

# Appendix

## Understanding Catalysis: A simplified simulation of catalytic reactors for CO<sub>2</sub> reduction

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The following student exercises provide suggestions for further exploration of the concepts discussed in the main text. They become progressively more challenging, and answers are provided. Exercises 1 and 2 review the computation, using tabulated values of the standard enthalpy of formation and entropy, of the free energy and enthalpy changes occurring in the production and combustion of C1 synthetic fuels and of the equilibrium constants for methanol and methane production. Exercises 3 – 5 treat the state of thermodynamic equilibrium for the hydrogenation of CO<sub>2</sub> to form methane, and Exercises 6 and 7 deal with introductory aspects of a kinetic model of methane formation. Exercise 8 poses a question for thought regarding the thermodynamics and kinetics of CO<sub>2</sub> hydrogenation. The numerical solution of the differential equations describing the operation of a plug flow reactor to produce methane is the subject of Exercises 9 and 10. Finally, Exercise 11 quantitatively determines the chemical paths followed by CO<sub>2</sub> during its conversion to CH<sub>4</sub>.

The Exercises generally require numerical computation: A simple spreadsheet is sufficient for Exercises 1,2, 5 and 6. Exercise 4 involves 3D plotting of a function of 2 variables and locating the position of its maximum. Following the scheme in Figure 6, Exercises 9 and 10 construct a computer program to numerically solve the differential equations describing the plug flow reactor, and the program is used in Exercise 11 to investigate details of the methanation process.

Not covered in the Exercises are the sections in the main text dealing with the continuously stirred tank reactor, the looped plug flow reactor and the sorption-enhanced plug flow reactor. These treatments, which are schematically described in the Figures 10, 12 and 14, involve self-consistent numerical calculations suitable for students with advanced programming skills.

## Exercises

### 1. Free energy of formation and enthalpy of oxidation of hydrocarbon fuels.

For standard conditions ( $T=25^{\circ}\text{C}$ ,  $P=1$  bar), compute the free energy of formation by hydrogenation reduction  $\Delta G_{\text{red}}$  and the enthalpy of oxidation  $\Delta H_{\text{oxid}}$  per mole of formic acid, formaldehyde, methanol and methane, and compare them with the Latimer-Frost diagram in Fig. 2. Make use of the following standard enthalpies of formation and entropies [Swaddle T. W. *Inorganic Chemistry – An Industrial and Environmental Perspective*, Academic Press: San Diego, 1997 and Lide, D. R. *CRC Handbook of Chemistry and Physics*; Chemical Rubber Publishing company: Cleveland, USA, 2009].

	$\Delta H^0$ [kJ/mol]	$S^0$ [J/mol K]
$\text{H}_2$ (g)	0	130.68
$\text{O}_2$ (g)	0	205.14
$\text{H}_2\text{O}$ (l)	-285.83	69.91
$\text{CO}_2$ (g)	-393.51	213.74
$\text{HCOOH}$ (l)	-409.2	129.0
$\text{HCHO}$ (g)	-115.9	218.7
$\text{CH}_3\text{OH}$ (l)	-238.66	126.80
$\text{CH}_4$ (g)	-74.81	186.26

Answer:

	$\Delta G_{\text{red}}$ [kJ/mol]	$-\Delta H_{\text{oxid}}$ [kJ/mol]
$\text{HCOOH}$	48.54	270.14
$\text{HCHO}$	47.38	563.44
$\text{CH}_3\text{OH}$	-9.02	726.51
$\text{CH}_4$	-130.60	890.36

### 2. Equilibrium constants for methanol and methane production reactions.

Using the thermodynamic data in Table 1, compute the equilibrium constants  $K_{1-3}^{eq}$  for the gas phase chemical reactions in Figures 3a and 3b. For methanol production, assume a reaction temperature of  $230^{\circ}\text{C}$ , and for methane, take  $T=400^{\circ}\text{C}$ . Compare the values with the plot in Figure 4, and confirm in both cases that  $K_1^{eq} \times K_2^{eq} = K_3^{eq}$ .

