

Example 4: Power Law Model Without Use of Effectiveness Factor

Sulfur Dioxide Oxidation

Effectiveness factors can be useful for simple, single reactions, but they are not useful for multiple reactions or even complex single reactions. In order to deal with the intraparticle gradients with multiple reaction systems, there are two possibilities: (1) develop kinetics with small catalyst particles and then integrate the mass balances in the catalyst particles at each point in the reactor model, or (2) develop kinetics on the commercial size catalyst which incorporate the intraparticle effects into the rate expression. The first option is not very practical due to the computational requirements which are difficult because of the two point boundary problem in addition to the extensive computations required. The second option is demonstrated in this example.

The example is a single reaction, but an accepted rate expression is quite complex, so it will be a good test. A power law rate expression will be developed for the model. Thus, this example is a test of both the adequacy of power law models and modeling without effectiveness factors.

The approach will be to use the "true" rate expression to develop reaction rate data at various concentrations and temperatures. Integration of the conservation equations for the catalyst pellet will produce a set of reaction rates for the various bulk concentrations. These data will be used in the second phase to develop the power law expressions.

The example studied is unique because commercially it is carried out in shallow beds with very low velocities to minimize pressure drop. This results in interfacial gradients for both the temperature and the concentrations. In this worksheet, velocities more typical of traditional fixed bed reactors will be assumed. The interfacial gradients will be checked to see whether or not they are significant. The assumption is that most systems will require a heat balance for the particle to account for the interfacial resistance of heat transfer, but that the lower mass transfer resistance will allow bulk concentrations to be used for the pellet surface concentrations.



This example draws extensively from data reported by Rase, **Vol 2**, Case 107, pf 86.

$$R_g = 1.987 \cdot \frac{\text{cal}}{\text{mol} \cdot \text{K}}$$

Bulk Conditions used for dimensionless variables

$$T_0 = 900 \text{ } ^\circ\text{F}$$

$$P_{tot} = 1 \cdot \text{atm}$$

Catalyst properties

$$\rho_p = 1.1729 \cdot \frac{\text{gm}}{\text{cm}^3}$$

cylinders

$$d_{ap} = .22 \cdot \text{in}$$

$$l_p = .40 \cdot \text{in}$$

$$V_p = \pi \cdot d_{ap}^2 \cdot l_p = 9.97 \times 10^{-4} L \quad \text{volume of particle}$$

effective diameter

$$d_p = 6 \cdot \frac{\frac{\pi}{4} \cdot d_{ap}^2 \cdot l_p}{\pi \cdot d_{ap} \cdot l_p + 2 \cdot \frac{\pi}{4} \cdot d_{ap}^2} = 0.26 \cdot \text{in}$$

effective radius

$$R_p = \frac{d_p}{2}$$

effective diffusivity

$$D_{eff} = 0.0286 \cdot \frac{\text{cm}^2}{\text{s}}$$

$$h_p = 0.015 \cdot \frac{\text{cal}}{\text{cm}^2 \cdot \text{s} \cdot \text{K}} \quad \text{assumed}$$

thermal conductivity of catalyst solid

$$k_s = 10^{-4} \cdot \frac{\text{cal}}{\text{s} \cdot \text{cm} \cdot \text{K}}$$

assumed based on typical range cited by Carberry (1976) pg 493

Thermophysical Data

Use Reid et al and compare with those used in the Rase example.

$$NC = 5$$

$$\begin{array}{l}
 \text{SO}_2 \\
 \text{SO}_3 \\
 \text{O}_2 \\
 \text{N}_2 \\
 \text{CO} \\
 2
 \end{array}
 \quad
 M_w = \begin{pmatrix} 64 \\ 80 \\ 32 \\ 28 \\ 44 \\ 2 \end{pmatrix} \cdot \frac{\text{gm}}{\text{mol}}
 \quad
 \Delta H_f = \begin{pmatrix} -70.95 \\ -94.47 \\ 0 \\ 0 \\ -94.05 \end{pmatrix} \cdot \frac{\text{kcal}}{\text{mol}}$$

Heat capacity

$$c_p = \begin{pmatrix} 5.697 & 1.6 \cdot 10^{-2} & -1.185 \cdot 10^{-5} & 3.172 \cdot 10^{-9} \\ 7.5 & 1.98 \cdot 10^{-2} & 1.91 \cdot 10^{-5} & 5.18 \cdot 10^{-9} \\ 6.713 & -8.79 \cdot 10^{-6} & 4.17 \cdot 10^{-6} & -2.544 \cdot 10^{-9} \\ 7.44 & -3.24 \cdot 10^{-2} & 6.4 \cdot 10^{-6} & -2.79 \cdot 10^{-9} \\ 4.728 & 1.754 \cdot 10^{-2} & -1.338 \cdot 10^{-5} & 4.097 \cdot 10^{-9} \end{pmatrix} \cdot \frac{\text{cal}}{\text{mol} \cdot \text{K}}$$

