Fundamentals of Material Balances

Process Classification
Balances on Reactive Systems

- Material balance no longer takes the form
  \[
  \text{INPUT} = \text{OUTPUT}
  \]

- Must account for the disappearance of reactants and appearance of products through stoichiometry.
Stoichiometric Equations

- The *stoichiometric equation* of a chemical reaction is a statement of the relative amounts of reactants and products that participate in the reaction.

\[ 2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3 \]

- A stoichiometric equation is valid only if the number of atoms of each atomic species is balanced.

\[ 2 \text{S} \rightarrow 2 \text{S} \]
\[ 4 \text{O} + 2 \text{O} \rightarrow 6 \text{O} \]
Stoichiometric Equations

- The *stoichiometric equation* of a chemical reaction is a statement of the relative amounts of reactants and products that participate in the reaction.

\[ 2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3 \]

- A *stoichiometric ratio* of two molecular species participating in a reaction is the ratio of their stoichiometric coefficients:

  - 2 mol SO\(_3\) generated /1 mol O\(_2\) consumed
  - 2 mol SO\(_3\) generated /2 mol SO\(_2\) consumed
Stoichiometric Equations

\[ \text{C}_4\text{H}_8 + 6 \text{ O}_2 \rightarrow 4 \text{ CO}_2 + 4 \text{ H}_2\text{O} \]

- Is this stoichiometric equation balanced?
- What is the stoichiometric coefficient of \( \text{CO}_2 \)?
- What is the stoichiometric ratio of \( \text{H}_2\text{O} \) to \( \text{O}_2 \)?
- How many lb-mol \( \text{O}_2 \) react to form 400 lb-mol \( \text{CO}_2 \)?

\[
400 \text{ lbmol CO}_2 \times \frac{6 \text{ lbmol O}_2}{4 \text{ lbmol CO}_2} = 600 \text{ lbmol O}_2
\]

- 100 lbmol/min \( \text{C}_4\text{H}_8 \) is fed and 50% reacts. At what rate is water formed?

\[
100 \frac{\text{lbmol C}_4\text{H}_8}{\text{min}} \times 0.50 \times \frac{4 \text{ lbmol H}_2\text{O}}{1 \text{ lbmol C}_4\text{H}_8} = 200 \frac{\text{lbmol H}_2\text{O}}{\text{min}}
\]
Limiting and Excess Reactants

- Two reactants are said to be in *stoichiometric proportion* if the ratio (moles A present/moles B present) equals the stoichiometric ratio from the balanced reaction equation.

\[2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3\]

- the feed ratio that would represent stoichiometric proportion is \(n_{\text{SO}_2}/n_{\text{O}_2} = 2:1\)

- If reactants are fed in stoichometric proportion, and the reaction proceeds to completion, all reactants are consumed.
Stoichiometric Proportion – Reactants are present in a ratio equivalent to the ratio of the stoichiometric coefficients.

\[ A + 2B \rightarrow 2C \]
**Limiting and Excess Reactants**

- *Limiting reactant* – A reactant is limiting if it is present in less than stoichiometric proportion relative to every other reactant.

  \[ A + 2B \rightarrow 2C \]

- *Excess reactant* – All other reactants besides the limiting reactant.
Limiting and Excess Reactants

- fractional excess \( (f_{XS}) \) – ratio of the excess to the stoichiometric proportion.

\[ A + 2B \rightarrow 2C \]

\[
f_{XS} = \frac{(n_A)_{\text{feed}} - (n_A)_{\text{stoich}}}{(n_A)_{\text{stoich}}} \]

\[
= \frac{5 - 4}{4} = 0.25
\]
Limiting and Excess Reactants

- *fractional conversion* \((f)\) – ratio of the amount of a reactant reacted, to the amount fed.

\[
\begin{align*}
A + 2B & \rightarrow 2C \\

f_A &= \frac{0}{5} = 0.0 \\

f_B &= \frac{0}{8} = 0.0 \\

f &= \frac{(n_A)_{\text{reacted}}}{(n_A)_{\text{fed}}} 
\end{align*}
\]
Limiting and Excess Reactants

- fractional conversion \((f)\) – ratio of the amount of a reactant reacted, to the amount fed.

\[
A + 2B \rightarrow 2C
\]

\[
f = \frac{(n_A)_{\text{reacted}}}{(n_A)_{\text{fed}}}
\]

\[
f_A = \frac{1}{5} = 0.2
\]

\[
f_B = \frac{2}{8} = 0.25
\]
Limiting and Excess Reactants

- **fractional conversion** \((f)\) – ratio of the amount of a reactant reacted, to the amount fed.

\[
A + 2B \rightarrow 2C
\]

\[
f = \frac{(n_A)_{\text{reacted}}}{(n_A)_{\text{fed}}}
\]

\[
f_A = \frac{2}{5} = 0.4
\]

\[
f_B = \frac{4}{8} = 0.5
\]
Limiting and Excess Reactants

- *fractional conversion* \( (f) \) – ratio of the amount of a reactant reacted, to the amount fed.

\[
A + 2B \rightarrow 2C
\]

\[
f = \frac{(n_\text{A})_{\text{reacted}}}{(n_\text{A})_{\text{fed}}}
\]

\[
f_A = \frac{3}{5} = 0.6
\]

\[
f_B = \frac{6}{8} = 0.75
\]
Limiting and Excess Reactants

- fractional conversion \((f)\) – ratio of the amount of a reactant reacted, to the amount fed.

\[
A + 2B \rightarrow 2C
\]

\[
f = \frac{(n_A)_{\text{reacted}}}{(n_A)_{\text{fed}}}
\]

\[
f_A = \frac{4}{5} = 0.8
\]

\[
f_B = \frac{8}{8} = 1.0
\]
extent of reaction ($\xi$) – an extensive quantity describing the progress of a chemical reaction.

\[ \nu = \text{stoichiometric coefficients: } \nu_A = -1, \nu_B = -2, \nu_C = 2 \]

\[ n_i = n_{i0} + \nu_i \xi \]

\[ A + 2B \rightarrow 2C \]

\[ \xi = 0 \]

\[ n_A = n_{A0} - \xi \]
\[ n_B = n_{B0} - 2\xi \]
\[ n_C = n_{C0} + 2\xi \]
extent of reaction \((\xi)\) – an extensive quantity describing the progress of a chemical reaction.

\[ \nu = \text{stoichiometric coefficients: } \nu_A = -1, \nu_B = -2, \nu_C = 2 \]

\[ n_i = n_{i0} + \nu_i \xi \]

\[ A + 2B \rightarrow 2C \]

\[ \xi = 0 \]

\[ n_A = 5 - \xi = 5 \]
\[ n_B = 8 - 2\xi = 8 \]
\[ n_C = 0 + 2\xi = 0 \]
**Extent of Reaction**

- **extent of reaction** ($\xi$) – an extensive quantity describing the progress of a chemical reaction.
- $\nu$ – stoichiometric coefficients: $\nu_A = -1$, $\nu_B = -2$, $\nu_C = 2$

$$\text{A} + 2\text{B} \rightarrow 2\text{C}$$

$$n_i = n_{i0} + \nu_i \xi$$

- $\xi = 1$

$n_A = 5 - \xi = 4$

$n_B = 8 - 2\xi = 6$

$n_C = 0 + 2\xi = 2$
**Extent of Reaction**

- *extent of reaction* ($\xi$) – an extensive quantity describing the progress of a chemical reaction.
- $\nu$ – stoichiometric coefficients: $\nu_A = -1$, $\nu_B = -2$, $\nu_C = 2$

$$A + 2B \rightarrow 2C$$

$$n_i = n_{i0} + \nu_i \xi$$

$$\xi = 2$$

$$n_A = 5 - \xi = 3$$  
$$n_B = 8 - 2\xi = 4$$  
$$n_C = 0 + 2\xi = 4$$
**Extent of Reaction**

- *extent of reaction* ($\xi$) – an extensive quantity describing the progress of a chemical reaction.
- $\nu$ – stoichiometric coefficients: $\nu_A = -1$, $\nu_B = -2$, $\nu_C = 2$

$$A + 2B \rightarrow 2C$$

\[
n_i = n_{i0} + \nu_i \xi
\]

\[
\xi = 4
\]

\[
n_A = 5 - \xi = 1
\]

\[
n_B = 8 - 2\xi = 0
\]

\[
n_C = 0 + 2\xi = 8
\]
Assume an equimolar reactant feed of 100 kmol:

- What is the limiting reactant?

