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EUROKIN spreadsheet on requirements for measurement of intrinsic kinetics in the gas-solid fixed-bed reactor

This document contains background information on the spreadsheet *EUROKIN_fixed-bed_html* developed for the assessment of transport limitations in a fixed bed reactor

Date issued: August 2012

DISCLAIMER

This spreadsheet and its functionality are not tested exhaustively and represent a beta-version. The use of the spreadsheet is at the user's own risk.

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SOURCE AND REFERENCE

The use of this spreadsheet is free. Please use the following reference: *EUROKIN_fixed-bed_html*, EUROKIN spreadsheet on requirements for measurement of intrinsic kinetics in the gas-solid fixed-bed reactor, 2012.

The Eurokin consortium, founded in 1998, is a consortium of industrial and academic members whose aim is the implementation of best practice in the area of chemical reaction kinetics, particularly in the industrial environment. This is achieved by carrying out work in a number of areas such as the design of experiments and the interpretation of kinetic data to make the latest knowledge in these fields available to the end user. In many cases this has resulted in the development of user-friendly tools to allow, for example, more efficient assessment of experimental conditions. Other work has been aimed at evaluating the software available for processing kinetic data while a number of leading academics and experts have been commissioned to produce reviews of the state-of-the-art in a number of chemical kinetics topics. For more information on the Eurokin consortium see: https://eurokin.org/.

The spreadsheet and this document have been composed by Rob Berger, Anaproc; c/o ChemE, Delft University of Technology, 2628 BL Delft, The Netherlands on behalf of the Eurokin consortium (https://eurokin.org/).

PURPOSE

This document provides explanation and help for use with the spreadsheet *EUROKIN_fixed-bed_html*. It contains additional information on the values to be specified by the user and it contains a complete description of the literature correlations used in the spreadsheet for the assessment of transport limitations and other disturbing phenomena such as axial dispersion.

The spreadsheet is aimed at the assessment of transport limitations in order to fulfill the requirements for direct measurement of intrinsic reaction kinetics. For allowing accurate measurement of the intrinsic reaction kinetics the effect of all transport limiting phenomena must be negligible. The general condition for allowing neglecting transport limitations is that the effect on the conversion rate is less than 5%. It is noted that the spreadsheet does not take into account combined effects of different transport phenomena.

Another application of the spreadsheet is to estimate the characteristics of industrial-scale beds.

It is stressed that many of the correlations used are only valid in a limited range of conditions. The use outside the validity ranges may lead to wrong conclusions. For this demonstration sheet we implemented, as far as available, a widely used and broadly applicable correlation for each parameter required. Of course there are many more correlations available in the open literature. These are available in the larger and more sophisticated version of this spreadsheet available for members of the Eurokin consortium only.

In order to demonstrate the use of and functions in the spreadsheet a specific example has been implemented, an example on the decomposition of nitrous oxide (N_2O) in a catalyst bed diluted with inert SiC particles. The spreadsheet shows that the example fulfils all requirements for direct measurement of intrinsic kinetics except the one for diffusion limitation inside the catalyst particles. The spreadsheet shows that the example fulfils all requirements for direct measurement of intrinsic kinetics except the one for diffusion limitation inside the catalyst particles.

The document also describes experimental checks for the presence of transport limitations that can be used to get more confidence, in particular for cases in which many catalyst characteristics are not available.

As mentioned above, this tool is a fully functional but limited version compared to the version available for Eurokin members. The table summarizes the differences between both.

Differences in functionality	This tool	Tool Eurokin members
Option for recycle	No	Yes
Number of components	4	7
Correlations for bed voidage	1	25
Correlations for pressure drop over the bed	1	15
Correlations for radial temperature gradient	1	28
Correlations for external temperature gradient	1	8
Correlations for radial dispersion / axial dispersion	0 / 1	7 / 12
Correlations for external concentration gradient	1	21
Calculation of mixture thermal conductivity and viscosity	No	Yes
Diffusivity	Bulk/Knudsen/simplified Stefan-Maxwell	
Criterion for axial temperature gradient	No	Yes
Criterion for inert bed dilution	Yes	Yes
Typical values of catalyst and inert diluent properties (porosity, tortuosity, thermal conductivity, density)	No	Yes
Option to store input data	No	Yes
Bright colours for indicating fulfillment of the criteria	No	Yes

CONTENTS

ADDITIONAL INFORMATION ON ITEMS IN THE SPREADSHEET

The spreadsheet *EUROKIN_fixed-bed_html* contains several references to background information and additional information. This information can be found at the items below.