The values for SO₃ were estimated based on the Reid SO₂ values and the ratio of the SO₂ and SO₃ enthalpy coefficients in Rase

$$C_p T f(T) = \left[1 \quad \frac{T}{K} \quad \left(\frac{T}{K} \right)^2 \quad \left(\frac{T}{K} \right)^3 \right]^T \quad \text{heat capacity temperature functions}$$

$$\nu = \begin{pmatrix} -1 & 1 & \frac{-1}{2} & 0 & 0 \end{pmatrix} \quad \text{stoichiometric matrix}$$

$$\nu \cdot M_w = 0 \frac{\text{kg}}{\text{mol}} \quad \text{check Mw}$$

Heats of reaction

$$\Delta H_o = \nu \cdot \Delta H_f \quad \text{standard state, at 298 K}$$

$$\Delta H_o = -9.85 \times 10^4 \cdot \frac{\text{J}}{\text{mol}}$$

$$\Delta C_p = \nu \cdot c_p$$

$$DHT(T) = \left(T \frac{T^2}{2 \cdot K} \frac{T^3}{3 \cdot K^2} \frac{T^4}{4 \cdot K^3} \right)^T$$

integrate the heat capacity function to obtain the enthalpy functions

$$\Delta H(T) = \Delta H_o + \Delta C_p \cdot (DHT(T) - DHT(298 \cdot K))$$

heat of reaction at T

$$\Delta H(T_o) = -8.02 \times 10^4 \cdot \frac{J}{mol}$$

Compare to Rase expression

$$\Delta H_{SO_2}(T) = - \left[4.19 \cdot 10^4 - 64.395 \cdot \frac{T}{R} + 7.522 \cdot 10^{-2} \cdot \left(\frac{T}{R} \right)^2 - 2.942 \cdot 10^{-5} \cdot \left(\frac{T}{R} \right)^3 \right] \cdot \frac{cal}{mol}$$

$$\Delta H_{SO_2}(T_o) = -8.14 \times 10^4 \cdot \frac{J}{mol}$$

Rankine temperatures and cal/mol were required for Rase expression in order to obtain comparable results.

Feed conditions

mole fractions

$$mf_{feed} = \begin{pmatrix} .0626 \\ 0 \\ 0.083 \\ 0.854 \\ 0 \end{pmatrix}$$

$$\sum mf_{feed} = 1$$

weight fractions

$$\omega_{feed} = \frac{\overrightarrow{(mf_{feed} \cdot Mw)}}{mf_{feed} \cdot Mw} \quad \omega_{feed} = \begin{pmatrix} 0.13 \\ 0 \\ 0.09 \\ 0.78 \\ 0 \end{pmatrix}$$

$$Mw_{feed} = mf_{feed} \cdot Mw = 0.03 \frac{kg}{mol}$$

molecular weight of feed mixture

$$\rho = \frac{P_{tot}}{Rg \cdot T_0} \cdot Mw_{feed} = 0.49 \frac{kg}{m^3}$$

nominal fluid density

$$T_{feed} = 867 \text{ } ^\circ F$$

$$tp_{feed} = \frac{T_{feed}}{T_0} = 0.98 \quad \text{dimensionless feed temperature}$$

Reaction data

"True" Kinetic Parameters

$$E = 47 \cdot \frac{kcal}{mol} \quad \text{Rase Vol 2 pg 89}$$

the following are from Rase Vol 2 pg 93

$$A = \exp\left(7.109 \cdot 10^{-4} \cdot \frac{E}{\frac{cal}{mol}} - 1.365\right) = 8.28 \times 10^{13}$$

$$k_{pm}(T) = A \cdot \exp\left(-\frac{E}{Rg \cdot T}\right) \cdot \frac{mol}{gm \cdot hr \cdot atm}$$

note change from Rase, but this is probably the form intended because that form results in numbers exceeding 10^{307}

$$K_M(T) = 2.3 \cdot 10^{-8} \cdot \exp\left(\frac{27200 \cdot \frac{cal}{mol}}{Rg \cdot \max(T, 200 \cdot K)}\right)$$

adsorption coefficient

$$K_p(T) = 10^{\left(\frac{5.1449 \cdot 10^3}{\frac{\max(T, 200 \cdot K)}{K}} - 4.888\right)} \cdot atm^{-\frac{1}{2}}$$

pressure based equilibrium coefficient

Rate Expression

$act = .05$

Higher activities causes the computations of the simulated experiments to fail. Possible reasons are (1) an inadequate initial guess for the concentration radial profiles in some of the cases and (2) possible complete reaction before reaching the particle center resulting in a flat concentration profile near the center. This failure does not detract from the method because in a real experiment, the calculation of the profiles in the pellet are not needed.

$$rxn(\omega, tp, P, act) = \frac{act \cdot \rho_p \cdot k_{pm}(tp \cdot T_0) \cdot K_M(tp \cdot T_0) \cdot \left[\frac{\frac{\omega_0}{Mw_0} \cdot P}{\sum \left(\frac{\omega}{Mw} \right)} \right]}{\left[\left[\frac{\frac{\omega_1}{Mw_1} \cdot P}{\sum \left(\frac{\omega}{Mw} \right)} \right]^{\frac{1}{2}} + \left[K_M(tp \cdot T_0) \cdot \frac{\frac{\omega_0}{Mw_0} \cdot P}{\sum \left(\frac{\omega}{Mw} \right)} \right]^{\frac{1}{2}} \right]^2} \cdot \left[\frac{\frac{\omega_2}{Mw_2} \cdot P}{\sum \left(\frac{\omega}{Mw} \right)} - \frac{\frac{\frac{\omega_1}{Mw_1} \cdot P}{\sum \left(\frac{\omega}{Mw} \right)}}{\frac{\max(\omega_0, 10^{-9})}{Mw_0} \cdot P \cdot K_p(tp \cdot T_0)} \right]^2$$

The above rate expression is written in terms of partial pressures but with mass fractions as the input. See Rase eq CS-7.2.