A reactant is limiting if it is present in less than stoichiometric proportion relative to every other reactant.

\[
\left( \frac{n_{C_2H_4}}{n_{O_2}} \right)_{stoich} = \frac{2}{1} = \text{ethylene}
\]

\[
\left( \frac{n_{C_2H_4}}{n_{O_2}} \right)_{feed} = \frac{1}{1}
\]
Assume an equimolar reactant feed of 100 kmol:

- What is the percentage excess of each reactant?

\[
f_{xs,O_2} = \frac{\left(n_{O_2}\right)_{feed} - \left(n_{O_2}\right)_{stoich}}{\left(n_{O_2}\right)_{stoich}}
\]

\[
= \frac{100 - 50}{50} = 1.00 = 100\%
\]
Assume an equimolar reactant feed of 100 kmol:

If the reaction proceeds to completion:

- (a) How much of the excess reactant will be left?

\[
n_{C_2H_4} = n_{C_2H_4}^0 + \nu_{C_2H_4} \xi \\
0 = 100 + (-2)\xi \\
\xi = 50
\]

- (b) How much \(C_2H_4O\) will be formed?

\[
n_{C_2H_4O} = n_{C_2H_4O}^0 + \nu_{C_2H_4O} \xi \\
n_{C_2H_4O} = 0 + (2)50 \\
n_{C_2H_4O} = 100
\]

- (c) What is the extent of reaction?

\[
2C_2H_4 + O_2 \rightarrow 2C_2H_4O
\]
Assume an equimolar reactant feed of 100 kmol:

- If the reaction proceeds to a point where the fractional conversion of the limiting reactant is 50%, how much of each reactant and product is present at the end? What is ξ?

\[
f = \frac{(n_{C_2H_4})_{reacted}}{(n_{C_2H_4})_{fed}} = 0.5
\]

\[
f = \frac{n^o_{C_2H_4} - n_{C_2H_4}}{n^o_{C_2H_4}} = 0.5
\]

\[
\frac{100 - n_{C_2H_4}}{100} = 0.5
\]

\[
n_{C_2H_4} = 50
\]
Assume an equimolar reactant feed of 100 kmol:

- If the reaction proceeds to a point where 60 mol of $O_2$ is left, what is the fractional conversion of $C_2H_4$? What is $\xi$?

\[
\begin{align*}
    n_{o_2} & = n_{o_2}^0 + v_{o_2} \xi \\
    60 & = 100 + (-1)\xi \\
    \xi & = 40 \\
    n_{C_2H_4} & = n_{C_2H_4}^0 + v_{C_2H_4} \xi \\
    n_{C_2H_4} & = 100 + (-2)(40) \\
    n_{C_2H_4} & = 20 \\
    f & = \frac{\left(n_{C_2H_4}\right)_{\text{reacted}}}{\left(n_{C_2H_4}\right)_{\text{fed}}} = \frac{100 - 20}{100} = 0.8
\end{align*}
\]
Incomplete Reaction

\[ \text{Sb}_2\text{S}_3 + 3\text{Fe} = 2\text{Sb} + 3\text{FeS} \]

From this reaction, suppose that 0.6 kg of stibnite and 0.25 kg of iron are heated together to give 0.2 kg of Sb metal. Determine:

A) the limiting reactant  
B) the percentage of excess reactant  
C) the degree of completion  
D) the percent conversion
Solution

\[ \text{Sb}_2\text{S}_3 + 3\text{Fe} = 2\text{Sb} + 3\text{FeS} \]

<table>
<thead>
<tr>
<th>Component</th>
<th>kg</th>
<th>MW</th>
<th>g mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(_2)S(_3)</td>
<td>0.6</td>
<td>339.7</td>
<td>(1.77 = \frac{600}{339.7})</td>
</tr>
<tr>
<td>Fe</td>
<td>0.25</td>
<td>55.85</td>
<td>(4.48 = \frac{250}{55.85})</td>
</tr>
<tr>
<td>Sb</td>
<td>0.2</td>
<td>121.8</td>
<td>(1.64 = \frac{200}{121.8})</td>
</tr>
<tr>
<td>FeS</td>
<td></td>
<td>87.91</td>
<td></td>
</tr>
</tbody>
</table>

1.77 g mol Sb\(_2\)S\(_3\)  
4.48 g mol Fe  

Reactor  

1.64 g mol Sb  

FeS
\[ \text{Sb}_2\text{S}_3 + 3\text{Fe} = 2\text{Sb} + 3\text{FeS} \]

A) to find the limiting reactant, examine ratio of \(\text{Sb}_2\text{S}_3\) to Fe, \(1/3 = 0.33\). In the actual reaction the ratio is \(1.77/4.48 = 0.4\), hence \(\text{Sb}_2\text{S}_3\) is the excess reactant and Fe is the limiting reactant. \(\text{Sb}_2\text{S}_3\) required to react with the Fe is \(4.48/3 = 1.49\) g mol

B) The percentage of excess reactant is
\[
\%\ \text{excess} = \frac{(1.77-1.49)}{1.49} \times 100 = 18.8\ \%\ \text{excess}\ \text{Sb}_2\text{S}_3
\]

C) Calculate how much Fe react from 1.64 Sb formed
\[
\begin{array}{c|c}
\text{1.64 g mol Sb} & \text{3 g mol Fe} \\
\hline
2 \text{ g mol Sb} & = 2.46 \text{ g mol Fe}
\end{array}
\]
Degree of completion = \(2.46/4.48 = 0.55\)
Sb₂S₃ + 3Fe = 2Sb + 3FeS

D) percent conversion of Sb₂S₃

\[
\frac{1.64 \text{ g mol Sb}}{2 \text{ g mol Sb}} \times \frac{1 \text{ g mol Sb₂S₃}}{1 \text{ g mol Sb}} = 0.82 \text{ g mol Sb₂S₃}
\]

\[
\% \text{ conversion} = \frac{0.82}{1.77} \times 100 = 46.3\%
\]

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<td>1.64</td>
</tr>
<tr>
<td>FeS</td>
<td></td>
<td>87.91</td>
<td></td>
</tr>
</tbody>
</table>
Acrylonitrile produced by reaction of ammonia, propylene, and O$_2$ at 30% conversion of limiting reactant:

\[
\begin{align*}
C_3H_6 + NH_3 + \frac{3}{2} O_2 & \rightarrow C_3H_3N + 3H_2O
\end{align*}
\]

