The Adiabatic CSTR

Accumulation = Input - Output + Production - Exchange

Steady state, \( W_s = 0 \):

Need to replace \( r = f(c_A, T) \):

Combine with mass balance:

Very important special case: adiabatic reactor operation \( \rightarrow U = 0 \)

\textbf{Adiabatic temperature rise:}
The Adiabatic PFR

Steady state EB:

Steady state MB:

Integration with initial condition $X=0, \ T=T_0$ yields:

Adiabatic temperature rise, PFR:
Adiabatic Temperature Rise

Simplified form:

The adiabatic temperature rise is:
- independent on the type of reactor
- independent on reaction rate \( r \)
-> a property of the reactant mixture!

More general form (introducing \( T \)-dependency and allowing for different heat capacities of reactants):

where \( C_p \) = integral mean heat capacity between (adiabatic) reactor temperature \( T \) and feed temperature \( T_0 \)
(often negligible correction...)

\[
\bar{C}_p = \frac{\int_{T_0}^{T} C_p(T) dT}{T - T_0}
\]

Since \( \Delta H_R(T) \) dependent on \( \Delta T_{ad} \) -> numerical/iterative solution
(for estimates, however, \( \Delta H_R(T_0) \) can often be used)
$\Delta T_{ad}$: Examples

Neglecting the temperature dependence of the heat of reaction as well as of the heat capacities of the gases, estimate the adiabatic temperature rise in the following systems, assuming complete conversion:

(I)\n
• Total oxidation of methane with air:
  \[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad \text{in a PFR with stoichiometric feed} \]

• Partial oxidation of methane with air:
  \[ \text{CH}_4 + 0.5 \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2 \quad \text{in a PFR with stoichiometric feed} \]

(II)\n
• $\text{H}_2 + 0.5 \text{O}_2 \rightarrow \text{H}_2\text{O} \quad \text{in a BR with}$
  \[ C_{\text{H}_2,0} = 2 \text{ mol/l}, C_{\text{O}_2,0} = 1 \text{ mol/l} \ (\text{i.e. stoichiometric}) \]

• same reaction, but now with air:
  \[ C_{\text{H}_2,0} = 2 \text{ mol/l}, C_{\text{O}_2,0} = 1 \text{ mol/l}, C_{\text{N}_2,0} = 4 \text{ mol/l} \]

Given:

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$</th>
<th>O$_2$</th>
<th>N$_2$</th>
<th>H$_2$</th>
<th>H$_2$O</th>
<th>CO</th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_f \ [\text{kJ/mol}]$</td>
<td>-75</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-240</td>
<td>-110</td>
<td>-394</td>
</tr>
<tr>
<td>$C_p \ [\text{J/(mol K)}]$</td>
<td>35</td>
<td>29</td>
<td>29</td>
<td>29</td>
<td>34</td>
<td>29</td>
<td>37</td>
</tr>
</tbody>
</table>
\( \Delta T_{ad} \): Examples...

(II) H\(_2\) oxidation

\[
H_2/O_2 = 2/1 \\
\Delta H_R =
\]

H\(_2\)/air (stoich.)

\[
\Delta H_R =
\]

(I) Methane oxidation

\[
\text{CH}_4/\text{air combustion} \\
\Delta H_R =
\]

\[
\text{CH}_4/\text{air} \rightarrow \text{syngas} + (4 \text{N}_2) \\
\Delta H_R =
\]
Calculating $T_{\text{ad}}$ with CHEMKIN

The equilibrium module in CHEMKIN (or any other equilibrium solver) can be used to calculate the adiabatic temperature rise of a reactive mixture, assuming...

...that the reaction goes to completion/equilibrium!
Another look at equilibrium limitations

We have previously looked into optimizing $S$ and $X$, but what about $r$?

- 'Optimization' with respect to $C_j$ obvious (depends on $m_j$).

**How about $T$?**

$$k = k_0 \exp\{-E_A/RT\}$$

**So, the higher $T$ the higher $r$?** Let's check $dr/dT$!

We know: $$\frac{dk_f}{dT} = \frac{E_A}{RT^2} k_f$$ and $$\frac{d\ln K_{eq}}{dT} = \frac{\Delta H_R}{RT^2}$$

Hence, the first term is always positive, the second term is:

- positive for endothermal reaction
- negative for exothermal reaction
So, we now know that for exothermal reactions a maximum in $r$ can exist. What is $T_{opt}$?

Temperature of maximum reaction rate in equilibrium-limited exothermal reaction

Phase trajectories in $\{X,T\}$-space
The blue lines are lines of constant reaction rate, the red line indicates the chemical equilibrium, i.e. $r = 0$. 

$T_{opt}$ for exothermal, reversible rctns
Adiabatic Reactor Operation: Trajectories

From $\Delta T_{ad}$:

$$T - T_0 = \left( -\frac{\Delta H_R}{\rho C_p} \right) C_{ad} X_d$$

Addition of inerts $\rightarrow$ same conversion at lower T!

What would that look like for an endothermic reaction?

What about equilibrium constraints??

Reversible, exothermic reaction

...with additional cooling

How can we realize an optimal trajectory?