$$rxn(\omega_{feed}, tp_{feed}, P_{tot}, act) = 1.29 \frac{mol}{s \cdot m^3}$$

$$Rxn(\omega, tp, P, act) = \nu^T \cdot rxn(\omega, tp, P, act)$$

molar production rates of the species

$$Rxn(\omega_{feed}, tp_{feed}, P_{tot}, act) = \begin{pmatrix} -1.29 \\ 1.29 \\ -0.65 \\ 0 \\ 0 \end{pmatrix} \frac{mol}{s \cdot m^3}$$

Catalyst Particle Model

$a = 3$ designate spherical collocation model, to be used in the included reference file below

☞ Reference: C:\Users\Harvey\Documents\Consulting\ebook single phase\Mathcad version - 3\gen diffusion N = 6.xmcd

quadrature weights

$$Wq = \begin{pmatrix} 9.83 \times 10^{-3} \\ 0.03 \\ 0.06 \\ 0.08 \\ 0.08 \\ 0.05 \\ 9.52 \times 10^{-3} \end{pmatrix}$$

collocation radial positions

$$x = \begin{pmatrix} 0.22 \\ 0.42 \\ 0.61 \\ 0.76 \\ 0.89 \\ 0.97 \\ 1 \end{pmatrix}$$

$N = 6$ number of interior collocation positions

These were produced by the reference worksheet. In addition, A and B matrices used below were produced.

The catalyst particle is isothermal. This was confirmed by another model.

The mass balance

$$\frac{1}{r^2} \cdot \frac{d}{dr} \left[r^2 \cdot \left(\frac{d}{dr} \omega_i \right) \right] + \frac{Mw_i \cdot R \cdot x_{n_i} \cdot Rp^2}{D_{eff} \cdot \rho} = 0$$

$$BC \quad \omega = \omega_b \quad \text{at } r=1$$

$$\frac{d}{dr} \omega_i = 0 \quad \text{at } r=0$$

where ω = mass fractions in catalyst

r = dimensionless radial position

ω_b = bulk mass fractions

The functions below are used to produce a matrix of production rates at all of the collocation points, including the surface point

$$Rvec(\omega, tp, P, act) = \left| \begin{array}{l} \text{for } c \in 0..NC-1 \\ \quad result_c \leftarrow Mw_c \cdot Rxn(\omega, tp, P, act)_c \\ result \end{array} \right.$$

$$Rmat(\omega, tp, P, act) = \left| \begin{array}{l} \text{for } j \in 0..N \\ \quad result_j \leftarrow Rvec(\omega^{(j)}, tp, P, act) \\ rmat \leftarrow result_0 \\ \text{for } j \in 1..N \\ \quad rmat \leftarrow augment(rmat, result_j) \\ rmat \end{array} \right.$$

Initial guesses at each collocation point

$rl = 0$ limiting reaction number

$lr = 0$ limiting reactant

Assume the extent of reaction of the feed is 0.4.

$$nf = 1 \cdot mol \cdot mf_{feed}$$

$$n_b = nf - \nu^T \cdot 0.4 \cdot \frac{nf \cdot lr}{\nu_{rl, lr}}$$

$$\omega_b = \frac{\overrightarrow{(n_b \cdot Mw)}}{\sum \overrightarrow{(n_b \cdot Mw)}} = \begin{pmatrix} 0.08 \\ 0.07 \\ 0.07 \\ 0.78 \\ 0 \end{pmatrix}$$

$$n_b = \begin{pmatrix} 0.04 \\ 0.03 \\ 0.07 \\ 0.85 \\ 0 \end{pmatrix} mol$$

$$\xi(x) = 1 - x^2$$

$$0 \leq \xi < 1$$

assumed extent as a function of radial position, x

$$n(x) = n_b - \nu^T \cdot \xi(x) \cdot \frac{n_{b,lr}}{\nu_{rl,lr}}$$

molar flows at radial positions

$$n(x_0) = \begin{pmatrix} 1.74 \times 10^{-3} \\ 0.06 \\ 0.05 \\ 0.85 \\ 0 \end{pmatrix} \text{ mol}$$

at first collocation pt. near center

$$n(1) = \begin{pmatrix} 0.04 \\ 0.03 \\ 0.07 \\ 0.85 \\ 0 \end{pmatrix} \text{ mol}$$

at surface

convert to mass fractions

$$wg(x) = \frac{\overrightarrow{(n(x) \cdot Mw)}}{\sum \overrightarrow{(n(x) \cdot Mw)}}$$

$$wg(x_0) = \begin{pmatrix} 3.65 \times 10^{-3} \\ 0.16 \\ 0.06 \\ 0.78 \\ 0 \end{pmatrix}$$

$$wg(1) = \begin{pmatrix} 0.08 \\ 0.07 \\ 0.07 \\ 0.78 \\ 0 \end{pmatrix}$$

$$\sum wg(x_0) = 1$$

$$\sum wg(1) = 1$$

$$\omega = \text{augment}(wg(x_0), wg(x_1), wg(x_2), wg(x_3), wg(x_4), wg(x_5), wg(x_6)))$$

create the guessed ω matrix

$$tp = tp_{feed}$$

given feed temperature

Solving the system of equations

Given

$$\left(B \cdot \omega^T \right)^T + \frac{Rp^2}{D_{eff} \cdot \rho} Rmat(\omega, tp, Ptot, act) = 0 \quad \text{in collocation form}$$

$$\omega^{\langle N \rangle} = \omega_b \quad \text{at surface}$$

$$\omega m(\omega_b, tp, Ptot) = Find(\omega) \quad \text{the problem solution has parameters: bulk fluid composition, particle temperature and pressure}$$

increasing radial position of collocation point from left to right

$$\omega m(\omega_b, tp, Ptot) = \begin{pmatrix} 0.05 & 0.05 & 0.06 & 0.07 & 0.07 & 0.08 & 0.08 \\ 0.1 & 0.1 & 0.09 & 0.08 & 0.07 & 0.07 & 0.07 \\ 0.07 & 0.07 & 0.07 & 0.07 & 0.07 & 0.07 & 0.07 \\ 0.78 & 0.78 & 0.78 & 0.78 & 0.78 & 0.78 & 0.78 \\ 3.23 \times 10^{-9} & 3.23 \times 10^{-9} & 3.23 \times 10^{-9} & 3.23 \times 10^{-9} & 3.23 \times 10^{-9} & 3.23 \times 10^{-9} & 3.23 \times 10^{-9} \end{pmatrix}$$

