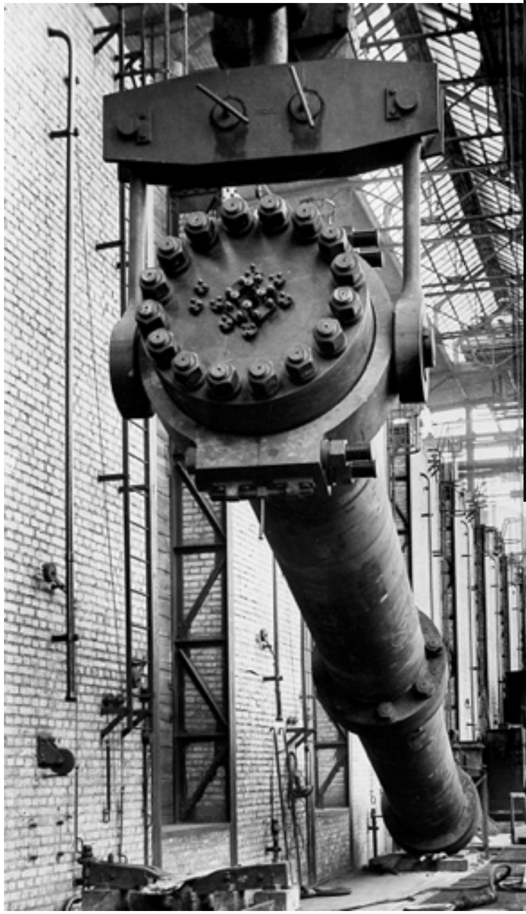
450°C						
p / bar	10	30	50	100	300	600
K_ϕ	0.994	0.975	0.942	0.877	0.688	0.496

D. A. Mc Quarrie, J. D. Simon, Physical Chemistry - A Molecular Approach S. 1080

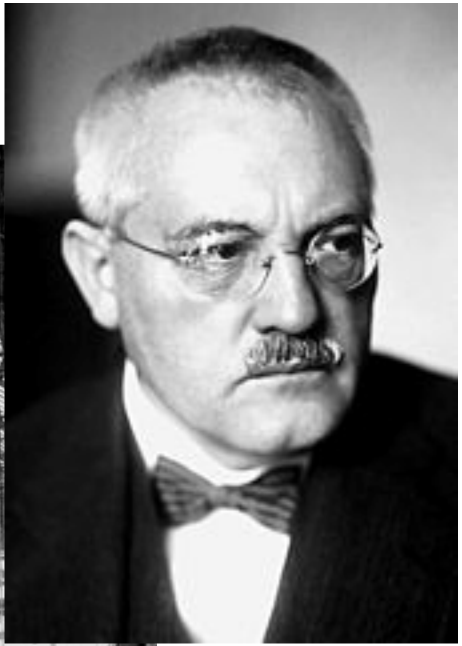
2.b. Catalytic Reactors for Thermodynamically Limited Reactions

Ammonia reactors:

reactor 1913



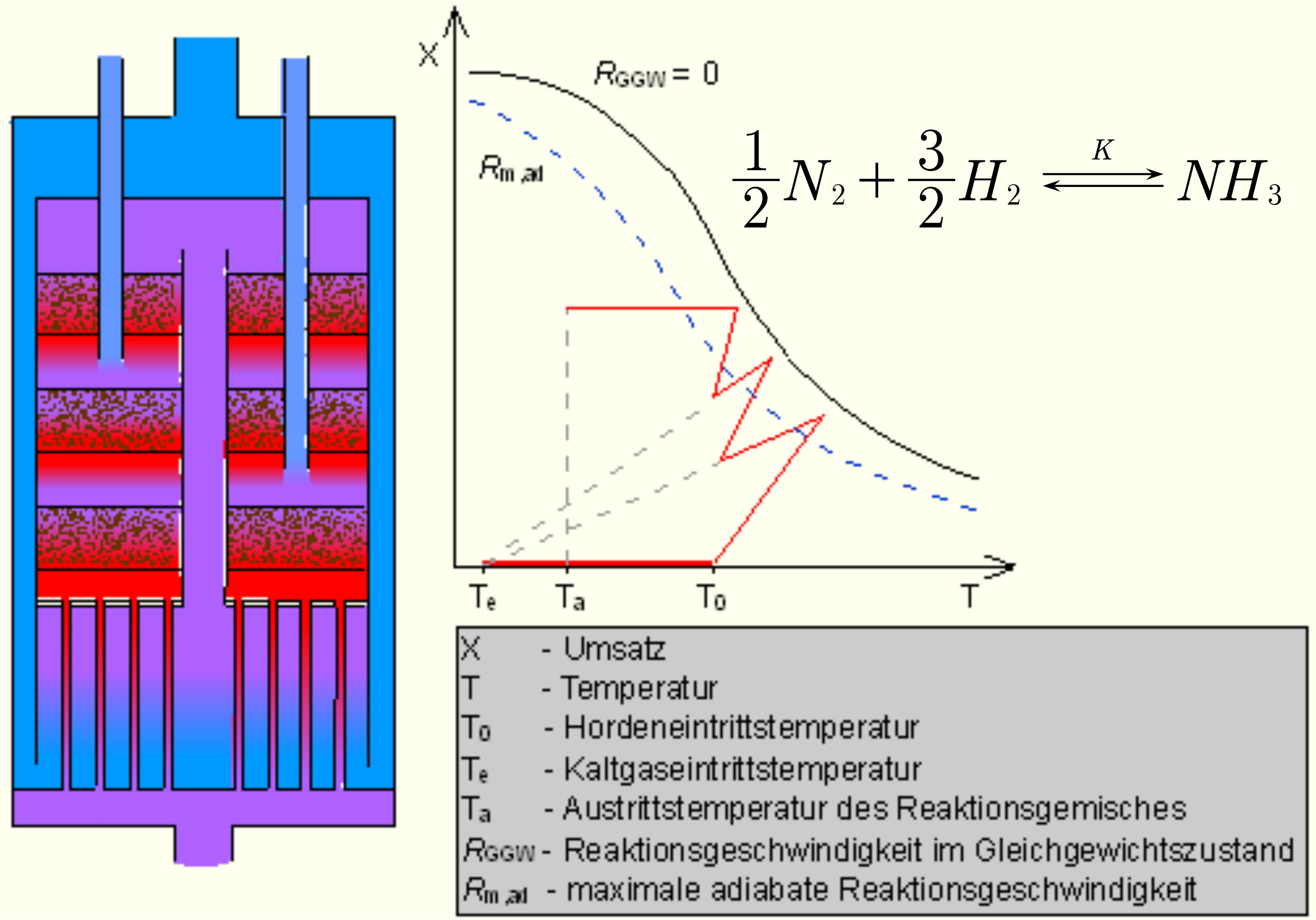
Carl Bosch



moderner NH_3 reactor

2.b. Catalytic Reactors for Thermodynamically Limited Reactions

Ammonia reactors inside:

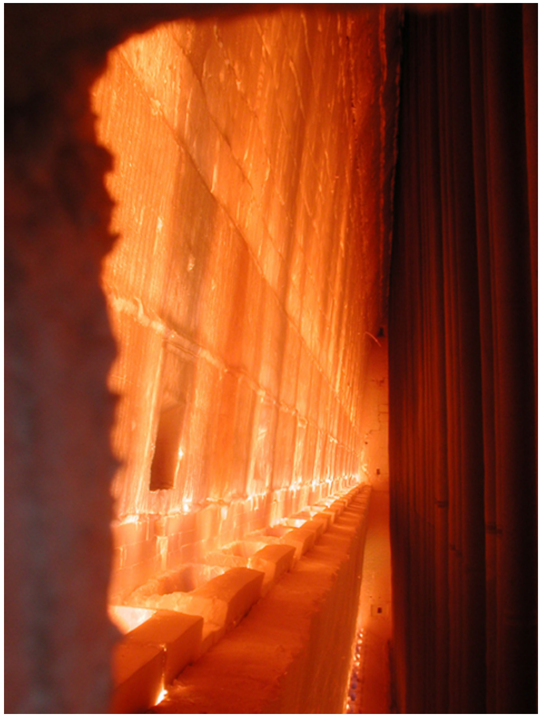


$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \xrightleftharpoons{K} NH_3$$