Determine limiting reactant

\[
\left(\frac{n_{NH_3}}{n_{C_3H_6}}\right)_0 = \left(\frac{0.120 \times 100}{0.100 \times 100}\right) = 1.20
\]

\[
\left(\frac{n_{NH_3}}{n_{C_3H_6}}\right)_{\text{stoich}} = \left(\frac{1}{1}\right) = 1
\]

\[
\left(\frac{n_{O_2}}{n_{C_3H_6}}\right)_0 = \left(\frac{0.780 \times 0.21 \times 100}{0.100 \times 100}\right) = 1.64
\]

\[
\left(\frac{n_{O_2}}{n_{C_3H_6}}\right)_{\text{stoich}} = \left(\frac{1.5}{1}\right) = 1.5
\]

\[
\text{stoich (mol C}_3\text{H}_3\text{N)} = \text{stoich (mol C}_3\text{H}_6) \times \left(\frac{n_{NH_3}}{n_{C_3H_6}}\right)_{\text{stoich}} = 1 \times 1 = 1
\]

\[
\text{stoich (mol } H_2O) = \text{stoich (mol C}_3\text{H}_6) \times 3 = 1 \times 3 = 3
\]
Acrylonitrile produced by reaction of ammonia, propylene, and $O_2$ at 30% conversion of limiting reactant:

Determine fractional excesses

\[
\begin{align*}
C_3H_6 + NH_3 + \frac{3}{2}O_2 & \rightarrow C_3H_3N + 3H_2O \\
\text{limiting} & \quad f_{XS} = 0.20 \\
\end{align*}
\]

\[
\begin{align*}
100 \text{ mol} & \\
0.100 \text{ mol C}_3\text{H}_6/\text{mol} & \\
0.120 \text{ mol NH}_3/\text{mol} & \\
0.780 \text{ mol air/mol} & \\
0.21 \text{ mol O}_2/\text{mol air} & \\
0.79 \text{ mol N}_2/\text{mol air} &
\end{align*}
\]

\[
\begin{align*}
\left(n_{C_3H_6}\right)_{\text{stoich}} &= 10.0 \text{ mol C}_3\text{H}_6 \left(\frac{1 \text{ mol NH}_3}{1 \text{ mol C}_3\text{H}_6}\right) = 10.0 \text{ mol NH}_3 \\
\left(f_{XS}\right)_{\text{NH}_3} &= \frac{(\text{NH}_3) - (\text{NH}_3)_{\text{stoich}}}{(\text{NH}_3)_{\text{stoich}}} = \frac{12.0 - 10.0}{10.0} = 0.2 \\
\left(n_{O_2}\right)_{\text{stoich}} &= 10.0 \text{ mol C}_3\text{H}_6 \left(\frac{1.5 \text{ mol O}_2}{1 \text{ mol C}_3\text{H}_6}\right) = 15.0 \text{ mol O}_2 \\
\left(f_{XS}\right)_{O_2} &= \frac{(\text{O}_2) - (\text{O}_2)_{\text{stoich}}}{(\text{O}_2)_{\text{stoich}}} = \frac{16.4 - 15.0}{15.0} = 0.093
\end{align*}
\]
Acrylonitrile produced by reaction of ammonia, propylene, and O₂ at 30% conversion of limiting reactant:

\[
C_3H_6 + NH_3 + \frac{3}{2}O_3 \rightarrow C_3H_3N + 3H_2O
\]

Determine the amount of propylene that leaves the reactor.

\[
f_{XS} = 0.20
\]

\[
n_{C_3H_6} = \left(1 - f\right) n_{C_3H_6}^0 = \left(1 - 0.30\right) (10.0 \text{ mol } C_3H_6) = 7.0 \text{ mol } C_3H_6
\]
Acrylonitrile produced by reaction of ammonia, propylene, and O\(_2\) at 30% conversion of limiting reactant:

\[ \text{limiting } f_{XS} = 0.20 \]

\[ C_3H_6 + NH_3 + \frac{3}{2} O_3 \rightarrow C_3H_3N + 3H_2O \]

\[ f_{XS} = 0.093 \]

\[ n_i = n_{i0} + \nu_i \xi \]

\[ n_{C_3H_6} = 7.0 \text{ mol } C_3H_6 \]

\[ n_{C_3H_6} = (n_{C_3H_6})_0 + (-1)\xi \]

\[ 7.0 \text{ mol} = 10.0 \text{ mol} - \xi \]

\[ \xi = 3 \text{ mol} \]
Acrylonitrile produced by reaction of ammonia, propylene, and O$_2$ at 30\% conversion of limiting reactant:

\[
\text{limiting } \quad f_{XS} = 0.20
\]

\[
\begin{align*}
\text{C}_3\text{H}_6 + \text{NH}_3 + \frac{3}{2}\text{O}_3 & \rightarrow \text{C}_3\text{H}_3\text{N} + 3\text{H}_2\text{O} \\
f_{XS} & = 0.093
\end{align*}
\]

Apply mole balance to all remaining species

\[
\xi = 3 \text{ mol} \quad n_i = n_{i0} + v_i \xi
\]

\[
\begin{align*}
n_{\text{NH}_3} & = (0.12)(100) + (-1)(3) = 9 \\
n_{\text{O}_2} & = (0.21)(0.78)(100) + (-\frac{3}{2})(3) = 11.9 \\
n_{\text{C}_3\text{H}_3\text{N}} & = (0) + (+1)(3.0) = 3 \\
n_{\text{N}_2} & = (0.79)(0.78)(100) + (0)(3) = 61.6 \\
n_{\text{H}_2\text{O}} & = (0) + (3)(3.0) = 9
\end{align*}
\]
Fuel for motor vehicles other than gasoline are being eyed because they generate lower levels of pollutants than does gasoline. Compressed propane has been suggested as a source of economic power for vehicles.

Suppose that in a test 22 kg of C$_3$H$_8$ is burned with 400 kg of air to produce 44 kg of CO$_2$ and 12 kg of CO.

a. What was the percent excess air?

b. The components in the product stream.
\[
\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (kg)</th>
<th>Molecular weight</th>
<th>Input (kg-mol)</th>
<th>Output (kg-mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_3)H(_8)</td>
<td>22</td>
<td>44</td>
<td>0.50</td>
<td>?</td>
</tr>
<tr>
<td>Air</td>
<td>400</td>
<td>29</td>
<td>13.80</td>
<td>?</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.21*13.80=2.90</td>
<td></td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.79*13.80=10.9</td>
<td></td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>CO(_2)</td>
<td>44</td>
<td>44</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>CO</td>
<td>12</td>
<td>28</td>
<td>-</td>
<td>0.43</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>18</td>
<td>18</td>
<td>-</td>
<td>?</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>29.87</td>
<td>?</td>
</tr>
</tbody>
</table>

\[
\text{Percent excess air} = \frac{(O_{2\text{Fed}} - O_{2\text{stoich}})}{(O_{2\text{stoich}})}
\]

\[
= \frac{(2.90 - 5*0.5)}{(5*0.5)} = 16\%
\]
$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad [1]$$

$$C_3H_8 + 7/2O_2 \rightarrow 3CO + 4H_2O \quad [2]$$

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<tbody>
<tr>
<td>$C_3H_8$</td>
<td>0.50</td>
<td>0.33</td>
<td>0.43/3=0.14</td>
<td>-</td>
<td>-</td>
<td>=0.55-(0.33+0.14)</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.21*13.80 =2.90</td>
<td>5*0.33= 1.65</td>
<td>3.5*0.14= 0.49</td>
<td>-</td>
<td>-</td>
<td>=2.90-(1.65+0.49)</td>
</tr>
<tr>
<td>$N_2$</td>
<td>0.79*13.80 =10.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.9</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>$CO$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.43</td>
<td>0.43</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>-</td>
<td>-</td>
<td>4*0.33= 1.32</td>
<td>4*0.14= 0.56</td>
<td>1.88</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>29.87</td>
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<td>15</td>
</tr>
</tbody>
</table>
A gas stream containing 80 mol% $\text{C}_2\text{H}_6$ and 20 mol% $\text{O}_2$ is burned in an engine with 200% excess air. If 80% of the ethane goes to $\text{CO}_2$, 10% goes to CO and the remaining unburned, determine the amount of the excess air per 100 moles of the feed gas.

$$\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \quad [1]$$

$$\text{C}_2\text{H}_6 + \frac{5}{2}\text{O}_2 \rightarrow 2\text{CO} + 3\text{H}_2\text{O} \quad [2]$$
A gas stream containing 80 mol\% C_2H_6 and 20 mol\% O_2 is burned in an engine with 200\% excess air. If 80\% of the ethane goes to CO_2, 10\% goes to CO and the remaining unburned, determine the amount of the excess air per 100 moles of the feed gas.