(1)   Default case

N_2O decomposition on Rh/Co_3O_4-Al_2O_3 at 550 K, 250 kPa, 0.04% N_2O in He, $W/F(N_2O)$ = 950 kg s / mol; 50 mg of catalyst diluted with 150 mg of non-porous SiC. The reaction rate was estimated at 1.0×10^{-4} mol-N_2O/kg-cat/s. This is also the standard case implemented.

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2 \tag{1}$$

The reaction order with respect to the reactant N_2O is one and with respect to all other compounds zero. The apparent activation energy amounts to 150 kJ/mol and the reaction enthalpy amounts to 81.5 kJ/mol. The stoichiometric numbers of the components involved in the reaction are -1, 1 and 0.5 for N_2O, N_2, and O_2, respectively.

The value of the reaction rate constant in the spreadsheet is calculated directly from the observed reaction rate ignoring any transport limitations.

(2)   Bulk void fraction

The typical value of the bed porosity or bulk void fraction is 0.38-0.40. Higher porosities occur if the particle size is less than one order of magnitude smaller than the bed diameter.

(3)   Conversion

The conversion in the spreadsheet is calculated with the assumption that the reaction is irreversible with a constant reaction order, and ignoring any transport limitations and the effect of the change of volume due to reaction. The influence of the change of volume due to reaction is in reality only negligible at low conversion or with much dilution with inert gas.

For a 1st order reaction applies:

$$X_A = 1 - \exp\left(k\frac{W}{F_{A,0}}p_{A,0} \right) \tag{2}$$

Where:
X_A = conversion of reactant A [-]
k = reaction rate constant [mol$_A$/Pa$_A$kg$_{cat}$s]
W = catalyst weight [kg$_{cat}$]
$F_{A,0}$ = feed molar flow of reactant A [mol/s]
$p_{A,0}$ = partial pressure of reactant A in the feed [Pa$_A$]

For other reaction orders the conversion follows from:

$$X_A = 1 - \left\{ 1 + k(n-1)\frac{W}{F_{A,0}}\left(p_{A,0}\right)^{n-1} \right\}^{\frac{1}{1-n}} \tag{3}$$

Where: n = reaction order with respect to reactant A [-]

(4)   Relative pressure drop over the catalyst bed

$$\Delta P < \frac{0.2P_{tot}}{n} \tag{4}$$

Where: ΔP = pressure drop over the catalyst bed [Pa]
P_{tot} = feed pressure [Pa]
n = reaction order [-]

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For estimating the pressure drop over the bed the widely applied correlation from Ergun [1] is used:

$$f_m = \frac{(1-\varepsilon_b)}{\varepsilon_b^3}\left(1.75 + 150\frac{(1-\varepsilon_b)}{Re}\right)$$ {5}

Where: f_m = modified friction factor

ε_b = bed porosity [m_{void}^3/m_{bed}^3]

Re = Reynolds number

The validation range of this correlation is $0.1 < Re < 1000$.

The Reynolds number is defined as:

$$Re = \frac{d_{pe}\,\rho_G u_0}{\mu_G}$$ {6}

Where: d_{pe} = diameter of sphere of equivalent specific surface, calculated as six times the ratio of the particle volume and the external surface area.

ρ_G = gas density [kg/m^3]

u_0 = superficial gas velocity [m/s]

μ_G = gas viscosity [kg/ms]

For simplicity, the equivalent particle diameter d_{pe} is in the spreadsheet set equal to the particle diameter, d_p.