Answer:

	$\text{CH}_3\text{OH}$ , $T=230^{\circ}\text{C}$ ( $1/T=0.00199$ $\text{K}^{-1}$ )	$\text{CH}_4$ , $T=400^{\circ}\text{C}$ ( $1/T=0.00149$ $\text{K}^{-1}$ )
$K_1^{eq}$	0.008071	60620
$K_2^{eq}$	0.008382	0.1006
$K_3^{eq}$	0.00006766	6101

### 3. Equilibrium degree of conversion for methanation I.

Modify the Equations (3-10) to describe the case of methane formation, instead of methanol formation, according to the reactions 2 and 3 in Figure 3b.

Answer:

$$K_2^{eq}(T) = Q_2 \equiv \frac{N_{CO} N_{H_2O}}{N_{H_2} N_{CO_2}}$$

$$K_3^{eq}(T) = Q_3 \equiv \frac{N_{CH_4} N_{H_2O}^2 N_{tot}^2 P_0^2}{N_{H_2}^4 N_{CO_2} P^2}$$

$$N_{CO} = \xi_2 N_{CO_2}^0$$

$$N_{CO_2} = (1 - \xi_2 - \xi_3) N_{CO_2}^0$$

$$N_{H_2} = (SN + 1 - \xi_2 - 4\xi_3) N_{CO_2}^0$$

$$N_{H_2O} = (\xi_2 + 2\xi_3) N_{CO_2}^0$$

$$N_{CH_4} = \xi_3 N_{CO_2}^0$$

$$N_{tot} = N_{CO} + N_{CO_2} + N_{H_2} + N_{H_2O} + N_{CH_4} = (SN + 2 - 2\xi_3) N_{CO_2}^0$$

### 4. Equilibrium degree of conversion for methanation II.

Express the "reaction quotients"  $Q_2$  and  $Q_3$ , from the previous exercise, in terms of the "degrees of reaction completion"  $\xi_2$  and  $\xi_3$ .

Answer:

$$Q_2 = \frac{\xi_2 (\xi_2 + 2\xi_3)}{(1 - \xi_2 - \xi_3)(1 - \xi_2 - 4\xi_3 + SN)}$$

$$Q_3 = \frac{\xi_3 (\xi_2 + 2\xi_3)^2 (2 - 2\xi_3 + SN)^2 P_0^2}{(1 - \xi_2 - \xi_3)(1 - \xi_2 - 4\xi_3 + SN)^4 P^2}$$

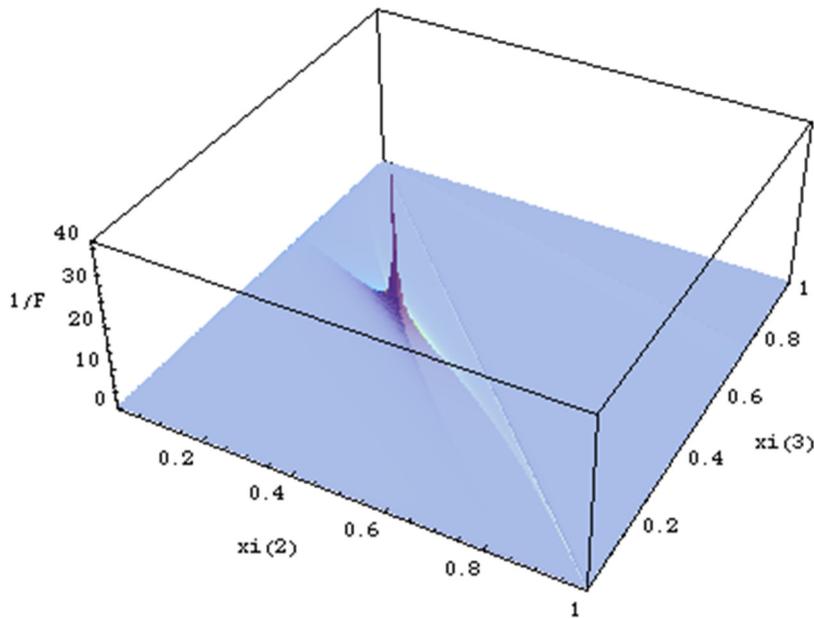
### 5. Equilibrium degree of conversion for methanation III.