Basis=100 mole feed gas

$$\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$$ \[1\]

Percent excess air (based on air):

$$(\text{O}_2 \text{ in} – \text{O}_2\text{used })/(\text{O}_2\text{used}) = 2 \quad (200\%)$$

O_2 theory (Eq 1) = 3.5*80 = 280

O_2 used (air) = O_2 theory (Eq 1) – 20 = 260 moles

$$(\text{O}_2 \text{ in (air)} – 260)/(260) = 2$$

O_2 in (air) = 260 + (2*260) = 780 moles

N_2 in = 3.76*780 = 2,933.1

Air stream = 4.76*780 = 3,712.8

<table>
<thead>
<tr>
<th>Component</th>
<th>Input Gas Stream</th>
<th>Output (kg-mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_2H_6</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>G_{air}= 4.76*780 = 3,712.8</td>
<td></td>
</tr>
<tr>
<td>O_2</td>
<td>20 + 0.21*G_{air} = 800</td>
<td></td>
</tr>
<tr>
<td>N_2</td>
<td>0.79*G_{air} = 2,933.1</td>
<td></td>
</tr>
<tr>
<td>CO_2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_2O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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$$\text{C}_2\text{H}_6 + \frac{7}{2}\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \quad [1]$$

$$\text{C}_2\text{H}_6 + \frac{5}{2}\text{O}_2 \rightarrow 2\text{CO} + 3\text{H}_2\text{O} \quad [2]$$

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_6$</td>
<td>80</td>
<td>$=80%\text{C}_2\text{H}_6$</td>
<td>10% goes to $\text{CO}$</td>
<td>-</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>800</td>
<td>$=64\times\frac{7}{2}$</td>
<td>$=8\times\frac{5}{2}$</td>
<td>-</td>
<td>-</td>
<td>556</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>2,933.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2,933.1</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>128</td>
<td>-</td>
<td>128</td>
</tr>
<tr>
<td>$\text{CO}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$=3\times64=192$</td>
<td>$=3\times8=24$</td>
<td>216</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>3812.8</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>3,505.1</strong></td>
</tr>
</tbody>
</table>
Given:

- a set of reactive species, and
- reaction conditions

Determine:

1) the final (equilibrium) composition of the reaction mixture.

2) how long the system takes to reach a specified state short of equilibrium.
Irreversible reaction

- reaction proceeds only in a single direction $A \rightarrow B$
- concentration of the limiting reactant eventually approaches zero (time duration can vary widely).

Equilibrium composition of an irreversible reaction is that which corresponds to complete conversion.
**Reversible reaction**
- reaction proceeds in both directions $A \rightleftharpoons B$
- net rate (forward – backward) eventually approaches zero (again, time can vary widely)

Equilibrium composition of a reversible reaction is that which corresponds to the *equilibrium conversion*. 
Equilibrium Composition

- An equilibrium reaction proceeds to an extent at temperature $T$ based on the equilibrium constant, $K(T)$.

$$K(T) = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}}$$

- where $y_i$ is the mole fraction of species $i$

**Example:**

- Water-gas shift reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

- Assume 1 mole CO and 2 mole H$_2$O
- $K(1105 \text{ K}) = 1.00$
Water-gas shift reaction:

\[
CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)
\]

- Assume 1 mole CO and 2 mole H₂O
- \( K(1105 \text{ K}) = 1.00 \)
Equilibrium Composition

- Water-gas shift reaction:

\[ CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \]

- Assume 1 mole CO and 2 mole H\(_2\)O
- \( K(1105 \text{ K}) = 1.00 \)

\[
\begin{align*}
\xi &= 0.667 \text{mol} \\
(\xi)(\xi) &= (1 - \xi)(2 - \xi) \\
K(T) &= \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} \\
y_i &= \frac{n_i}{n_{\text{total}}} \\
n_i &= n_{i0} + v_i \xi \\
\end{align*}
\]
Water-gas shift reaction:

\[ CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \]

- Assume 1 mole CO and 2 mole H\(_2\)O
- \(K(1105 \text{ K}) = 1.00\)

Equilibrium Composition

\[
\begin{align*}
\nu_2 &= 0.333/3 = 0.111 \\
\xi &= 0.333 \\
n_{\text{CO}} &= 1 - \xi = 0.333 \\
n_{\text{H}_2\text{O}} &= 2 - \xi = 1.333 \\
n_{\text{CO}_2} &= \xi = 0.667 \\
n_{\text{H}_2} &= \xi = 0.667 \\
n_{\text{total}} &= 3
\end{align*}
\]

\[
K(T) = \frac{y_{\text{CO}_2} y_{\text{H}_2}}{y_{\text{CO}} y_{\text{H}_2\text{O}}}
\]

\[
y_i = \frac{n_i}{n_{\text{total}}}
\]

\[
n_i = n_{i0} + \nu_i \xi
\]
Water-gas shift reaction:

\[ CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_2(g) + H_2(g) \]

- Assume 1 mole CO and 2 mole H\(_2\)O
- \( K(1105 \text{ K}) = 1.00 \)

**limiting reactant is CO**

\( \gamma_{CO} = 0.333/3 = 0.111 \)
\( \gamma_{H_2O} = 1.333/3 = 0.444 \)
\( \gamma_{CO_2} = 0.667/3 = 0.222 \)
\( \gamma_{H_2} = 0.667/3 = 0.222 \)
\( n_{\text{total}} = 3 \)

At equilibrium, \( \xi = 0.667 \text{ mol} \)

\( n_i = n_{i0} + v_i \xi \)
\( n_{CO} = 1 + (-1)(0.667) = 0.333 \text{ mol} \)

Fractional conversion at equilibrium:

\[ f = \frac{n_{CO} - n_{CO}}{n_{CO}} \]
\[ f = \frac{1.00 - 0.333}{1.00} = 0.667 \]
Multiple Reactions

\[ C_2H_4 + \frac{1}{2} O_2 \rightarrow C_2H_4O \]
\[ C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \]

For \( j \) reactions of \( i \) species, mole balance becomes:

\[ n_i = (n_i)_0 + \sum_j v_{ij} \xi_j \]

\[ n_{C_2H_4} = (n_{C_2H_4})_0 + (-1)\xi_1 + (-1)\xi_2 \]
\[ n_{O_2} = (n_{O_2})_0 + (-\frac{1}{2})\xi_1 + (-3)\xi_2 \]
\[ n_{C_2H_4O} = (n_{C_2H_4O})_0 + (+1)\xi_1 \]
\[ n_{CO_2} = (n_{CO_2})_0 + (+2)\xi_2 \]
\[ n_{H_2O} = (n_{H_2O})_0 + (+2)\xi_2 \]
Multiple Reactions

\[ C_2H_4 + \frac{1}{2} O_2 \rightarrow C_2H_4O \]
\[ C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \]

for \( j \) reactions of \( i \) species, mole balance becomes:

\[ n_i = (n_i)_0 + \sum_j v_{ij}\xi_j \]

\[ \text{yield} = \frac{\text{moles of desired product}}{\text{moles formed at 100\% conversion (with no side reactions)}} \]

\[ \text{selectivity} = \frac{\text{moles of desired product}}{\text{moles of undesired product}} \]
Multiple Reactions

- 100 moles A fed to a batch reactor
- product composition: 10 mol A, 160 B, 10 C

What is:

1. \( f_A \) ?
2. \( Y_B \) ?
3. \( S_{B/C} \) ?
4. \( \xi_1, \xi_2 \)

\[ f_A = \frac{100 - 10}{100} = 0.9 \]

EXAMPLE: Consider the following pair of reactions.
A → 2B (desired)
A → C (undesired)

100 moles of A are fed to a batch reactor and the final product contains 10 mol of A, 160 mol of B and 10 mol of C. Calculate (1) fractional conversion for A \( f_A \) (2) percentage yield of B, (3) the selectivity of B relative to C (4) the extents of the reactions.
EXAMPLE: Consider the following pair of reactions.
\[
A \rightarrow 2B \text{ (desired)} \\
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100 moles of A are fed to a batch reactor and the final product contains 10 mol of A, 160 mol of B and 10 mol of C. Calculate: (1) fractional conversion for A \( f_A \) (2) percentage yield of B, (3) the selectivity of B relative to C (4) the extents of the reactions.

\[Y_B: \]
moles of desired product (B) formed = 160
moles of desired product formed if there were no side reactions and the limiting reactant:

\[
\text{react completely} = 100 \text{ moles } A \times \frac{2 \text{ moles of } B \text{ produced}}{1 \text{ mole of } A \text{ reacted}} = 200 \text{ mol}
\]

\[
Y_B = \frac{160}{200} \times 100 = 80\%
\]
Multiple Reactions

EXAMPLE: Consider the following pair of reactions.

\[ A \rightarrow 2B \text{ (desired)} \]
\[ A \rightarrow C \text{ (undesired)} \]

100 moles of A are fed to a batch reactor and the final product contains 10 mol of A, 160 mol of B and 10 mol of C. Calculate:

1. fractional conversion for A \( f_A \)
2. percentage yield of B
3. the selectivity of B relative to C
4. the extents of the reactions.

\[ S_{B/C} := \]

moles of desired product (B) formed = 160

moles of undesired product (C) formed = 10

\[ S_{B/C} = \frac{160}{10} = 16 \]
Multiple Reactions

EXAMPLE: Consider the following pair of reactions.

\[ A \rightarrow 2B \text{ (desired)} \]
\[ A \rightarrow C \text{ (undesired)} \]

100 moles of A are fed to a batch reactor and the final product contains 10 mol of A, 160 mol of B and 10 mol of C. Calculate: (1) fractional conversion for A \( \xi_A \) (2) percentage yield of B, (3) the selectivity of B relative to C (4) the extents of the reactions.

**Extent of Reactions \((\xi_1, \xi_2)\):**

\[
\begin{align*}
n_B &= n_{B_0} + \nu_{B_1} \xi_1 \\
160 &= 0 + 2 \xi_1 \\
\xi_1 &= 80
\end{align*}
\]

\[
\begin{align*}
n_A &= n_{A_0} + \nu_{A_1} \xi_1 + \nu_{A_2} \xi_2 \\
10 &= 100 - \xi_1 - \xi_2 \\
\xi_2 &= 90 - \xi_1 = 10
\end{align*}
\]
• Continuous, steady-state dehydrogenation of ethane
• Total mass balance still has \textbf{INPUT = OUTPUT} form
• Molecular balances contain consumption/generation
• Atomic balances (H and C) also have simple form

\[ \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]
Continuous, steady-state dehydrogenation of ethane

First consider molecular balances:

**Molecular H₂ balance:** generation = output
\[ \text{generation } H_2 = 40 \text{ kmol } H_2/\text{min} \]

**C₂H₆ balance:** input = output + consumption
\[ 100 \text{ kmol } C_2H_6/\text{min} = n_1 (\text{kmol } C_2H_6/\text{min}) + (\text{C}_2\text{H}_6 \text{ consumed}) \]

**C₂H₄ balance:** generation = output
\[ \text{generated } C_2H_4 = n_2 \]

\[ C_2H_6 \rightarrow C_2H_4 + H_2 \]

100 kmol C₂H₆/min → 40 kmol H₂/min
\[ i_1 (\text{kmol } C_2H_6/\text{min}) \]
\[ i_2 (\text{kmol } C_2H_4/\text{min}) \]
• Continuous, steady-state dehydrogenation of ethane

Atomic C balance:  \( \text{input} = \text{output} \)

\[
100 \text{ mol } C_2H_6 \left( \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right) = \dot{n}_1 \left( \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right) + \dot{n}_2 \left( \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_4} \right)
\]

Atomic H balance:  \( \text{input} = \text{output} \)

\[
100 \text{ mol } C_2H_6 \left( \frac{6 \text{ mol H}}{1 \text{ mol } C_2H_6} \right) = 40 \left( \frac{2 \text{ mol H}}{1 \text{ mol } H_2} \right) + \dot{n}_1 \left( \frac{6 \text{ mol H}}{1 \text{ mol } C_2H_6} \right) + \dot{n}_2 \left( \frac{4 \text{ mol H}}{1 \text{ mol } C_2H_4} \right)
\]

\[C_2H_6 \rightarrow C_2H_4 + H_2\]
Independent Equations

- To understand the number of independent species balances in a reacting system requires an understanding of independent algebraic equations.
- Algebraic equations are independent if you cannot obtain any of them by adding/subtracting multiples of the others.

\[
\begin{align*}
  x + 2y &= 4 \quad [1] \\
  3x + 6y &= 12 \quad [2] \\
  x + 2y &= 4 \quad [3] \\
  2x - z &= 2 \quad [4] \\
  4y + z &= 6 \quad [5]
\end{align*}
\]

\[
\]
Independent Equations

To understand the number of independent species balances in a reacting system requires an understanding of independent algebraic equations.

Algebraic equations are independent if you cannot obtain any of them by adding/subtracting multiples of the others.

\[
\begin{align*}
x + 2y &= 4 \quad [1] \\
3x + 6y &= 12 \quad [2]
\end{align*}
\]
\[
\begin{align*}
3(4 - 2y) + 6y &= 12 \\
(12 - 6y) + 6y &= 12
\end{align*}
\]

\[
12 = 12
\]
Independent Species

- If two molecular or atomic species are in the same ratio to each other wherever they appear in a process and this ratio is incorporated in the flowchart labeling, balances on those species will not be independent equations.

\[ \dot{n}_1 = \dot{n}_3 \]
\[ 3.76\dot{n}_1 = 3.76\dot{n}_3 \]
When using molecular species balances or extents of reaction to analyze a reactive system, the degree of freedom analysis must account for the number of independent chemical reactions among the species entering and leaving the system.
Independent Chemical Reactions

Chemical reactions are independent if the stoichiometric equation of any one of them cannot be obtained by adding and subtracting multiples of the stoichiometric equations of the others.

\[ A \rightarrow 2B \ \ [1] \]
\[ B \rightarrow C \ \ [2] \]
\[ A \rightarrow 2C \ \ [3] \quad 2 \times [2] + [1] = [3] \]
Solving Reactive Systems

There are 3 possible methods for solving balances around a reactive system:

1. Molecular species balances require more complex calculations than the other methods and should be used only for simple (single reaction) systems.
2. Atomic species balances generally lead to the most straightforward solution procedure, especially when more than one reaction is involved.
3. Extents of reaction are convenient for chemical equilibrium problems.
To use molecular species balances to analyze a reactive system, the balances must contain generation and/or consumption terms.