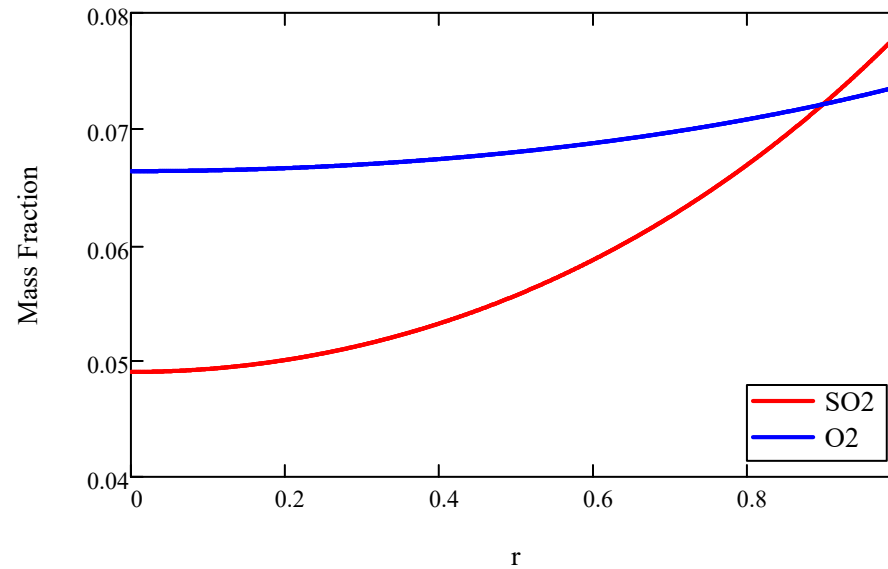
$$\left[\left(A \cdot \omega m(\omega_b, tp, Ptot)^T \right)^T \right]^{\langle N \rangle} = \begin{pmatrix} 0.07 \\ -0.08 \\ 0.02 \\ -3.03 \times 10^{-12} \\ -5.71 \times 10^{-12} \end{pmatrix} \quad \text{derivatives at outer radius will be used to compute the rate of reaction for the pellet}$$

$$comp = 0..NC - 1$$

$$d = \left(Q^{-1} \cdot \omega m(\omega_b, tp, Ptot)^T \right) \quad \text{the polynomial coefficients, d, are fit to the results, } \omega$$

$$\omega r(r, comp) = \sum_{i=0}^N \left(d_{i, comp} \cdot r^{2 \cdot i} \right) \quad \text{using the polynomial to obtain a continuous function}$$

Fig. E4.1: Radial Profile Reactant Mass Fractions



CSTR Model using the rates from the particle model

CSON

$$Atom = \begin{pmatrix} 0 & 1 & 2 & 0 \\ 0 & 1 & 3 & 0 \\ 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 2 \\ 1 & 0 & 2 & 0 \end{pmatrix} \begin{matrix} SO_2 \\ SO_3 \\ O_2 \\ N_2 \\ CO_2 \end{matrix}$$

$$V_p = \frac{4}{3} \cdot \pi \cdot R_p^3 = 1.49 \times 10^{-4} L$$

$$\rho_b = 10^1 \cdot \frac{kg}{m^3}$$

$$\rho_b = 10 \cdot \frac{gm}{L}$$

catalyst bulk density in reactor

$$\text{resid}(X, \omega_0, \tau, Tr, P_{tot}) = \begin{bmatrix}
(\omega_{0_0} - X_0) - \left[\left[\left(A \cdot \omega m \left(X, \frac{Tr}{T_0}, P_{tot} \right)^T \right)^T \right]^{(N)} \right]_0 \cdot \frac{D_{eff} \cdot 4 \cdot \pi \cdot R_p \cdot \rho_b}{V_p \cdot \rho_p} \cdot \tau \\
\omega_{0_1} - X_1 - \left[\left[\left(A \cdot \omega m \left(X, \frac{Tr}{T_0}, P_{tot} \right)^T \right)^T \right]^{(N)} \right]_1 \cdot \frac{D_{eff} \cdot 4 \cdot \pi \cdot R_p \cdot \rho_b}{V_p \cdot \rho_p} \cdot \tau \\
(\omega_{0_2} - X_2) - \left[\left[\left(A \cdot \omega m \left(X, \frac{Tr}{T_0}, P_{tot} \right)^T \right)^T \right]^{(N)} \right]_2 \cdot \frac{D_{eff} \cdot 4 \cdot \pi \cdot R_p \cdot \rho_b}{V_p \cdot \rho_p} \cdot \tau \\
(\omega_{0_3} - X_3) - \left[\left[\left(A \cdot \omega m \left(X, \frac{Tr}{T_0}, P_{tot} \right)^T \right)^T \right]^{(N)} \right]_3 \cdot \frac{D_{eff} \cdot 4 \cdot \pi \cdot R_p \cdot \rho_b}{V_p \cdot \rho_p} \cdot \tau \\
0 \\
1 - \sum X \\
\left[Atom^T \cdot \left(\frac{\omega_0 - X}{Mw} \right) \right]_0 \cdot \frac{gm}{mol} \\
\left[Atom^T \cdot \left(\frac{\omega_0 - X}{Mw} \right) \right]_1 \cdot \frac{gm}{mol} \\
\left[Atom^T \cdot \left(\frac{\omega_0 - X}{Mw} \right) \right]_2 \cdot \frac{gm}{mol}
\end{bmatrix}$$

wt fractions must sum to 1

These last constraints are C, S and O balances. Since the method used to solve the reactor balances is an optimization routine, there is danger that the results may not be realistic. These atom balances provide an additional constraint on the solution.

