

A First Course on Kinetics and Reaction Engineering

Example 17.1

Problem Purpose

This problem illustrates the derivation of a mole balance design equation for a reactor that is similar to a PFR.

Problem Statement

It has been proposed that the water-gas shift reaction, equation (1), be run in a membrane reactor. The membrane reactor is similar to a tubular plug flow reactor, the only difference is that the wall of the reactor is permeable to hydrogen. That is, if the space outside the reactor is evacuated to a low partial pressure of hydrogen, the hydrogen flux through the wall at any axial position, z , will be proportional to its local partial pressure, equation (2). Assuming the reactor to be isothermal and to operate at steady state, and assuming plug flow and perfect radial mixing still prevail, derive a steady state mole balance on hydrogen.



$$N_{\text{H}_2}(z) = D_{\text{eff}} P_{\text{H}_2} \quad (2)$$

Problem Solution

As was done in deriving the mole balance for a plug flow reactor, the mole balance is written for a differential element of reactor volume and then the limit is taken as the size of this element goes to zero. Here, we will assume that the reactor is cylindrical with a constant diameter, D , and a length, L . Figure 1 shows such a reactor, highlighting a differentially thick cross section that will be used in formulating the mole balance for the membrane.

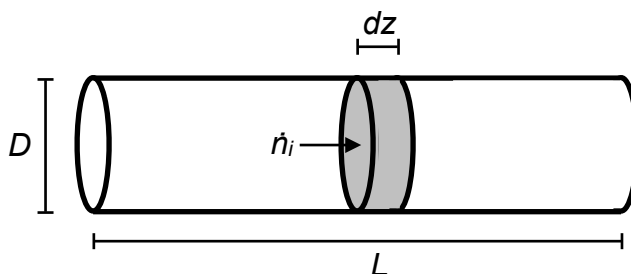


Figure 1 Volume element used in deriving the ideal PFR design equations.

As with a PFR, it is assumed that there is perfect mixing in the radial direction and no mixing in the axial direction. With these assumptions, the environmental variables will be uniform throughout the entire differential element shown in Figure 1 (or, put differently, the differential element shown in Figure 1 is

perfectly mixed). The derivation of the mole balance on species i begins with the balance equation, applied to the differential element.

$$\text{INPUT} + \text{GENERATION} = \text{OUTPUT} + \text{ACCUMULATION}$$

The input and output terms include the molar flow rate, evaluated at the “front” and “back” of the differential element. In contrast to the PFR, here there is a second output term corresponding to the permeation of the species through the wall of the reactor. This term is equal to the flux through the membrane wall times the area of that wall.

$$\dot{n}_i|_z + \text{GENERATION} = \dot{n}_i|_{z+dz} + D_{eff,i} P_i (\pi D dz) + \text{ACCUMULATION}$$

If we assume that there is a single fluid within the reactor in which all reactions take place, then the total rate of generation of species i per unit fluid volume is equal to $\sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j$. The differential element

is perfectly mixed, and therefore the rate is the same anywhere within its volume. Therefore, the total generation of moles of species i within the element is equal to the volume of the differential element times the total rate per volume, $\frac{\pi D^2 (dz)}{4} \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j$, where we have further assumed that every

reaction rate has been normalized per unit fluid volume.

$$\dot{n}_i|_z + \frac{\pi D^2 (dz)}{4} \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j = \dot{n}_i|_{z+dz} + D_{eff,i} P_i (\pi D dz) + \text{ACCUMULATION}$$

Since we're interested in a steady-state mole balance, the accumulation term can be set equal to zero.

$$\dot{n}_i|_z + \frac{\pi D^2 (dz)}{4} \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j = \dot{n}_i|_{z+dz} + D_{eff,i} P_i (\pi D dz)$$

This equation can be rearranged.

$$\frac{\dot{n}_i|_{z+dz} - \dot{n}_i|_z}{dz} = \frac{\pi D^2}{4} \sum_{\substack{j=all \\ reactions}} \nu_{i,j} r_j - D_{eff,i} P_i (\pi D)$$

In the limit of an infinitesimally thin volume element, $\lim_{dz \rightarrow 0} \left(\frac{\dot{n}_i|_{z+dz} - \dot{n}_i|_z}{dz} \right) = \frac{\partial \dot{n}_i}{\partial z}$.

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \sum_{\substack{j=all \\ reactions}} v_{i,j} r_j - D_{eff,i} P_i (\pi D)$$

Finally, we were asked for a mole balance on hydrogen, so we set i equal to H_2 , insert the value of the stoichiometric coefficient of hydrogen, +1, and note that there is only one reaction in the summation. Notice that if the membrane was perfectly *permselective*, that is if only hydrogen could pass through it, then the mole balances for the species other than hydrogen would be exactly the same as for a PFR.

$$\frac{\partial \dot{n}_{H_2}}{\partial z} = \frac{\pi D^2}{4} r_1 - D_{eff,H_2} P_{H_2} (\pi D)$$