At a reaction temperature  $T=800^{\circ}\text{C}$ , the equilibrium constants for methanation have the values:  $K_2^{eq} = 1.562$  and  $K_3^{eq} = 0.1034$ . Assume a reactor pressure of  $P=10$  bar and an (ideal) initial stoichiometry number of  $SN=3$ . In order to (numerically) solve the two equations in the two unknown degrees of reaction completion,  $\xi_2$  and  $\xi_3$ , form the function to minimize:

$$F \equiv \left| \ln \left[ K_2^{eq} \right] - \ln \left[ Q_2 \left( \xi_2, \xi_3 \right) \right] \right| + \left| \ln \left[ K_3^{eq} \right] - \ln \left[ Q_3 \left( \xi_2, \xi_3 \right) \right] \right|$$

Show that a 2-dimensional plot of  $1/F$  as a function of  $\xi_2$  and  $\xi_3$  has a maximum at the  $\xi_2$  and  $\xi_3$  values we are searching for, and compute the corresponding equilibrium reduced partial pressures  $p_i = P N_i / P_0 N_{tot}$  of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_4$ . ( $P_0$  is the pressure 1 bar.)

Answer:



$$T = 800^{\circ}\text{C}, P=10 \text{ bar}, SN=3$$

$$\xi_2 = 0.3351, \quad \xi_3 = 0.4957$$

$$p_{\text{CO}} = 0.84$$

$$p_{\text{CO}_2} = 0.42$$

$$p_{\text{H}_2} = 4.21$$

$$p_{\text{H}_2\text{O}} = 3.32$$

$$p_{\text{CH}_4} = 1.24$$

### 6. Kinetic model of methanation.

According to the model of Xu and Froment [Xu, J.; Froment, G. F. Methane Steam Reforming, Methanation and Water-Gas Shift: I. Intrinsic Kinetics. *AIChE J.* **1989**, 35 (1), 88 – 96.], the reaction and component creation rates corresponding to the expressions for methanol in Eqs. (12-16) are:

$$r_1 = -\frac{k_1}{p_{H_2}^{5/2}} \frac{(p_{CH_4} p_{H_2O} - p_{H_2}^3 p_{CO} K_1^{eq})}{denom}$$

$$r_2 = -\frac{k_2}{p_{H_2}} \frac{(p_{CO} p_{H_2O} - p_{H_2} p_{CO_2} K_2^{eq})}{denom}$$

$$r_3 = -\frac{k_3}{p_{H_2}^{7/2}} \frac{(p_{CH_4} p_{H_2O}^2 - p_{H_2}^4 p_{CO_2} K_3^{eq})}{denom}$$

$$denom = \left( 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} \frac{p_{H_2O}}{p_{H_2}} \right)^2$$

$$\mathbf{R} = (R_{CO}, R_{CO_2}, R_{H_2}, R_{H_2O}, R_{CH_4})$$

$$= (-r_1 + r_2, -r_2 - r_3, -3r_1 - r_2 - 4r_3, r_1 + r_2 + 2r_3, r_1 + r_3)$$

Note that we use here the reciprocal of the equilibrium constants appearing in the work of Xu, et al. This is because we assume a reversed direction for the chemical reactions. The fitted Arrhenius parameters for the kinetic rates are:

	a	b (J/mol)
$k_1$	$4.225 \times 10^{15} \frac{mol}{kg \ s}$	$-2.401 \times 10^5$
$k_2$	$1.955 \times 10^6 \frac{mol}{kg \ s}$	$-0.6713 \times 10^5$
$k_3$	$1.020 \times 10^{15} \frac{mol}{kg \ s}$	$-2.439 \times 10^5$
$K_{CO}$	$8.23 \times 10^{-5}$	$0.7065 \times 10^5$
$K_{H_2}$	$6.12 \times 10^{-9}$	$0.8290 \times 10^5$
$K_{CH_4}$	$6.65 \times 10^{-4}$	$0.3828 \times 10^5$
$K_{H_2O}$	$1.77 \times 10^5$	$-0.8868 \times 10^5$

In Exercise 5, we found for the reactor conditions: T=800°C, P=10 bar, SN=3, the equilibrium reduced partial pressures  $\mathbf{p}$  of the 5 chemical species in the methanation reactor. Compute from these the reaction rates  $r_i$  and the component creation rates  $R_i$ , per mol/kg s, for the initial conditions ( $p_{CO} = p_{H_2O} = p_{CH_3OH} = p_{CH_4} = 0, p_{CO_2} = 2, p_{H_2} = 8$ ) and for the conditions at thermodynamic equilibrium.