Solve block

$X = \omega_b$ initial guesses for outlet weight fractions and temperature

$$Tr = 700 \cdot K$$

$$\tau = 800 \cdot s$$

Given

$$\text{resid}(X, \omega_{feed}, \tau, Tr, P_{tot}) = 0$$

$CSTR(\omega_{feed}, \tau, Tr, P_{tot}, \omega_b) = \text{Find}(X)$ use Levenberg-Marquardt method (right click on Find to check or change method)

The result, $CSTR$, is a the outlet weight fraction vector as a function of τ , Tr , and ω_{feed} .

End of solve block

$$CSTR(\omega_{feed}, 200 \cdot s, Tr, P_{tot}, \omega_b) = \begin{pmatrix} 0.1 \\ 0.04 \\ 0.08 \\ 0.78 \\ -3.96 \times 10^{-8} \end{pmatrix} \quad \omega_{feed} = \begin{pmatrix} 0.13 \\ 0 \\ 0.09 \\ 0.78 \\ 0 \end{pmatrix}$$

Design the "Experiments"

The CO₂ and N₂ have been shown to have no effect on the kinetics during the catalyst development. Thus, they will be left out of the design to simplify. N₂ will be included as a feed to keep the reaction rate and therefore the heat effect low.. Otherwise, the activation energy would have to be estimated along with the powers...a difficult task due to the extreme non-linearity.

Once the powers of the concentration terms have been determined under nearly isothermal conditions, the temperature will be varied. The centerpoint concentration will be used for this series.

The procedure below creates an experimental design which varies the flow rates of the species in the feed. For each case, the CSTR exit composition is

determined and then the overall reaction rates are determined by material balance on the CSTR. Using the reaction rates and the exit compositions, the parameter estimation is conducted.

Note that the design varies the feed flow rates of the individual species, not the mass or mole fractions. The reason for this is that the fractions have to sum to one so that it is not possible to independently vary the fractions of all species. Flows, however, can be varied independently.

`des = taguchi(4,3)`

A three level Taguchi design is an efficient design. A fractional factorial design was also tested and the results were similar.

`nf = rows(des)`

`centerpt = (nf 1 2 2 2 2)`

Add a centerpoint experiment to the design. In the Taguchi design, the center level is level 2. In a fractional factorial design, the center level is 0.

`des = stack(des,centerpt)`

`vals =`

"SO2"	0.5	1.25	2
"SO3"	0.2	1.1	2
"O2"	0.5	1.25	2
"P"	1.	1.5	2

This is where the ranges of each variable are set. The values for the species are relative flow rates and the pressure is atm.

add labels and values, low, center, and high

`labeled = doelabel(des,vals)`

`labeled =`

	0	1	2	3	4	5
0	"Run"	"Block"	"SO2"	"SO3"	"O2"	"P"
1	1	1	0.5	0.2	0.5	1
2	2	1	0.5	1.1	1.25	1.5
3	3	1	0.5	2	2	2
4	4	1	1.25	0.2	1.25	2
5	5	1	1.25	1.1	2	1
6	6	1	1.25	2	0.5	1.5
7	7	1	2	0.2	2	1.5
8	8	1	2	1.1	0.5	2
9	9	1	2	2	1.25	1
10	10	1	1.25	1.1	1.25	1.5

The design without the N2 and CO2

The third experiment would not converge so it is eliminated below.

$$labeled1 = submatrix(labeled, 0, 2, 0, 5)$$

$$labeled2 = submatrix(labeled, 4, 10, 0, 5)$$

$$labeled = stack(labeled1, labeled2)$$

Separate the flows from the design and then add N2 and CO2 constant flows

$$NE = rows(labeled) - 1 \qquad NE = 9 \qquad \text{number of experiments}$$

$$flow = submatrix(labeled, 0, NE, 2, 4)$$

$$ncol = cols(flow)$$

$$flow_{0, ncol} = "N2" \qquad flow_{0, ncol+1} = "CO2"$$

$$i = 1 .. NE$$

$$flow_{i, ncol} = 9 \qquad flow_{i, ncol+1} = 0$$

$flow =$

	0	1	2	3	4
0	"SO2"	"SO3"	"O2"	"N2"	"CO2"
1	0.5	0.2	0.5	9	0
2	0.5	1.1	1.25	9	0
3	1.25	0.2	1.25	9	0
4	1.25	1.1	2	9	0
5	1.25	2	0.5	9	0
6	2	0.2	2	9	0
7	2	1.1	0.5	9	0
8	2	2	1.25	9	0
9	1.25	1.1	1.25	9	0

These are the relative flow rates for the species in the feed

Compute the mole and mass fractions for the model "experiments".