X - Umsatz
T - Temperatur
T_0 - Hordeneintrittstemperatur
T_e - Kaltgaseintrittstemperatur
T_a - Austrittstemperatur des Reaktionsgemisches
R_{GGW} - Reaktionsgeschwindigkeit im Gleichgewichtszustand
$R_{m,ad}$ - maximale adiabate Reaktionsgeschwindigkeit

2.a. Calculating Thermodynamic Equilibrium for Multiple Reactions

Example 3: Calculate the equilibrium composition for methane steam reforming at 1000K and 1bar pressure. The reaction mixture consists of CH_4, H_2O, CO, CO_2 and H_2. The feed consists of $n_{0,CH4}$=2mol and $n_{0,H2O}$=3mol. All gases can be treated as ideal gases.



2.a. Calculating Thermodynamic Equilibrium for Multiple Reactions

Theory: To calculate chemical equilibrium we have to solve the following minimization problem:

$$(G)_{T,p} = G(n_1, n_2, .n_i., n_S)_{T,p} = \min$$

The n_i cannot vary independently of each other, because we cannot loose or create atoms!

$$\sum_{i=1}^{S} a_{ki} n_i = b_k$$

total mol of atoms of sort k in the reaction mixture

number of atoms of sort k in species i

mol species i

We have to perform the minimization of G by accounting for k constraints!

constraints:

$$\sum_{i=1}^{S} a_{ki} n_i - b_k = 0$$

2.a. Calculating Thermodynamic Equilibrium for Multiple Reactions

We introduce k Lagrange multiplies:

constraints	Lagrange multipliers
$\sum_{i=1}^{S} a_{ki} n_i - b_k = 0$	$\lambda_k \left(\sum_{i=1}^{S} a_{ki} n_i - b_k \right) = 0 \quad \sum_{k=1}^{M} \lambda_k \left(\sum_{i=1}^{S} a_{ki} n_i - b_k \right) = 0$

Formulation of the Lagrange function:

$$L = (G)_{T,p} + \sum_{k=1}^{M} \lambda_k \left(\sum_{i=1}^{S} a_{ki} n_i - b_k \right)$$

Minimization of the Lagrange function yields:

$$\left(\frac{\partial L}{\partial n_i} \right)_{T,p,n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} + \sum_{k=1}^{M} \lambda_k a_{ki} = \mu_i + \sum_{k=1}^{M} \lambda_k a_{ki} = 0$$

2.a. Calculating Thermodynamic Equilibrium for Multiple Reactions

This translates into the solution of the following system of equations:

$$\mu_i^\circ + RT\ln a_i + \sum_{k=1}^{M} \lambda_k a_{ki} = 0$$

S-equations (one for each species)

$$\sum_{i=1}^{S} a_{ki} n_i - b_k = 0$$

M-equations (one for each sort of atom)

solve this system of non-linear equations for the mole numbers of all species and the Langrange multipliers

We need the chemical potentials of the species in their standard states:

Spezies	**CH_4**	**H_2O**	**CO**	**CO_2**	**H_2**
$\mu_i°=\Delta G_f°$ (1000K) / $J \cdot mol^{-1}$	19475	-192603	-200281	-395865	0

2.a. Calculating Thermodynamic Equilibrium for Multiple Reactions

Let‘s formulate the system of equations:

$$\sum_{i=1}^{S} a_{ki} n_i - b_k = 0$$

$$\mu_i^{\circ} + RT \ln a_i + \sum_{k=1}^{M} \lambda_k a_{ki} = 0 \quad \Rightarrow \quad \frac{\Delta G_{f,i}^{\circ}}{RT} + \ln a_i + \sum_{k=1}^{M} \frac{\lambda_k}{RT} a_{ki} = 0$$

$$a_i = \frac{p_i}{1bar} = \frac{x_i \cdot p}{1bar} = \frac{x_i \cdot 1bar}{1bar} = x_i = \frac{n_i}{\sum_{i=1}^{S} n_i}$$

atom balances ($n_{0,CH4}$=2mol, $n_{0,H2O}$=3mol, $n_{0,CO}$=$n_{0,CO2}$=$n_{0,H2}$=0mol) ➔ b_C=2mol, b_H=14mol, b_O=3mol