The pressure drop follows from:

$$\frac{\Delta P}{h_{bed}} = \frac{f_m\,\rho_G\,u_0^2}{d_{pe}}$$ {7}

Where: h_{bed} = height catalyst bed [m]

(5)   Axial dispersion

Mears [2] and Gierman [3] defined the following criterion for the bed height for allowing neglection of the axial dispersion and thus allowing the assumption of plug-flow behaviour:

$$\frac{h_{bed}}{d_p} > \frac{8}{Bo}\,n\ln\left\{\frac{1}{1-X_A}\right\}$$ {8}

Where: d_p = particle diameter [m]

Bo = Bodenstein number [-]

X_A = conversion of the reactant [-]

The Bodenstein number for axial mass transport, or Pe_p the Péclet number referring to the particle, is defined as:

$$Bo \equiv Pe_p = \frac{u_0\,d_p}{D_{A,ax}}$$ {9}

Where: $D_{A,ax}$ = axial dispersion coefficient of A in the bed [m^2/s]

A widely valid correlation for the Bodenstein number comes from Wakao et al. [4]:

$$\frac{1}{Bo} = \frac{\varepsilon_b D_{A,m}}{\tau_b d_p u_0} + 0.5 \equiv \frac{\varepsilon_b}{\tau_b ReSc} + 0.5$$ {10}

Where: ε_b = bed porosity [m^3/m_{bed}^3]

$D_{A,m}$ = molecular diffusivity of A in the gas mixture [m^2/s]

τ_b = bed tortuosity [-]

Sc = Schmidt number [-], defined as $\mu_G/(\rho_G D_{A,m})$

Re = Reynolds number [-], defined as $d_p\rho_G u_0/\mu_G$

For the tortuosity of the bed the correlation reported by Puncochar & Drahos [5] can be used:

$$\tau_b = \frac{1}{\sqrt{\varepsilon_b}} \qquad \{11\}$$

(6) Radial dispersion

Chu & Ng [6] showed that the following criterion is valid for the bed diameter and the particle diameter for allowing the assumption of absence of radial concentration gradients:

$$d_t / d_p \;>\; 8 \qquad \{12\}$$

Where: d_t = catalyst bed diameter [m]

(7) Inert bed dilution

Berger et al. [7] defined the following criterion for the fraction of inert bed dilution:

$$\Delta = \left(\frac{b}{1-b} \right) \frac{x_{dil}\, d_p}{2\, h_{bed}} \qquad \{13\}$$

Where: Δ = relative deviation of the conversion in comparison with the conversion that would be obtained if the catalytic activity would be homogeneously distributed over the bed [-]

   b = volume of inert material as fraction of total solids volume [m³$_{inert}$/m³$_{inert+cat}$]

   x_{dil} = conversion obtained with the diluted bed [-]

The volumetric dilution, b, can be calculated with:

$$b = \frac{W_{dil} / \rho_{dil}}{W_{cat} / \rho_{cat} + W_{dil} / \rho_{dil}} \qquad \{14\}$$

Where: W_{dil} = amount of inert dilution material [kg].

   ρ_{dil} = density of dilution particles [kg/m³$_{pellet}$]

   W_{cat} = amount of catalyst [kg]

   ρ_{cat} = density of catalyst particles [kg/m³$_{catpellet}$]

With the maximum accepted deviation set at 0.05 follows:

$$b < \frac{1}{1 + 10\, x_{dil}\, d_p / L} \qquad \{15\}$$

(8) External mass transfer limitation

The extent of external mass transfer limitation, i.e. mass transfer limitation over the gas film surrounding the catalyst particles is expressed using the Carberry number, defined as (Mears [8]):

$$Ca \;=\; \frac{R_{v,A}^{obs}}{k_g\, a_v\, C_{A,b}} \;=\; \frac{C_{A,b} - C_{A,s}}{C_{A,b}} \;<\; \frac{0.05}{n} \qquad (n > 0) \qquad \{16\}$$

Where: Ca = Carberry number [-]

   $R_{v,A}^{obs}$ = observed volumetric reaction rate per unit of catalyst pellet volume [mol/m³$_{catpellet}$s]

   k_G = external mass transfer coefficient [-]

   a_v = specific external surface area of a single catalyst particle [m²/m³$_{pellet}$]; for a spherical particle equal to 6/d_p.