Answer:

a) initial conditions:

$$\xi_2 = 0, \quad \xi_3 = 0$$

$$r_1 = 0$$

$$r_2 = 3294 \text{ mol/kg s}$$

$$r_3 = 800 \text{ mol/kg s}$$

$$R_{CO} = 3294 \text{ mol/kg s}$$

$$R_{CO_2} = -4094 \text{ mol/kg s}$$

$$R_{H_2} = -6496 \text{ mol/kg s}$$

$$R_{H_2O} = 4895 \text{ mol/kg s}$$

$$R_{CH_4} = 800 \text{ mol/kg s}$$

b) equilibrium conditions:

$$\xi_2 = 0.3351, \quad \xi_3 = 0.4957$$

$$r_1 = r_2 = r_3 = 0$$

$$R_{CO} = R_{CO_2} = R_{H_2} = R_{H_2O} = R_{CH_4} = 0$$

Note:  
because  
there is  
initially no  
CO  
present,  
reaction  
rate  $r_1 = 0$ ,  
and at

equilibrium, all reaction and component creation rates vanish.

## 7. Equilibrium condition on the kinetic rate expressions.

We saw in the previous exercise that at thermodynamic equilibrium, all kinetic reaction rates vanish. Show, both for the case of methanol production, Eqs (12-15), and of methanation, Exercise 6, that the condition for zero reaction rate  $r_i$  implies the equality between the equilibrium constant and the reaction quotient:  $K_i^{eq} = Q_i$ . Recall that the reduced partial pressure  $p_j$  for each chemical component is related to its molar concentration  $N_j$  by  $p_j = PN_j/P_oN_{tot}$ .

## 8. A question to ponder.

In our discussion of thermodynamic equilibrium, we considered only two of the three reactions in Figure 3, invoking the “degrees of completion”,  $\xi_2$  and  $\xi_3$ . We justified this by stating that only 2 of the 3 reactions are “independent”. But in our models for the *kinetics* of methanol and methane production, we took account of all three reactions. Why are two reactions sufficient for thermodynamics but three are necessary for kinetics?

Answer:

As mentioned in a footnote in the main text, the “degrees of completion”,  $\xi_2$  and  $\xi_3$ , are in reality only book-keeping devices, which serve to guarantee that the stoichiometry, i.e., the number of atoms of each element, is preserved. The equilibrium condition, at a given pressure  $P$ , temperature  $T$  and initial stoichiometry number  $SN$ , defines a particular combination of molar concentrations  $N_{CO}, N_{CO_2}, N_{H_2}, N_{H_2O}, N_{CH_3OH/CH_4}$ , representing 5 unknowns. This takes account of three stoichiometry constraints, one for each element C, H and O. In order to determine the equilibrium state, two additional constraints are thus required, and we took these to be the two equations  $K_2^{eq} = Q_2$  and  $K_3^{eq} = Q_3$ . Note that the third equation of this type,  $K_1^{eq} = Q_1$ , is simply a linear combination of the other two.

The equilibrium state only gives us the corresponding molar concentrations. Thermodynamics cannot tell us how we got there, e.g., whether the methanol or methane we obtained was produced directly from  $CO_2$  (reaction 3) or via CO from the reverse water gas shift reaction (reactions 2 and 1). For this information, we need to know the individual kinetic reaction rates of all three reactions. (See Exercise 11 below.)

## 9. PFR simulation I.

Based on the computation scheme in Figure 6, we want to build our own computer routine to numerically simulate the operation of a simplified plug flow reactor (PFR) for methane production. As in the main text, we assume all chemical components are ideal gases, at a uniform temperature  $T$  and pressure  $P$ .

In a first step, set up a routine which, given the molar flow rates  $\dot{\mathbf{N}} = (\dot{N}_{CO}, \dot{N}_{CO_2}, \dot{N}_{H_2}, \dot{N}_{H_2O}, \dot{N}_{CH_4})$ , computes the component creation rates  $\mathbf{R}(\dot{\mathbf{N}})$  (see Exercise 6). For this, it will be necessary, from the flow rates, to compute the component-specific reduced partial pressures  $p_j = P\dot{N}_j / \sum_k \dot{N}_k$ . As in the main text, we use the reactor parameters:

$$\begin{aligned} T &= 800 \text{ }^\circ\text{C} \\ P &= 10 \text{ bar} \\ SN &= 3 \\ A_{tubes} &= 10 * \pi(0.02)^2 / 4 \text{ m}^2 \\ v_{flow} &= 5 \text{ m/s} \\ L_{tube} &= 1 \text{ m} \\ \rho_{catalyst} &= 1000 \text{ kg/m}^3 \end{aligned}$$