C-balance $$1 \cdot n_{CH_4} + 0 \cdot n_{H_2O} + 1 \cdot n_{CO} + 1 \cdot n_{CO_2} + 0 \cdot n_{H_2} - 2 = 0$$

H-balance $$4 \cdot n_{CH_4} + 2 \cdot n_{H_2O} + 0 \cdot n_{CO} + 0 \cdot n_{CO_2} + 2 \cdot n_{H_2} - 14 = 0$$

O-balance $$0 \cdot n_{CH_4} + 1 \cdot n_{H_2O} + 1 \cdot n_{CO} + 2 \cdot n_{CO_2} + 0 \cdot n_{H_2} - 3 = 0$$

2.a. Calculating Thermodynamic Equilibrium for Multiple Reactions

CH_4

$$\frac{19475}{8.314 \cdot 1000} + \ln\left(\frac{n_{CH_4}}{\sum_i n_i}\right) + \frac{\lambda_C}{8.314 \cdot 1000} + \frac{4 \cdot \lambda_H}{8.314 \cdot 1000} = 0$$

H_2O

$$\frac{-192603}{8.314 \cdot 1000} + \ln\left(\frac{n_{H_2O}}{\sum_i n_i}\right) + \frac{2 \cdot \lambda_H}{8.314 \cdot 1000} + \frac{\lambda_O}{8.314 \cdot 1000} = 0$$

CO

$$\frac{-200281}{8.314 \cdot 1000} + \ln\left(\frac{n_{CO}}{\sum_i n_i}\right) + \frac{\lambda_C}{8.314 \cdot 1000} + \frac{\lambda_O}{8.314 \cdot 1000} = 0$$

CO_2

$$\frac{-395865}{8.314 \cdot 1000} + \ln\left(\frac{n_{CO_2}}{\sum_i n_i}\right) + \frac{\lambda_C}{8.314 \cdot 1000} + \frac{2 \cdot \lambda_O}{8.314 \cdot 1000} = 0$$

H_2

$$\ln\left(\frac{n_{H_2}}{\sum_i n_i}\right) + \frac{2 \cdot \lambda_H}{8.314 \cdot 1000} = 0$$

2.a. Calculating Thermodynamic Equilibrium for Multiple Reactions

Initial values for the Langrange multipliers can be guesses using physico-chemical knowledge that mole fractions take on values between 0 and 1: e.g. for x_{H2}=0.5

$$\ln\left(\frac{n_i}{\sum_{i=1}^{S} n_i}\right) + \frac{2 \cdot \lambda_H}{8.314 \cdot 1000} = 0 \xrightarrow{with\ x_{H2}=0.5} \lambda_{H,0} = -\frac{8.314 \cdot 1000 \cdot \ln 0.5}{2} = 2881$$

Solving this non-linear system of equations yields (e.g. Matlab ‚fsolve‘):

Equilibrium composition for steam reforming at 1000K and 1bar starting from 2mol CH_4 and 3mol H_2O.

$$n_{CH_4} = 0.175\,mol$$
$$n_{H_2O} = 0.856\,mol$$
$$n_{CO} = 1.507\,mol$$
$$n_{CO_2} = 0.319\,mol$$
$$n_{H_2} = 5.795\,mol$$
$$\sum_i n_i = 8.651\,mol$$

⇒

$$x_{CH_4} = 0.0202$$
$$x_{H_2O} = 0.0990$$
$$x_{CO} = 0.1742$$
$$x_{CO_2} = 0.0368$$
$$x_{H_2} = 0.6698$$
$$\sum_i x_i = 1$$

Thank you very much for your attention!