   $C_{A,b}$ = bulk concentration of reactant A [mol/m³$_{gas}$]

$C_{A,s}$ = concentration of reactant *A* at the external pellet surface [mol/m³_{gas}]

The criterion is that the resistance due to external mass transfer is less than 5% of the resistance due to chemical reaction. For a first-order reaction, the efficiency follows from:

$$\eta = 1 - Ca \quad \text{(for } n > 0\text{)} \tag{17}$$

Where: η = catalyst efficiency (concerning external mass transfer limitation) [-]

There are many empirical correlations available for the mass transfer coefficient between pellet and gas bulk (k_g). The correlation from Wakao et al. [4], validated in the range 0.1 < *Re* < 100, is used here:

$$Sh = 2 + 1.1 Re^{0.6} Sc^{\frac{1}{3}} \tag{18}$$

In which the Sherwood number (*Sh*) is defined according to:

$$Sh = \frac{k_G \, d_p}{D_{A,m}} \tag{19}$$

It is noted that this calculation does not take into account the effect of limitation by any other transport phenomenon.

(9) Internal diffusion limitation

The extent of internal diffusion limitation, i.e. pore diffusion limitation inside the catalyst particles, is expressed using the Weisz-Prater criterion (Froment & Bischoff [9]):

$$\Phi = \left(\frac{n+1}{2}\right) \frac{R_{v,A}^{obs} \left(d_p/6\right)^2}{D_{A,eff} \, C_{A,s}} \tag{20}$$

Where: Φ = Weisz modulus [-]
$R_{v,A}^{obs}$ = observed volumetric reaction rate per unit of catalyst pellet volume [mol/m³_{catpellet}s]
$D_{A,eff}$ = effective diffusivity inside the catalyst particles [m²/s], see (16)
$C_{A,s}$ = concentration of reactant A at the external catalyst particle surface [mol$_A$/m³]

The deviation caused by pore diffusion limitation is smaller than 5% if $\Phi < 0.08$. For a zero-order reaction, however, Φ should be < 0.33 (Anderson & Pratt [10]).

The Weisz modulus expresses the ratio between the observed rate and the 'diffusion rate' as follows:

$$\Phi = \eta \phi^2 \tag{21}$$

where: η = effectiveness factor

ϕ = Thiele modulus $= \dfrac{d_p}{6} \sqrt{\left(\dfrac{n+1}{2}\right) \dfrac{R_{v,A}}{D_{A,eff} \, C_{a,s}}}$ (for spherical particles)

If Φ is known, η and ϕ can be calculated (by using a solver).
For a first order reaction, thus $n = 1$, η can be determined analytically from ϕ:

$$\eta = \frac{1}{\phi}\left(\frac{1}{\tanh(3\phi)} - \frac{1}{3\phi}\right) \tag{22}$$

η can then be determined via trial & error (or using a solver).
For $\Phi < 0.1$, η will be almost 1 and ϕ can be estimated simply from $\phi = \sqrt{\Phi}$.
For simplicity this has been implemented in the spreadsheet.

It is noted that this calculation does not take into account the effect of limitation by any other transport phenomenon.

(10) External heat transfer limitation

The criterion for external heat transfer limitation, i.e. heat transfer limitation over the gas film surrounding the catalyst particles is according to Mears [8]) expressed as follows:

$$\Delta T_{film} = \frac{R_{v,A}^{obs} \left| \Delta_r H \right| d_p}{6\, \alpha_p} < \frac{0.05\, R T_G^2}{E_a}$$ {23}

Where: ΔT_{film} = temperature difference over the film surrounding the catalyst particles [K]

$\Delta_r H$ = reaction enthalpy [J/mol$_A$]

α_p = particle heat transfer coefficient [W/mK]

R = ideal gas constant [J/mol K]

T_G = bulk gas temperature [K]

E_a = (apparent) activation energy of the reaction [J/mol]

There are many empirical correlations available for α_p, the heat transfer coefficient between pellet and fluid bulk. A widely applicable correlation is the one from Wakao et al. [4], which is similar to the one for external mass transfer limitation. It has been validated in the range 0.1 < *Re* < 100.