From the component creation rates  $\mathbf{R}$ , one can calculate the spatial derivative of the molar flow rates:

$$\frac{d\dot{\mathbf{N}}}{dx} = \rho_{catalyst} A_{tubes} \mathbf{R}(\dot{\mathbf{N}})$$

These are the coupled differential equations, which describe the PFR operation. At the entrance to the reactor ( $x=0$ ), show that the initial values of the partial pressures  $\mathbf{p}$ , the molar flow rates  $\dot{\mathbf{N}}$  and the component creation rates  $\mathbf{R}$  are:

$$\mathbf{p}^{initial} = P \left( 0, \frac{1}{2 + SN}, \frac{1 + SN}{2 + SN}, 0, 0 \right)$$

$$\dot{\mathbf{N}}^{initial} = \frac{A_{tubes} v_{flow}}{RT} \mathbf{p}^{initial}$$

$$A_{tubes} \rho_{catalyst} \mathbf{R}(\dot{\mathbf{N}}^{initial}) = A_{tubes} \rho_{catalyst} \begin{pmatrix} -r_1[\mathbf{p}^{initial}] + r_2[\mathbf{p}^{initial}] \\ -r_2[\mathbf{p}^{initial}] - r_3[\mathbf{p}^{initial}] \\ -3r_1[\mathbf{p}^{initial}] - r_2[\mathbf{p}^{initial}] - 4r_3[\mathbf{p}^{initial}] \\ r_1[\mathbf{p}^{initial}] + r_2[\mathbf{p}^{initial}] + 2r_3[\mathbf{p}^{initial}] \\ r_1[\mathbf{p}^{initial}] + r_3[\mathbf{p}^{initial}] \end{pmatrix}$$

Using the results of Exercise 6 and the kinetic model of Xu and Froment [Xu, J.; Froment, G. F. Methane Steam Reforming, Methanation and Water-Gas Shift: I. Intrinsic Kinetics. *AIChE J.* **1989**, 35 (1), 88 – 96.], and the reactor parameters above, find the numerical values of these three vector quantities.

Answer:

$$\mathbf{P}^{initial} = (0, 2, 8, 0, 0) \text{ bar}$$

$$\dot{\mathbf{N}}^{initial} = (0, 0.356, 1.427, 0, 0) \text{ mol/s}$$

$$A_{tubes} \rho_{catalyst} \mathbf{R}(\dot{\mathbf{N}}^{initial}) = (10350, -12860, -20410, 15380, 2514) \text{ mol/s/m}$$

## 10. PFR simulation II.

For the PFR reactor, in order to compute the degree of conversion of the initial CO<sub>2</sub> to product species, we must numerically integrate the PFR equation:

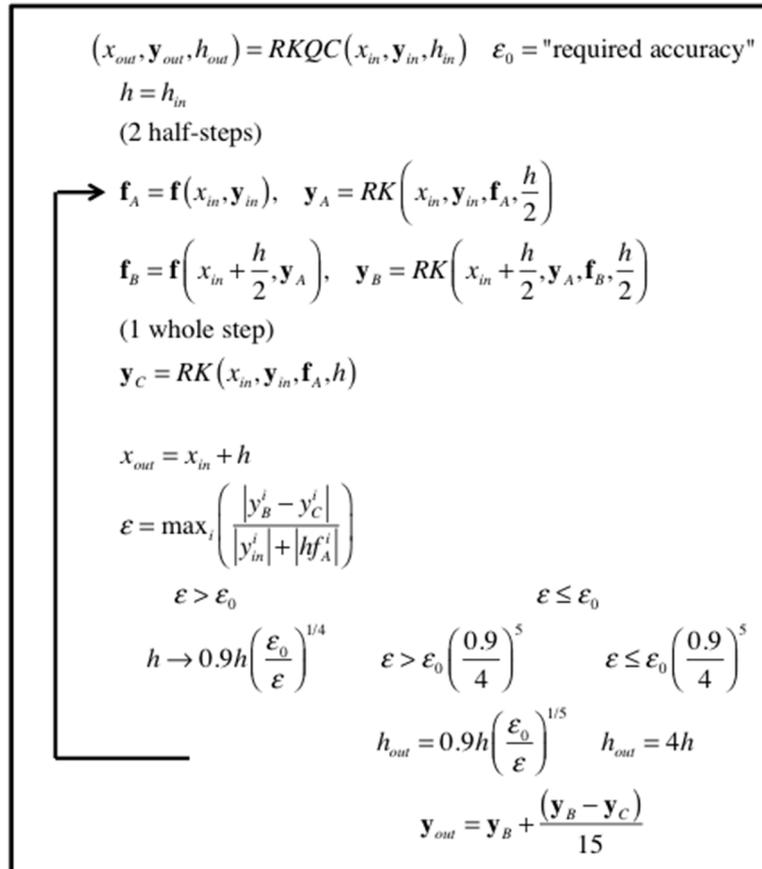
$$\frac{d\dot{\mathbf{N}}}{dx} = \rho_{catalyst} A_{tubes} \mathbf{R}(\dot{\mathbf{N}})$$