$$i = 0..NE - 1 \quad j = 0..NC - 1$$

$$Y_{feed\,i,j} = \frac{flow_{i+1,j}}{\sum_{k=0}^{NC-1} flow_{i+1,k}} \quad X_{feed\,i,j} = \frac{Y_{feed\,i,j} \cdot Mw_j}{\sum_{k=0}^{NC-1} (Y_{feed\,i,k} \cdot Mw_k)} \quad P = \text{submatrix}(\text{labeled}, 1, NE, 5, 5)$$

Conduct the Experiments

Each row of Xb is an experiment, or run.

$$Results(X_{feed}, Y_{feed}, \tau, P, tp) = \left| \begin{array}{l} NE \leftarrow \text{rows}(X_{feed}) \\ \text{for } run \in 0..NE - 1 \\ \quad x_{feed} \leftarrow (X_{feed}^T)^{\langle run \rangle} \\ \quad nf \leftarrow 1 \cdot \text{mol} \cdot (Y_{feed}^T)^{\langle run \rangle} \\ \quad \xi \leftarrow .2 \\ \quad n_b \leftarrow nf - \nu^T \cdot \xi \cdot \frac{nf \cdot lr}{\nu_{rl, lr}} \\ \quad \omega_b \leftarrow \frac{\overrightarrow{(n_b \cdot Mw)}}{\sum [\overrightarrow{(n_b \cdot Mw)}]} \\ \quad \omega \leftarrow CSTR(x_{feed}, \tau, tp_{run} \cdot T_0, P_{run} \cdot atm, \omega_b) \\ \quad \text{"mass balance on reactant to determine rxn rate"} \\ \quad \text{"mol/m}^3\text{/s"} \\ \quad \text{""} \\ \quad \dots \end{array} \right.$$


```

****
rate0 ←  $\frac{(x_{feed_0} - \omega_0) \cdot \rho}{Mw_0 \cdot \tau}$ 
ΔT ←  $\frac{rate0 \cdot (-\Delta H (tp_{run} \cdot T_0)) \cdot \rho_p \cdot V_p}{h_p \cdot 4 \cdot \pi \cdot Rp^2 \cdot \rho_b}$ 
"partial pressure in reactor"
for c ∈ 0..NC - 1
  |
  |  $y_c \leftarrow \frac{\omega_c}{Mw_c}$ 
  |  $\sum \left( \frac{\omega}{Mw} \right)$ 
  |
  | resultrun,c ← yc · Prun
  |
resultrun,NC ←  $\frac{rate0}{\frac{mol}{m^3 \cdot s}}$ 
resultrun,NC+1 ←  $\frac{\Delta T}{K}$ 
resultrun,NC+2 ← Prun
resultrun,NC+3 ←  $\frac{tp_{run} \cdot T_0}{K}$ 
run = 0..NE - 1
resultrun,j = Yfeedrun,j · Prun

```

tp_{run} = *tp_{feed}*

the tp argument is a vector

heading = ("P SO2" "P SO3" "P O2" "P N2" "P CO2" "rate" "ΔT K" "Ptot atm" "T K")

data = Results(*X_{feed}*, *Y_{feed}*, 200·s, *P*, *tp*)

To save time while editing for printing, the results of this operation were saved to a file, ex4 data.prn.

$res = WRITEPRN("ex4 data", data)$

$data = READPRN("ex4 data.prn")$ ■

$datah = stack(heading, data)$

$datah =$

	0	1	2	3	4	5
0	"P SO2"	"P SO3"	"P O2"	"P N2"	"P CO2"	"rate"
1	0.03	0.04	0.04	0.89	$1.37 \cdot 10^{-7}$	$1.59 \cdot 10^{-3}$
2	0.02	0.18	0.14	1.15	$3.74 \cdot 10^{-7}$	$1.92 \cdot 10^{-3}$
3	0.09	0.17	0.15	1.59	$5.42 \cdot 10^{-7}$	$4.81 \cdot 10^{-3}$
4	0.04	0.14	0.13	0.69	$-1.13 \cdot 10^{-7}$	$3.41 \cdot 10^{-3}$
5	0.12	0.27	0.04	1.07	$-2.88 \cdot 10^{-8}$	$1.37 \cdot 10^{-3}$
6	0.1	0.16	0.17	1.07	$-6.04 \cdot 10^{-7}$	$6.07 \cdot 10^{-3}$
7	0.26	0.25	0.05	1.45	$-2.31 \cdot 10^{-7}$	$2.13 \cdot 10^{-3}$
8	0.1	0.19	0.07	0.64	$-2.79 \cdot 10^{-7}$	$2.5 \cdot 10^{-3}$
9	0.08	0.21	0.12	1.1	$-1.52 \cdot 10^{-9}$...

$NE = rows(data)$

Estimate the Parameters

The concentration powers

$Pdata = submatrix(data, 0, NE - 1, 0, NC - 1)$

$rateobs = data^{(5)}$

The model

$T = tp_{feed} \cdot T_0$ all runs were conducted at this temperature

$$model1(P, pk) = \frac{pk_3}{atm^{1.5}} \cdot (P_0)^{pk_0} \cdot (P_1)^{pk_1} \cdot (P_2)^{pk_2} \cdot \left[P_0 \cdot (P_2)^{.5} \cdot atm^{1.5} - \frac{P_1 \cdot atm}{K_p(T)} \right]$$

The above model includes the equilibrium driving force. However, the high value of the equilibrium coefficient, K_p , suggests that the following model may be adequate. Both models will be used and the results compared.

$$model2(P, pk) = pk_3 \cdot (P_0)^{pk_0} \cdot (P_1)^{pk_1} \cdot (P_2)^{pk_2}$$

$$G = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 10^{-6} \end{pmatrix} \quad \text{guess values for the parameters in the model}$$