$$Nu = 2 + 1.1 Re^{0.6} Pr^{1/3}$$ {24}

Where: Pr = Prandtl number [-], defined as $c_{p,G}\mu_G/\lambda_G$ (with $c_{p,G}$ = gas heat capacity in J/kg K)

In which the Nusselt number (*Nu*) is defined according to:

$$Nu = \frac{\alpha_p\, d_p}{\lambda_G}$$ {25}

Where: λ_G = thermal conductivity of the gas mixture [W/m K]

(11) Radial heat transfer limitation

According to Mears [8], the following criterion is valid concerning radial heat transport limitation in the catalyst bed:

$$\Delta T_{rad} = \frac{R_{v,A}^{obs} \left| \Delta_r H \right| (1-\varepsilon_b)(1-b) d_t^2}{32\, \lambda_{er}} < \frac{0.05\, R T_w^2}{E_a}$$ {26}

Where: ΔT_{rad} = temperature difference between the bed near the wall and the average in the bed [K]

$\Delta_r H$ = reaction enthalpy [J/mol$_A$]

b = volume of inert material as fraction of total solids volume [m$^3_{inert}$/m$^3_{inert+cat}$]

λ_{er} = effective radial thermal conductivity in the bed [W/mK]

If the reactor wall temperature is measured instead of the temperature at the centerline of the bed, the following criterion applies:

$$\Delta T = \left(1 + \frac{8}{Bi_w}\right) \frac{R_{v,A}^{obs} \left| \Delta_r H \right| (1-\varepsilon_b)(1-b) d_t^2}{32\, \lambda_{er}} < \frac{0.05 R T_w^2}{E_a}$$ {27}

Where: Bi_w = Biot number [-]

The Biot number at the internal reactor wall is defined as follows:

$$Bi_w = \frac{\alpha_w\, d_t}{\lambda_{er}}$$ {28}

Where: α_w = heat transfer coefficient at the internal reactor wall [W/m²K]

Since this second criterion is more difficult to fulfill, the experimentator is always recommended to measure the catalyst bed temperature directly, e.g. by a thermocouple in the catalyst bed or in the thermowell in the centre of the bed.

There are many empirical correlations available for the effective radial heat conductivity, λ_{er}, and the heat transfer coefficient at the internal reactor wall, α_w, to describe the radial heat transfer in the reactor. A correlation validated at $Re > 40$ is the one from Specchia et al. [11].

The effective radial thermal conductivity in the bed (λ_{er}) is estimated as follows:

$$\frac{\lambda_{er}}{\lambda_G} = \frac{\lambda_{b,0}}{\lambda_G} + \frac{\lambda_{conv}}{\lambda_G} \qquad \{29\}$$

Where:

$$\frac{\lambda_{conv}}{\lambda_G} = \frac{Re_p\, Pr}{Pe_{rif}} \quad \text{with: } Pe_{rif} = 8.65\left[1 + 19.4\left(\frac{d_p}{d_t}\right)^2\right] \qquad \{30\}$$

and

$$\frac{\lambda_{b,0}}{\lambda_G} = \varepsilon_b + \frac{1 - \varepsilon_b}{0.220\varepsilon_b^2 + \frac{2}{3}\left(\frac{\lambda_G}{\lambda_p}\right)} \qquad \{31\}$$

Where: $\lambda_{b,0}$ = static contribution effective radial thermal conductivity [W/m K]

λ_{conv} = convective contribution to radial thermal conductivity [W/m K]

d_p = pellet diameter [m]

λ_p = thermal conductivity of the particles in the bed [W/m K]

Note that λ_p is the average thermal conductivity of the particles in the bed. In the presence of inert bed dilution this bed dilution influences this value. The way in which this influence is accounted for can be found at **(12)** on page 11.