beginning at  $x=0$  with the initial molar flow rates  $\dot{\mathbf{N}}^{initial}$ , until we reach the end of the reactor at  $x=L_{tube}$ . This is an example of coupled first-order ordinary differential equations with given initial conditions, and a standard algorithm for the numerical integration is the Runge-Kutta method [Press, W. H. *Numerical recipes: the art of scientific computing*, Cambridge University Press, Cambridge, UK, 2007]. Here discrete steps of size  $h$  in the independent variable  $x_n$  are made, and the dependent variables are updated from  $\mathbf{y}_n$  to  $\mathbf{y}_{n+1}$ . The “fourth-order” Runge-Kutta method requires 4 evaluations of the derivative function  $\mathbf{f}(x, \mathbf{y})$  for each step. The procedure RK to make a single step, outlined below requires as input the values  $x_n, \mathbf{y}_n, \mathbf{f}_0 = \mathbf{f}(x_n, \mathbf{y}_n)$  and  $h$ :

$$\begin{aligned} \frac{d\mathbf{y}}{dx} &= \mathbf{f}(x, \mathbf{y}) \\ (x_{n+1}, \mathbf{y}_{n+1}) &= RK(x_n, \mathbf{y}_n, \mathbf{f}_0, h) \\ k_a &= h \mathbf{f}_0 \\ k_b &= h \mathbf{f}\left(x_n + \frac{h}{2}, \mathbf{y}_n + \frac{k_a}{2}\right) \\ k_c &= h \mathbf{f}\left(x_n + \frac{h}{2}, \mathbf{y}_n + \frac{k_b}{2}\right) \\ k_d &= h \mathbf{f}(x_n + h, \mathbf{y}_n + k_c) \\ \mathbf{y}_{n+1} &= \mathbf{y}_n + \frac{1}{6}(k_a + 2k_b + 2k_c + k_d) \\ x_{n+1} &= x_n + h \end{aligned}$$

For a simulation of the plug flow reactor, where rapid changes occur at the beginning of the reactor and much slower changes occur at the end, the standard Runge-Kutta procedure, with a fixed step size  $h$ , is insufficient. We need to extend the method to dynamically adjust the step size, as required. The "quality control" Runge-Kutta procedure RKQC accomplishes this by comparing the effect of making two small RK steps with that of making a single step and adjusting the step size accordingly. An additional input parameter,  $\epsilon_0$ , specifies the required relative accuracy of the dependent variables.

Implement the RK and RKQC procedures and use them, for the methanation PFR parameters given in Exercise 9, to compute the degree of conversion from  $\text{CO}_2$  to  $\text{CH}_4$ ,  $\dot{N}_{\text{CH}_4}(x = L_{\text{tube}}) / \dot{N}_{\text{CO}_2}^{\text{initial}}$ , for a sequence of reactor temperatures,  $T = 200, 300, 400, 500, 600, 700$  and  $800^\circ\text{C}$ , and compare it with



the corresponding values  $\xi_3$  from equilibrium thermodynamics (Exercise 5). Use  $\epsilon_0 = 0.001$ . Compare with Figure 7b.