The degree-of-freedom analysis is as follows:

- # unknown labeled variables
- + # independent chemical reactions
- - # independent molecular species balances
- - # other equations relating unknown variables

# of degrees of freedom
Example:

\[ \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]

2 unknown labeled variables
+ 1 independent chemical reactions
- 3 independent molecular species balances
- 0 other equations relating unknown variables
0 degrees of freedom
Molecular Species Balances

At steady state

H₂ Balance: generation = output

\[
\text{gen}_{\text{H}_2} = 40 \text{ kmol H}_2
\]

C₂H₆ Balance: input = output + consumption

\[
100 \text{ kmol C}_2\text{H}_6/\text{min} = \dot{n}_1 \frac{\text{kmol C}_2\text{H}_6}{\text{min}} + \left(40 \frac{\text{kmol H}_2}{\text{min}}\right) \left(1 \frac{\text{kmol C}_2\text{H}_6}{1 \text{kmol H}_2}\right)
\]

\[
\dot{n}_1 = 60
\]

C₂H₄ Balance: generation = output

\[
\dot{n}_2 = \left(40 \frac{\text{kmol H}_2}{\text{min}}\right) \left(1 \frac{\text{kmol C}_2\text{H}_4}{1 \text{kmol H}_2}\right)
\]

\[
\dot{n}_2 = 40 \frac{\text{kmol C}_2\text{H}_4}{\text{min}}
\]
All atomic species balances take the form:

\[
\text{INPUT} = \text{OUTPUT}
\]

Degree-of-freedom analysis, \( n_{df} = \)

- # unknown labeled variables
- # independent atomic species balances
- # molecular balances on independent nonreactive species
- # other equations relating unknown variables
• All atomic species balances take the form

\[ \text{INPUT} = \text{OUTPUT} \]

• Degree-of-freedom analysis, \( n_{df} = 0 = 2 \) unknown labeled variables
  - 2 independent atomic species balances
  - 0 molecular balances on independent nonreactive species
  - 0 other equations relating unknown variables
Atomic Species Balances

\[ C_2H_6 \rightarrow C_2H_4 + H_2 \]

**C Balance:** input = output

\[
100 \left( \frac{k\text{mol}C_2H_6}{\text{min}} \right) \left( \frac{2\text{kmolC}}{1\text{kmol}C_2H_6} \right) = \dot{n}_1 \left( \frac{k\text{mol}C_2H_6}{\text{min}} \right) \left( \frac{2\text{kmolC}}{1\text{kmol}C_2H_6} \right) + \dot{n}_2 \left( \frac{k\text{mol}C_2H_4}{\text{min}} \right) \left( \frac{2\text{kmolC}}{1\text{kmol}C_2H_4} \right)
\]

\[ 100 \text{ kmol} = \dot{n}_1 + \dot{n}_2 \]

**H Balance:** input = output

\[
100 \left( \frac{k\text{mol}C_2H_6}{\text{min}} \right) \left( \frac{6\text{kmolH}}{1\text{kmol}C_2H_6} \right) = 40 \left( \frac{k\text{mol}H_2}{\text{min}} \right) \left( \frac{2\text{kmolH}}{1\text{kmol}H_2} \right) + \dot{n}_1 \left( \frac{k\text{mol}C_2H_6}{\text{min}} \right) \left( \frac{6\text{kmolH}}{1\text{kmol}C_2H_6} \right)
\]

\[ + \dot{n}_2 \left( \frac{k\text{mol}C_2H_4}{\text{min}} \right) \left( \frac{4\text{kmolH}}{1\text{kmol}C_2H_4} \right) \]

\[ 600 \text{ kmol} = 80 \text{ kmol} + 6\dot{n}_1 + 4\dot{n}_2 \]
Solve simultaneously

C: 100 kmol = \( \dot{n}_1 + \dot{n}_2 \)

H: 600 kmol = 80 kmol + 6\( \dot{n}_1 \) + 4\( \dot{n}_2 \)

\( \dot{n}_1 = 60 \text{ kmol } C_2H_6/\text{min} \)

\( \dot{n}_2 = 40 \text{ kmol } C_2H_4/\text{min} \)
The 3\textsuperscript{rd} method by which to determine molar flows in a reactive system is using expressions for each species flow rate in terms of extents of reaction ($\xi$).

\[ n_i = (n_i)_0 + \sum_j v_{ij} \xi_j \]

Degree-of-freedom analysis for such an approach:

\[ n_{df} = \# \text{ of unknown labeled variables} \]
\[ + \# \text{ independent reactions} \]
\[ - \# \text{ independent nonreactive species} \]
\[ - \# \text{ other relationships or specifications} \]
Incomplete Combustion of CH$_4$

Example

Methane is burned with air in a continuous steady-state reactor to yield a mixture of carbon monoxide, carbon dioxide, and water.

\[
\begin{align*}
\text{CH}_4 + \frac{3}{2} \text{O}_2 & \rightarrow \text{CO} + 2 \text{ H}_2 \text{O} \\
\text{CH}_4 + 2 \text{ O}_2 & \rightarrow \text{CO}_2 + 2 \text{ H}_2 \text{O}
\end{align*}
\]

The feed to the reactor contains 7.80 mol% CH$_4$, 19.4 mol% O$_2$, 72.8 mol% N$_2$. Methane undergoes 90.0% conversion, and the effluent gas contains 8 mol CO$_2$ per mole CO.
\[ \text{CH}_4 + \frac{3}{2} \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2\text{O} \]
\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]

\[ f_{\text{CH}_4} = 0.9 \]

\[ \begin{align*}
100 \text{ mol} & \quad 0.0780 \text{ mol CH}_4/\text{mol} \\
0.194 \text{ mol O}_2/\text{mol} & \quad 0.728 \text{ mol N}_2/\text{mol} \\
\end{align*} \]

The feed to the reactor contains 7.80 mol% CH\(_4\), 19.4 mol% O\(_2\), 72.8 mol% N\(_2\). Methane undergoes 90.0% conversion, and the effluent gas contains 8 mol CO\(_2\) per mole CO.

\[ n_{\text{df}} = 5 \text{ unknowns} + 2 \text{ independent reactions} \]
- 5 expressions for \( \xi \) (CH\(_4\), O\(_2\), CO, CO\(_2\), H\(_2\)O)
- 1 nonreactive species balance (N\(_2\))
- 1 specified methane conversion

\[ = 0 \]
\[
\begin{align*}
\text{CH}_4 + \frac{3}{2}\text{O}_2 &\rightarrow \text{CO} + 2\text{H}_2\text{O} \\
\text{CH}_4 + 2\text{O}_2 &\rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

\[f_{\text{CH}_4} = 0.9\]

\[n_{\text{CH}_4} = \frac{0.780}{\text{mol CH}_4/\text{mol}} \times (100 \text{ mol}) = 78.0 \text{ mol CH}_4\]

\[n_{\text{O}_2} = (0.194)(100 \text{ mol}) = 19.4 \text{ mol O}_2\]
\[ \text{CH}_4 + \frac{3}{2} \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2\text{O} \]
\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \]

**Extent of reaction mole balances:**

\[
\begin{align*}
n_{\text{CH}_4} &= (n_{\text{CH}_4})_0 + (-1)\xi_1 + (-1)\xi_2 \\
n_{\text{CO}} &= (n_{\text{CO}})_0 + (+1)\xi_1 \\
n_{\text{CO}_2} &= (n_{\text{CO}_2})_0 + (+1)\xi_2 \\
n_{\text{H}_2\text{O}} &= (n_{\text{H}_2\text{O}})_0 + (+2)\xi_1 + (+2)\xi_2 \\
n_{\text{O}_2} &= (n_{\text{O}_2})_0 + (-\frac{3}{2})\xi_1 + (-2)\xi_2 \\
0.78 &= 7.80 - \xi_1 - \xi_2 \\
n_{\text{CO}} &= \xi_1 \\
n_{\text{CO}_2} &= 8n_{\text{CO}} = \xi_2 \\
n_{\text{H}_2\text{O}} &= 2\xi_1 + 2\xi_2 \\
n_{\text{O}_2} &= 19.4 - \frac{3}{2} \xi_1 - 2\xi_2
\end{align*}
\]