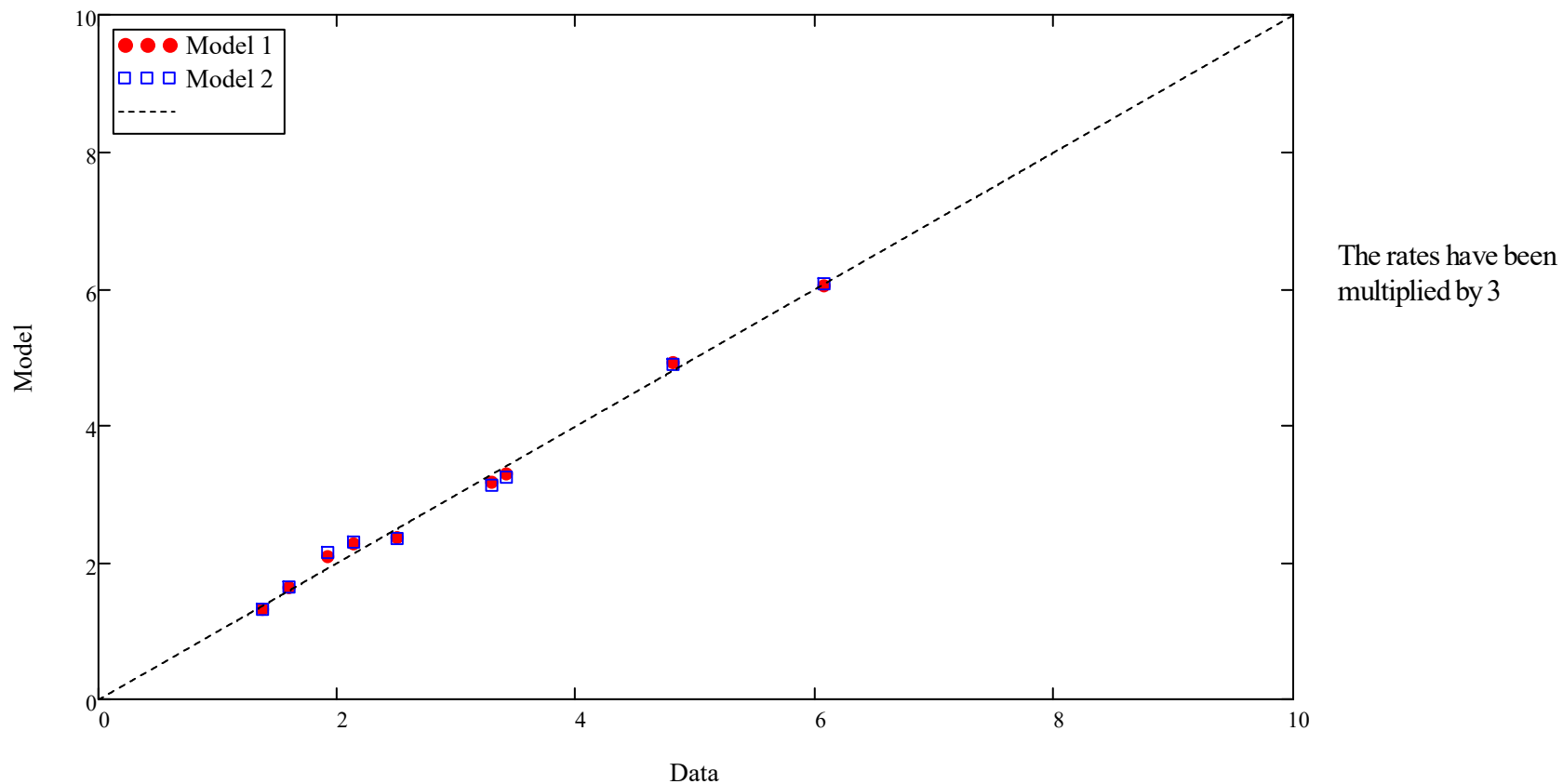
Fit to the data

$$pk2 = \text{multifit}(Pdata, rateobs, G, model2)$$

$$pk1 = \text{multifit}(Pdata, rateobs, pk2, model1)$$

$pk1 = \begin{pmatrix} -0.56 \\ -0.45 \\ 0.41 \\ 0.04 \end{pmatrix}$	$pk2 = \begin{pmatrix} 0.52 \\ -0.53 \\ 0.94 \\ 0.04 \end{pmatrix}$	SO2 SO3 O2 kp	results
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Fig. E4.2: Model vs Data for Reaction Rate



As suspected, the equilibrium term is not needed for this reaction, as indicated by the nearly identical results for the two models. This behavior is typical for oxidation reactions which tend to go to completion.

The activation energy and pre-exponential constant

The centerpoint conditions are repeated at other temperatures. The model will have the powers fixed to the above estimates.

$$Te = \begin{pmatrix} 800 \\ 850 \\ 900 \\ 950 \end{pmatrix} \text{ } ^\circ F$$

The third temperature is a repeat of the centerpoint case already run. Thus, this "experiment" would not have to be run in the lab..

