
Consider the liquid phase reaction n-butane $\leftrightarrow$ iso-butane. The feed comes at a rate of 163 kmol/h and 90 mol% is n-butane, and 10 mol% is i-pentane. The latter is an inert. The feed comes at 330 K. The following data are available.

$A \leftrightarrow B$ and inert is P.

$C_{p-A} = C_{p-B} = 141$ J/mol/K, $C_{p-P} = 161$ J/mol/K.

$\Delta H = -6900$ J/mol $A$ reacted.

Rate constant is $k = 31.1$ h$^{-1}$ at 360 K, and activation energy is 65.7 kJ/mol. The equilibrium constant is $K_C = 3.03$ at 60 °C and the concentration of A in the feed is $C_{A-in} = 9.3$ kmol/m$^3$. You are also given that $K_C = K_C^0 e^{\frac{\Delta H}{RT}}$.

**Solution:**

First we will write the parameters in standard form. For the reaction $A \leftrightarrow k_{-1} B$, the rate constant is given by $k_1 = k_{10} e^{\frac{E}{RT}}$

At 360 K, $k = 31.1$ h$^{-1}$ and $E = 65.7$ kJ/mol implies that $k = 1.0615 \times 10^{11} e^{\frac{65700}{8.314T}} = 1.0615 \times 10^{11} e^{\frac{7902.3}{T}}$ h$^{-1}$

At 60 °C, $K_C = 3.03$. $\Delta H = 6500$ J/mol. This means that $K_C^0 = 0.2506$.

$k_{-1} = \frac{k_1}{K_C} = \frac{k_{10} e^{\frac{(E-\Delta H)}{RT}}}{K_C^0} = 4.2351 \times 10^{11} e^{\frac{8732.3}{T}}$

Design equation: For a CSTR, $F_{A-in} + V (r_A) = F_{A-out}$. For a PFR $\frac{dF_A}{dV} = r_A = -k_i C_A + k_{-1} C_B$. Since this is a liquid phase reaction with negligible density change, and since the feed does not contain any B, we can write that $C_A = C_{A-in} (1-x)$ and $C_B = C_{A-in} x$

Hence the design equation is $\frac{dx}{dV} = k_i C_A - k_{-1} C_B = k_i C_{A-in} (1-x) - k_{-1} C_{A-in} x$

Note that the rate constants are functions of temperature.

Energy balance equation:
Choose any point ‘V’ in the reactor. The conversion at that point is ‘x’ and the temperature is ‘T’. The heat released until that point is the same as the heat needed to bring the feed to that temperature.

\[ F_{A-in} \Delta H |_{T} = \int_{T_n}^{T} \sum_{i} F_{i-in} C_{p-i} dT \]

Since \( C_{p-A} = C_{p-B} \), \( \Delta H \) is not a function of temperature. \( F_{A-in} = 90\% \) of Feed = 146.7 kmol/h. \( F_{P-in} = 16.3 \) kmol/h. Therefore,

\[ \sum_{i} F_{i-in} C_{p-i} dT = (F_{A-in} C_{p-A} + F_{P-in} C_{p-P}) dT = 23309 dT \text{ kJ/h} \]

\[ \int_{T_n}^{T} \sum_{i} F_{i-in} C_{p-i} dT = \int_{T_n}^{T} 23309 dT = 23309(T - T_n) \]

\[ F_{A-in} \Delta H |_{T} = 1.0122 \times 10^6 x \]

Therefore, \( T = 330 + 43.4253 x \). The book gives a value of \( 330 + 43.3 x \).

In order to find the relationship between the reactor volume and conversion, we have to integrate

\[ V = \int dV = F_{A-in} \int \frac{dx}{-r_A} \]

We need to create a table of \( x \) vs \((1/-r_A)\) and then integrate. We also want to keep track of equilibrium conversion, so that we don’t try to go above it.

At equilibrium \( r_A = 0 \). Therefore, \( k_1 C_{A-in} (1-x_e) - k_{-1} C_{A-in} x_e = 0 \), which means that \( x_e = \frac{k_1}{k_1 + k_{-1}} \)

<table>
<thead>
<tr>
<th>( x )</th>
<th>( T )</th>
<th>( K_1 )</th>
<th>( k_{-1} )</th>
<th>( x_e )</th>
<th>(-r_A )</th>
<th>( 1/(-r_A) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>330</td>
<td>4.2421</td>
<td>1.3639</td>
<td>0.7567</td>
<td>39.45</td>
<td>0.0253</td>
</tr>
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<td>0.2</td>
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<td>2.688</td>
<td>0.7446</td>
<td>53.32</td>
<td>0.0188</td>
</tr>
<tr>
<td>0.4</td>
<td>347.4</td>
<td>14.05</td>
<td>5.122</td>
<td>0.733</td>
<td>59.33</td>
<td>0.0169</td>
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<td>0.6</td>
<td>356</td>
<td>23.5</td>
<td>9.5</td>
<td>0.722</td>
<td>38.3</td>
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</tr>
<tr>
<td>0.65</td>
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<td>28</td>
<td>10.97</td>
<td>0.7184</td>
<td>24.8</td>
<td>0.0403</td>
</tr>
<tr>
<td>0.7</td>
<td>360.4</td>
<td>32</td>
<td>12.7</td>
<td>0.7156</td>
<td>6.5</td>
<td>0.1546</td>
</tr>
</tbody>
</table>

If we integrate this, we find that the volume to get 0.7 conversion is about 3.4 m\(^3\). The last bit of conversion takes a lot of volume. In the beginning the increase in temperature helps. Near the end, the reverse reaction is slowing down the conversion of A, since we are close to equilibrium.

If we want 40% conversion in the PFR, we need 1.15 m\(^3\) volume.
If we conduct this in a CSTR and want the same 40% conversion, we will have $T = 347.4 \text{ K}$ (same as in PFR). $k_1$ and $k_{m1}$ are known and hence the rate is known. From the design equation we can write

$$V = \frac{F_{A-in}x}{-r_A} = \frac{F_{A-in}x}{k_1 \times C_{A-in} \times (1 - x) - k_{-1} \times C_{A-in} \times x}$$

$$= \frac{146.7 \times 0.4}{14.05 \times 9.3 \times (1 - 0.4) - 5.122 \times 9.3 \times 0.4}$$

$$= 0.988 \text{ m}^3$$