The feed to the reactor contains 7.80 mol% CH\(_4\), 19.4 mol% O\(_2\), 72.8 mol% N\(_2\). Methane undergoes 90.0\% conversion, and the effluent gas contains 8 mol CO\(_2\) per mole CO.
Two definitions of **reactant conversion** are used in the analysis of chemical reactors with product separation and recycle of unconsumed reactants.

\[
\text{overall conversion} = \text{reactant} \left( \frac{\text{input to process} - \text{output from process}}{\text{input to process}} \right)
\]

\[
\text{single pass conversion} = \text{reactant} \left( \frac{\text{input to reactor} - \text{output from reactor}}{\text{input to reactor}} \right)
\]
Overall conversion = \left( \frac{75 \text{ mol A/min} - 0}{75 \text{ mol A/min}} \right) \times 100\% = 100\%

Single pass conversion = \left( \frac{100 \text{ mol A/min} - 25 \text{ mol A/min}}{100 \text{ mol A/min}} \right) \times 100\% = 75\%
Catalytic Propane Dehydrogenation

95% overall conversion

Fresh feed
100 mol C\textsubscript{3}H\textsubscript{8}

\begin{align*}
n_1 & (\text{mol C}_3\text{H}_8) \\
n_2 & (\text{mol C}_3\text{H}_6)
\end{align*}

\text{REACTOR}

\begin{align*}
n_3 & (\text{mol C}_3\text{H}_8) \\
n_4 & (\text{mol C}_3\text{H}_6) \\
n_5 & (\text{mol H}_2)
\end{align*}

\text{SEPARATOR}

\begin{align*}
n_6 & (\text{mol C}_3\text{H}_8) \ (0.555\% \ of \ n_3) \\
n_7 & (\text{mol C}_3\text{H}_6) \\
n_8 & (\text{mol H}_2)
\end{align*}

\text{Product}

\text{Recycle}

\begin{align*}
n_9 & (\text{mol C}_3\text{H}_8) \\
n_10 & (\text{mol C}_3\text{H}_6) \ (5\% \ of \ n_7)
\end{align*}

\[
C_3H_8 \rightarrow C_3H_6 + H_2
\]
95% overall conversion

Catalytic Propane Dehydrogenation

Overall Process

Fresh feed 100 mol C\textsubscript{3}H\textsubscript{8} → C\textsubscript{3}H\textsubscript{6} + H\textsubscript{2}

C\textsubscript{3}H\textsubscript{8} → C\textsubscript{3}H\textsubscript{6} + H\textsubscript{2}

Recycle

\begin{align*}
n_1 (\text{mol C}_3\text{H}_8) \\
n_2 (\text{mol C}_3\text{H}_6)
\end{align*}

\begin{align*}
n_3 (\text{mol C}_3\text{H}_8) \\
n_4 (\text{mol C}_3\text{H}_6) \\
n_5 (\text{mol H}_2)
\end{align*}

\begin{align*}
n_6 (\text{mol C}_3\text{H}_8) \text{ (0.555\% of } n_3) \\
n_7 (\text{mol C}_3\text{H}_6) \\
n_8 (\text{mol H}_2)
\end{align*}

\begin{align*}
n_9 (\text{mol C}_3\text{H}_8) \\
n_{10} (\text{mol C}_3\text{H}_6) \text{ (5\% of } n_7)
\end{align*}

\text{n}_{\text{df}} = 3 \text{ unknowns (n}_6, n_7, n_8) \\
\quad \text{ 2 independent atomic balances (C and H)} \\
\quad \text{ 1 relation (overall conversion)} \\
\quad = 0

Consider n\textsubscript{6}, n\textsubscript{7}, n\textsubscript{8} known for further DOF analyses
Catalytic Propane Dehydrogenation

95% overall conversion

\[ \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2 \]

Mixing point

\[ n_{df} = 4 \text{ unknowns (} n_9, n_{10}, n_1, n_2) \]

\[ = 2 \text{ balances (C}_3\text{H}_8 \text{ and C}_3\text{H}_6) \]

\[ = 2 \]
95% overall conversion

\[ \text{n}_{\text{df}} = 5 \text{ unknowns (n}_3, \text{n}_4, \text{n}_5, \text{n}_1, \text{n}_2) \]
- 2 balances (C and H)

\[ = 3 \]
\[ n_{\text{df}} = 5 \text{ unknowns (} n_3, n_4, n_5, n_9, n_{10} \) }

- 3 balances (\( \text{C}_3\text{H}_8, \text{C}_3\text{H}_6, \text{and H}_2 \))
- 2 relations (reactant and product recovery fractions)

\[ = 0 \]
$n_6 = (1 - 0.95)(100 \text{ mol}) = 5 \text{ mol } C_3H_8$

95% overall conversion

Overall conversion relationship

Fresh feed
100 mol $C_3H_8$

$C_3H_8 \rightarrow C_3H_6 + H_2$

$C_3H_8 \rightarrow C_3H_6 + H_2$

Recycle

$n_1 (\text{mol } C_3H_8)$
$n_2 (\text{mol } C_3H_6)$
$n_3 (\text{mol } C_3H_8)$
$n_4 (\text{mol } C_3H_6)$
$n_5 (\text{mol } H_2)$

$REACTOR$

$SEP\text{ARATOR}$

Product

$n_6 (\text{mol } C_3H_8) \ (0.555\% \text{ of } n_3)$
$n_7 (\text{mol } C_3H_6)$
$n_8 (\text{mol } H_2)$
95% overall conversion

\[ C_3H_8 \rightarrow C_3H_6 + H_2 \]

overall C atomic balance

\[
(100 \text{ mol } C_3H_8) \left( \frac{3 \text{ mol } C}{1 \text{ mol } C_3H_8} \right) = (5 \text{ mol } C_3H_8) \left( \frac{3 \text{ mol } C}{1 \text{ mol } C_3H_8} \right) + n_7 \text{ mol } C_3H_8 \left( \frac{3 \text{ mol } C}{1 \text{ mol } C_3H_6} \right)
\]

\[ n_7 = 95 \text{ mol } C_3H_6 \]
95% overall conversion

\[ (100 \text{ mol } C_3H_8) \left( \frac{8 \text{ mol H}}{1 \text{ mol } C_3H_8} \right) = (5 \text{ mol } C_3H_8) \left( \frac{8 \text{ mol H}}{1 \text{ mol } C_3H_8} \right) \]
\[ + (95 \text{ mol } C_3H_6) \left( \frac{6 \text{ mol H}}{1 \text{ mol } C_3H_6} \right) + n_8 \text{ mol } H_2 \left( \frac{2 \text{ mol H}}{1 \text{ mol } H_2} \right) \]
\[ n_8 = 95 \text{ mol } H_2 \]
Given Relations

\[ n_6 = (0.00555)n_3 \rightarrow n_3 = 900 \text{ mol} \text{C}_3\text{H}_8 \]
\[ n_{10} = (0.0500)n_7 \rightarrow n_{10} = 4.75 \text{ mol} \text{C}_3\text{H}_6 \]
95% overall conversion

Fresh feed
100 mol C₃H₈

n₁ (mol C₃H₈)
n₂ (mol C₃H₆)

C₃H₈ → C₃H₆ + H₂

Recycle

n₉ (mol C₃H₈)

n₁₀ = 4.75 mol C₃H₆

n₃ = n₆ + n₉ → n₉ = 895 mol C₃H₈

Separator

Propane balance

Product
n₆ = 5 mol C₃H₈ (0.555% of n₃)
n₇ = 95 mol C₃H₆
n₈ = 95 mol H₂

Propane balance

n₃ = n₆ + n₉ → n₉ = 895 mol C₃H₈
\[ \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2 \]