The heat transfer coefficient at the wall based on a model in which the heat conduction through the bed is also accounted for, α_w, is estimated as follows:

$$\alpha_w = \alpha_w^0 + \alpha_{w,conv} \qquad \{32\}$$

Where:

$$\frac{\alpha_w^0\, d_p}{\lambda_G} = 2\varepsilon_b + \frac{1 - \varepsilon_b}{0.0024\left(\frac{d_t}{d_p}\right)^{1.58} + \frac{1}{3}\left(\frac{\lambda_G}{\lambda_p}\right)} \qquad \{33\}$$

and:

For $Re_p < 1200$: $\quad \alpha_{w,conv} = 0.0835\dfrac{\lambda_G}{d_p}Re_p^{0.91}\left(\dfrac{Pr}{Pr_{air,80°C}}\right)^{1/3}$

$$\{34\}$$

For $Re_p \geq 1200$: $\quad \alpha_{w,conv} = 1.23\dfrac{\lambda_G}{d_p}Re_p^{0.53}\left(\dfrac{Pr}{Pr_{air,80°C}}\right)^{1/3}$

Where: α_w = heat transfer coefficient gas - reactor wall [W/m² K]

α_w^0 = static contribution heat transfer coefficient gas-wall [W/m² K]

$\alpha_{w,conv}$ = convective contribution heat transfer coefficient gas-wall [W/m² K]

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It is noted that the correlation above for λ_{er} and α_w, are not validated at $Re < 40$, occurring in most lab-reactor applications. Nevertheless it appears that the correlation does give a reasonable estimates at lower values of Re. The correlation is also not validated at $Re > 10,000$.

N.B. The effect of heat transfer by radiation is neglected. Depending on geometry and application, the contribution by radiation is negligible at temperatures below 1100-1400 K.

(12) Intraparticle heat transport limitation

According to Mears [8] the following criterion is valid concerning internal thermal conduction in the catalyst particles:

$$\Delta T_{int} = \frac{R_{v,A}^{obs} |\Delta_r H| d_p^2}{60 \lambda_p} < \frac{0.05 \, R \, T^2}{E_a} \tag{35}$$

Where: ΔT_{int} = Temperature difference between the edge and the average in the particle [K]
$\qquad \lambda_p$ = thermal conductivity of the catalyst particle [W/m K]

The average pellets heat conductivity (λ_p) can be calculated from the conductivity of the catalyst pellets (λ_{cat}) and the dilution pellets (λ_{dil}) by using the volume-weighted mean of the heat conductivity resistances :

$$\frac{1}{\lambda_p} = \frac{1-b}{\lambda_{cat}} + \frac{b}{\lambda_{dil}} \tag{36}$$

(13) Adiabatic temperature rise

A parameter of general interest is the adiabatic temperature rise (ΔT_{ad} [K]), which is easily calculated from:

$$\Delta T_{ad} = \frac{|\Delta_r H| y_A X_A}{C_{p,G}} \tag{37}$$

Where: y_A = molar fraction of reactant A in the feed [-]
$\qquad \Delta_r H$ = reaction enthalpy [J/mol$_A$]
$\qquad X_A$ = conversion of reactant A [-]
$\qquad C_{p,G}$ = heat capacity of the gas mixture [J/mol K]

(14) Axial temperature gradient

A criterion concerning the axial temperature profile in a fixed bed is normally not necessary since the effect of the axial temperature gradient in the bed is smaller than that for the radial temperature profile if the reactor wall can be assumed isothermal over the length of the catalyst bed.

(15) Bulk diffusivity

Binary molecular diffusivity in gases (bulk diffusivity)

The binary molecular diffusivity of gas A in gas B, D_{AB}, can be estimated with the semi-empirical correlation from Fuller, Schettler and Giddings (Perry et al. [12])

$$D_{AB} = \frac{3.2 \times 10^{-11} \, T^{1.75} \sqrt{\frac{1}{m_A} + \frac{1}{m_B}}}{P_{tot} \left\{ (\Sigma v)_A^{1/3} + (\Sigma v)_B^{1/3} \right\}^2} \tag{38}$$

where : D_{AB} = diffusivity of A in B [m^2/s]
$\qquad\qquad T$ = temperature   [K]
$\qquad\qquad m_i$ = molecular mass of i [kg/mol]
$\qquad\qquad P_{tot}$ = total pressure   [kPa]
$\qquad\qquad (\Sigma v)_i$ = diffusion volume of i [m^3/mol]

Table: *Diffusion volumes for estimation of the molecular diffusivity [10^{-6} m^3/mol]*