Answer:

T [°C]	Equilibrium	PFR
	$\xi_3$	$\dot{N}_{\text{CH}_4}(x = L_{\text{tube}}) / \dot{N}_{\text{CO}_2}^{\text{initial}}$
200	0.996	0
300	0.983	0.171
400	0.954	0.953
500	0.901	0.901
600	0.816	0.816
700	0.684	0.684
800	0.496	0.496

### 11. Does the CH<sub>4</sub> come from reaction 1 or reaction 3?

As discussed in Exercise 8, in order to determine how much of the product CH<sub>4</sub> is produced directly from the hydrogenation of CO<sub>2</sub> and how much indirectly via CO from the reverse water gas shift reaction, we need to consider the reaction kinetics in the plug flow reactor. To this end, we introduce modified expressions to the PFR equations:

$$\mathbf{p} = (p_{CO}, p_{CO_2}, p_{H_2}, p_{H_2O}, p_{CH_4(total)})$$

$$\dot{\mathbf{N}} = (\dot{N}_{CO}, \dot{N}_{CO_2}, \dot{N}_{H_2}, \dot{N}_{H_2O}, \dot{N}_{CH_4(total)}, \dot{N}_{CH_4(1)}, \dot{N}_{CH_4(3)})$$

$$R_{CH_4(total)} = r_1[\mathbf{p}] + r_3[\mathbf{p}]$$

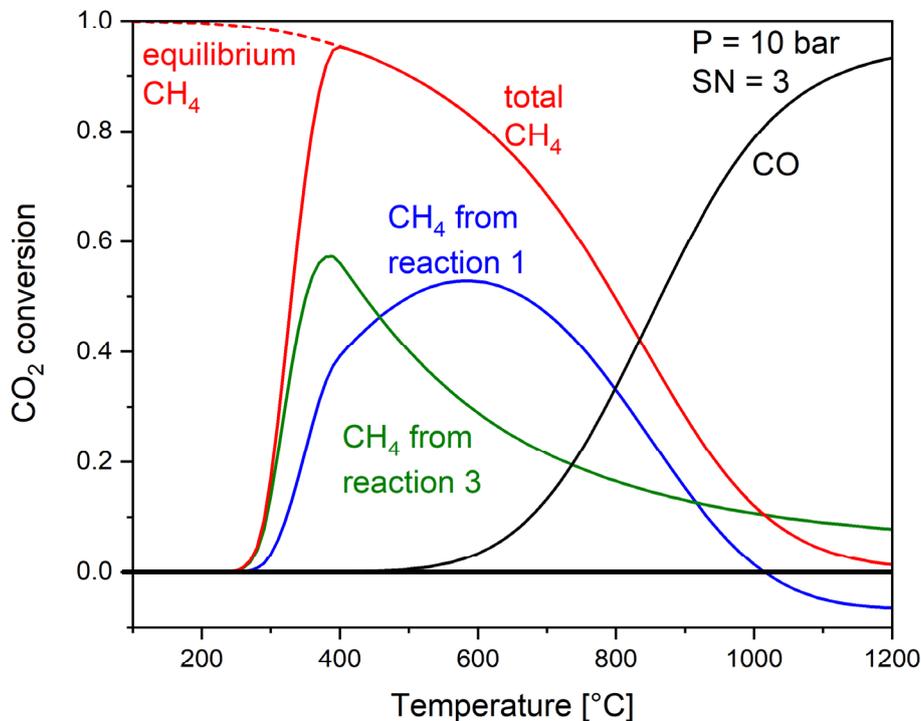
$$R_{CH_4(1)} = r_1[\mathbf{p}]$$

$$R_{CH_4(3)} = r_3[\mathbf{p}]$$

While the 5-component reduced partial pressure vector  $\mathbf{p}$  is unchanged, we have added two CH<sub>4</sub> components, specific to reactions 1 and 3, to the molar flow and component creation rate vectors.

Use the Runge-Kutta routines from Exercise 10 to integrate the 7-component PFR equation, and plot the resulting CO<sub>2</sub> to CH<sub>4</sub> degrees of conversion as a function of reactor temperature. Discuss the results.

Answer:



We note the following two features: a) At the lowest reaction temperatures, the exothermic reaction 1 is principally responsible for the CH<sub>4</sub> production, b) At very high temperatures, the conversion via reaction 1 is *negative*, implying that the CH<sub>4</sub> produced by reaction 3 is “back-converted” to CO via the inverse of reaction 1.