$$Te = \begin{pmatrix} 699.82 \\ 727.59 \\ 755.37 \\ 783.15 \end{pmatrix} K$$

$$tpT = \frac{Te}{T_0}$$

$$NT = \text{rows}(Te)$$

$$t = 0..NT - 1 \quad j = 0..NC - 1$$

$$PT_t = P_8 \quad XbT_{t,j} = Xfeed_{8,j} \quad YbT_{t,j} = Yfeed_{8,j} \quad \text{The centerpoint conditions were run 9 (8 index) of the design data set.}$$

$$dataT = \text{Results}(XbT, YbT, 200 \cdot s, PT, tpT) \quad \text{simulate the cases}$$

$$dataT = \begin{pmatrix} 0.12 & 0.17 & 0.13 & 1.08 & 1.03 \times 10^{-7} & 1.49 \times 10^{-3} & 0.03 & 1.5 & 699.82 \\ 0.09 & 0.2 & 0.12 & 1.09 & 6.59 \times 10^{-8} & 2.85 \times 10^{-3} & 0.05 & 1.5 & 727.59 \\ 0.06 & 0.23 & 0.11 & 1.1 & -4.84 \times 10^{-7} & 3.99 \times 10^{-3} & 0.07 & 1.5 & 755.37 \\ 0.05 & 0.24 & 0.1 & 1.11 & 5.79 \times 10^{-8} & 4.57 \times 10^{-3} & 0.07 & 1.5 & 783.15 \end{pmatrix}$$

$$PdataT = \text{submatrix}(dataT, 0, NT - 1, 0, NC - 1)$$

$$rateobsT = dataT^{(5)}$$

The model for exploring temperature effect

The model below omits the forward rate parameter, previously included as pk_3 but is called kp below.

$$modelT(P, T) = 1 \cdot (P_0)^{pk2_0} \cdot (P_1)^{pk2_1} \cdot (P_2)^{pk2_2}$$

based on Model 2 used in the experiments above

$$i = 0 \dots NT - 1$$

$$kp_i = \frac{rateobsT_i}{modelT\left[\left(PdataT^T\right)^{\langle i \rangle}, Te_i\right]}$$

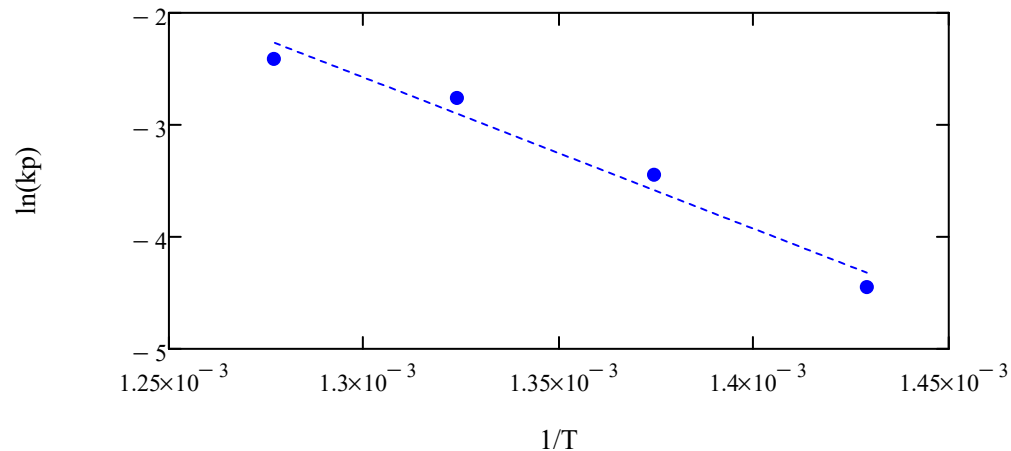
dividing the results of the full model by the result of modelT, kp is obtained for each experiment

$$kp = \begin{pmatrix} 0.01 \\ 0.03 \\ 0.06 \\ 0.09 \end{pmatrix}$$

$$\ln(kp) = \begin{pmatrix} -4.45 \\ -3.44 \\ -2.76 \\ -2.41 \end{pmatrix}$$

$$lfit = line\left(\frac{1}{Te}, \ln(kp)\right) = \begin{pmatrix} 14.98 \\ -1.35 \times 10^4 \end{pmatrix}$$

Fig. E4.3: Determination of the Overall Activation Energy



$$E_a = -\text{slope}\left(\frac{1}{T_e}, \ln(kp)\right) \cdot Rg$$

The slope of a line determined by minimization of squared errors determines the activation energy.

measured (apparent)

$$E_a = 26.83 \cdot \frac{\text{kcal}}{\text{mol}}$$

actual value for the activation energy in the particle pore model

$$E = 47 \cdot \frac{\text{kcal}}{\text{mol}}$$

As expected, the apparent activation energy is less than that for the pore surface reaction. This is partly due to the diffusion effect, but it is also influenced by the adsorption terms which were not explicitly included in the power law model.

The apparent activation energy determined by this method compares favorably with the value of 31 kcal/mol reported on pg 286 of Rase, **Vol 1**. The Rase value is an apparent activation energy for an industrial catalyst.

The pre-exponential constant

The rates currently are for the reactor total volume. Determine the pre-exponential constant on a catalyst weight basis. Use the centerpoint data.

$$kpm = \frac{kp_2 \cdot \frac{\text{mol}}{\text{m}^3 \cdot \text{s}}}{\rho_b} = 6.35 \times 10^{-3} \frac{\text{mol}}{\text{s} \cdot \text{kg}}$$

$$k_o = kpm \cdot \exp\left(\frac{E_a}{Rg \cdot T_{e2}}\right) = 3.67 \times 10^5 \frac{\text{mol}}{\text{s} \cdot \text{kg}}$$

Conclusion

A reaction with a very complex reaction rate in a large pellet has been successfully modeled with a simple power law model. The number of runs needed for the parameter estimation were 13 by design, only 12 actually used. A few exploratory runs prior to executing the design would probably be needed to check the extent of reaction and adjust total flow or amount of catalyst.

References

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