H_2	D_2	He	N_2	O_2	Air	Ne	Ar	Kr	Xe
7.07	6.70	2.88	17.9	16.6	20.1	5.59	16.1	22.8	37.9
CO	CO_2	N_2O	NH_3	H_2O	CCl_2F_2	SF_5	Cl_2	Br_2	SO_2
18.9	26.9	35.9	14.9	12.7	114.8	69.7	37.7	67.2	41.1

Table: *Atomic and structural diffusion volume increments for use with organic molecules for estimation of the molecular diffusivity [10^{-6} m^3/mol]*

C	H	O	N	Cl	S	Aromatic ring	Heterocyclic ring
16.5	1.98	5.48	5.69	19.5	17.0	-20.2	-20.2

N.B. The Fuller-Schettler-Giddings equation is not valid for polar mixtures or at high pressures; alternative equations can be found in Perry et al. [12].

Bulk diffusivity in gas mixtures

A simple equation for the bulk diffusivity of a component in a gas mixture containing more than two molecules (D_{Am}) can be estimated from the individual binary diffusivities (D_{Ai}) according to the Wilke-equation (Perry et al. [12]):

$$D_{Am} = \left(1 - x_A\right)\left(\sum_{i=1(i \neq A)}^{N_c} \frac{x_i}{D_{Ai}}\right)^{-1} \qquad \{39\}$$

where : N_c = total number of components
x_i = molar fraction of component i

Unfortunately, the Wilke-equation is only valid in diluted mixtures in a stagnant medium. Particularly in cases in which the gas is diluted with a fast-diffusing gas such as hydrogen or helium, the equation is only valid for very highly diluted mixtures.

Therefore, it is in most cases more accurate to use the Stefan-Maxwell equation since this takes into account the effect of the diffusion of the other compounds. Compounds that diffuse in the same direction have less influence than components that diffuse in the opposite direction (or inert components that show no net diffusion). In order to do so, however, one needs to include the stoichiometry of the reaction taking place (which determines the values of v_i).

$$D_{Am}^{\circ} = \frac{1 - x_A \sum_{i=1}^{N_c} \frac{v_i}{v_A}}{\sum_{i=1(i \neq A)}^{N_c} \left\{\frac{1}{D_{Ai}}\left(x_i - x_A \frac{v_i}{v_A}\right)\right\}} \qquad \{40\}$$

where : D_{Am}° = reduced molecular diffusivity of A
v_i = stoichiometric coefficient of component i (positive for products, negative for reactants)

$$f_A = \frac{\left(x_{A,i} - x_A\right)\sum_{i=1}^{N_c}\left(\frac{v_i}{v_A}\right)}{\ln\left\{\frac{1 - x_A \sum_{i=1}^{N_c}\left(\frac{v_i}{v_A}\right)}{1 - x_{A,i} \sum_{i=1}^{N_c}\left(\frac{v_i}{v_A}\right)}\right\}} \qquad \{41\}$$

where : f_A = so-called film factor (for component A)
$x_{A,i}$ = molar fraction of component i at the gas-solid interface (for external diffusion limitation)

The effective diffusivity is then calculated according to:

$$D_{Am} = \frac{D_{Am}^{\circ}}{f_A} \qquad \{42\}$$

Unfortunately, accurate use of this equation requires an iteration loop since the mole fraction of A at the gas-solid interface is not known beforehand and depends on the diffusivity. For equimolar counterdiffusion (which occurs if there is no net consumption of production of molecules), the film factor f_A reduces to one, and thus $D_{Am} = D^{\circ}{}_{Am}$.

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If the effect of transport limitation is assumed to be small (i.e. $x_{A,i} \cong x_A$), the film factor f_A reduces to $f_{A,app}$:

$$f_{A,app} = 1 - x_A \sum_{i=1}^{N_c} \left(\frac{v_i}{v_A} \right) \qquad \{43\}$$

where :
$f_{A,app}$ = approximate film factor (for component A)

Particularly in diluted gas mixtures, this approximation stays reasonably accurate up to situations with significant or even strong transport limitations. Therefore this equation has been implemented the spreadsheet.

(16) Effective diffusivity

The effective diffusivity in the catalyst particle pores, $D_{A,eff}$, is lower than the bulk diffusivity due to the restriction caused by the solid material. It is estimated from the molecular diffusivity of A in the mixture, $D_{A,m}$, the catalyst porosity (ε_p) and the catalyst pore tortuosity (τ_p) according to:

$$D_{A,eff} = \frac{\varepsilon_p}{\tau_p} D_A$$

With gases and in case of catalysts with narrow pores, which applies to most catalysts, the limitation due to Knudsen diffusion has to be taken into account according to e.g. Satterfield [13] by means of :

$$D_{eA} = \frac{\varepsilon_p / \tau_p}{\dfrac{1}{D_{A,m}} + \dfrac{1}{D_{A,k}}}$$

Knudsen diffusivity

A diffusion process is called Knudsen diffusion if the transport of the gas molecules is limited by molecule-wall collisions and not by molecule-molecule collisions as in bulk diffusion. Knudsen diffusion becomes slower than bulk diffusion if the pore size is smaller than the mean free path of the gas molecules, amounting to app. 10 nm at atmospheric pressure.

$$D_{A,K} = \frac{2}{3} \bar{r} \sqrt{\frac{8RT}{\pi m_A}}$$

where :
$D_{A,K}$ = Knudsen diffusivity of A [m²/s]
$\bar{r}$ = (average) pore radius   [m]
R = gas constant   [J/mol K]
T = temperature   [K]
m_A = molecular mass of A [kg/mol]

If long cylindrical pores with uniform pore diameter are assumed, average pore radius $\bar{r}$ can be calculated according to:

$$\bar{r} = \frac{2\varepsilon_p}{\rho_p S}$$

where :
ε_p = pellet porosity   [-]
ρ_p = pellet density   [kg/m$_{pellet}^3$]
S = specific internal surface area   [m²/kg-cat]

REFERENCES

[1]   Ergun S., Fluid flow through packed columns, *Chem. Eng. Progr.* **48** (1952) 89-92.

[2]   Mears D.E., Role of axial dispersion in trickle-flow laboratory reactors, *Chem. Eng. Sci.* **26**, (1971) 1361-1366.

[3]   Gierman, H., Design of laboratory hydrotraeting reactors – Scaling down of trickle-flow reactors, *Appl. Catal.*, **43** (1988) 277-286.

[4]   Wakao N.; Kaguei S.; Funazkri, T.; Effect of fluid dispersion coefficients on particle-to-fluid heat-transfer coefficients in packed-beds – Correlation of Nusselt numbers. *Chem. Eng. Sci.* **34** (1979) 325-336.

[5]   M. Puncochar and J. Drahos, The tortuosity concept in fixed and fluidized-bed, *Chem. Eng. Sci.* **48** (1993) 2173-2175.

[6]   Chu, C.F., K.M. Ng, Flow in packed tubes with a small tube to particle diameter ratio, *AIChE. J.* **35** (1989) 148-158.

[7]   Berger, R.J., Pérez-Ramírez, J., Kapteijn, F. and Moulijn, J.A., Catalyst performance testing: bed dilution revisited, *Chem. Eng. Sci.*, 57 (2002) 4921-4932.

[8]   Mears D.E., Diagnostic criteria for heat transport limitations in fixed bed reactors, *J. Catal.* **20** (1971) 127-131.

[9]   Froment G.F., Bischoff K., *Chemical Reactor Analysis and Design*, J. Wiley & Sons, New York, 1990.

[10] Anderson J.R. and Pratt K.C., *Introduction to characterization and testing of catalysts*, Academic Press, Sydney, 1985.

[11] Specchia V., Baldi G., Sicardi S., Heat transfer in packed bed reactors with one phase flow, *Chem. Eng. Commun.*, 4 (1980) 361-380.

[12] Perry R.H., Green D.W., Perry's Chemical Engineers' Handbook, 7th Ed. McGraw-Hill, New York, 1997.

[13] Satterfield C.N., Mass Transfer in heterogeneous catalysis, MIT Press, Cambridge, Mass. (1970).

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