**Propane balance**

\[ 100 + n_9 = n_1 \rightarrow n_1 = 995 \text{ mol C}_3\text{H}_8 \]

**95\% overall conversion**
\[ C_3H_8 \rightarrow C_3H_6 + H_2 \]

**Mixer**

**propylene balance**

\[ n_{10} = n_2 \rightarrow n_2 = 4.75 \text{ mol C}_3\text{H}_6 \]

**95% overall conversion**

- Fresh feed: 100 mol C\textnormal{\textsubscript{3}}\textnormal{H\textsubscript{8}}
- Reactor:
  - \( n_1 = 995 \text{ mol C}_3\text{H}_8 \)
  - \( n_2 = \text{mol C}_3\text{H}_6 \)
  - \( n_3 = 900 \text{ mol C}_3\text{H}_8 \)
  - \( n_4 = \text{mol C}_3\text{H}_6 \)
  - \( n_5 = \text{mol H}_2 \)
- Separator:
  - \( n_6 = 5 \text{ mol C}_3\text{H}_8 \)
  - \( n_7 = 95 \text{ mol C}_3\text{H}_6 \)
  - \( n_8 = 95 \text{ mol H}_2 \)
- Product:
  - \( n_9 = 895 \text{ mol C}_3\text{H}_8 \)
  - \( n_{10} = 4.75 \text{ mol C}_3\text{H}_6 \)
C\textsubscript{3}H\textsubscript{8} → C\textsubscript{3}H\textsubscript{6} + H\textsubscript{2}

\[
\begin{align*}
(995 \text{ mol C}_3\text{H}_8) & \times \left(\frac{3 \text{ mol C}}{1 \text{ mol C}_3\text{H}_8}\right) + (4.75 \text{ mol C}_3\text{H}_6) \times \left(\frac{3 \text{ mol C}}{1 \text{ mol C}_3\text{H}_6}\right) \\
& = (900 \text{ mol C}_3\text{H}_8) \times \left(\frac{3 \text{ mol C}}{1 \text{ mol C}_3\text{H}_8}\right) + (n_4) \times \left(\frac{3 \text{ mol C}}{1 \text{ mol C}_3\text{H}_6}\right) \\
n_4 & = 99.75 \text{ mol C}_3\text{H}_6
\end{align*}
\]
\[(995 \text{ mol } \text{C}_3\text{H}_8) \left( \frac{8 \text{ molH}}{1 \text{ molC}_3\text{H}_8} \right) + (4.75 \text{ mol } \text{C}_3\text{H}_6) \left( \frac{6 \text{ molH}}{1 \text{ molC}_3\text{H}_6} \right) \]

\[= (900 \text{ mol } \text{C}_3\text{H}_8) \left( \frac{8 \text{ molH}}{1 \text{ molC}_3\text{H}_8} \right) + (99.75 \text{ mol } \text{C}_3\text{H}_6) \left( \frac{6 \text{ molH}}{1 \text{ molC}_3\text{H}_6} \right) + n_5 \left( \frac{2 \text{ molH}}{1 \text{ molH}_2} \right) \]

\[n_5 = 95 \text{ mol } \text{H}_2\]
$C_3H_8 \rightarrow C_3H_6 + H_2$

$\text{Fresh feed} \ 100 \text{ mol } C_3H_8$

$n_1 = 995 \text{ mol } C_3H_8$
$n_2 = 4.75 \text{ mol } C_3H_6$

$n_3 = 900 \text{ mol } C_3H_8$
$n_4 = 99.75 \text{ mol } C_3H_6$
$n_5 = 95 \text{ mol } H_2$

$n_9 = 895 \text{ mol } C_3H_8$
$n_{10} = 4.75 \text{ mol } C_3H_6$

$\text{Product}$
$n_6 = 5 \text{ mol } C_3H_8 \ (0.555\% \text{ of } n_3)$
$n_7 = 95 \text{ mol } C_3H_6$
$n_8 = 95 \text{ mol } H_2$

$\text{Overall conversion} = 95\%$

$\text{Single-pass conversion}$

$f_{\text{single-pass}} = \frac{(995 \text{ mol } C_3H_8) - (900 \text{ mol } C_3H_8)}{995 \text{ mol } C_3H_8} \times 100\% = 9.55\%$
\[
R = \frac{n_9 + n_{10}}{\text{100 mol fresh feed}} = \frac{(895 \text{ mol}) + (4.75 \text{ mol})}{\text{100 mol}} = 9.0 \frac{\text{mol recycle}}{\text{mol fresh feed}}
\]

95% overall conversion

\[
C_3H_8 \rightarrow C_3H_6 + H_2
\]

\[
n_1 = 995 \text{ mol } C_3H_8 \quad n_4 = 99.75 \text{ mol } C_3H_6 \\
n_2 = 4.75 \text{ mol } C_3H_6 \quad n_5 = 95 \text{ mol } H_2 \\
n_3 = 900 \text{ mol } C_3H_8 \\
n_6 = 5 \text{ mol } C_3H_8 \quad (0.555\% \text{ of } n_3) \\
n_7 = 95 \text{ mol } C_3H_6 \\
n_8 = 95 \text{ mol } H_2
\]

Recycle ratio

\[
f_{\text{single-pass}} = 9.55\%
\]
Purging

 Necessary with recycle to prevent accumulation of a species that is both present in the fresh feed and is recycled rather than separated with the product.

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

mixed fresh feed and recycle is a convenient basis selection

\begin{align*}
 n_0 &= 100 \text{ mol} \\
 x_{OC} &= (0.996 - x_{OC}) (\text{mol} \, \text{H}_2/\text{mol}) \\
 0.00400 \text{ mol l/mol}
\end{align*}

\begin{align*}
 n_1 &= \text{mol CO}_2 \\
 n_2 &= \text{mol H}_2 \\
 n_3 &= 2.0 \text{ mol l} \\
 n_4 &= \text{mol CH}_3\text{OH} \\
 n_5 &= \text{mol H}_2\text{O}
\end{align*}
Methanol Synthesis

- \( n_{df} = 7 \) unknowns \((n_0, x_{0C}, n_p, x_{5C}, x_{5H}, n_3, n_4) + 1 \) rxn
- 5 independent species balances = 3
\( n_{df} = 4 \) unknowns \((n_1, n_2, n_3, n_4) + 1\) rxn

– 4 independent species balances
– 1 single pass conversion = 0

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

\( f_{\text{single-pass}} = 60\% \)
\( n_{df} = 3 \) unknowns \((n_5, x_{5C}, x_{5H})\)

- 3 independent species balances
  \[ = 0 \]

\[ \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \]

\[ f_{\text{single-pass}} = 60\% \]

\[ n_0 \text{(mol)} \]

\[ n_{10} \text{(mol CO}_2\text{/mol)} \]

\[ 0.280 \text{ mol CO}_2\text{/mol} \]

\[ 0.700 \text{ mol H}_2\text{/mol} \]

\[ 0.020 \text{ mol l/mol} \]

\[ n_{1\text{mol CO}} \]

\[ x_{5C} \text{(mol CO}_2\text{/mol)} \]

\[ x_{5H} \text{(mol H}_2\text{/mol)} \]

\[ (1 - x_{5C} - x_{5H}) \text{(mol l/mol)} \]

\[ n_1 \text{(mol CO}_2\text{)} \]

\[ n_2 \text{(mol H}_2\text{)} \]

\[ 2.0 \text{ mol l} \]

\[ n_3 \text{(mol CH}_3\text{OH)} \]

\[ n_4 \text{(mol H}_2\text{O)} \]

\[ n_5 \text{(mol CO}_2\text{)} \]

\[ x_{5C} \text{(mol CO}_2\text{/mol)} \]

\[ x_{5H} \text{(mol H}_2\text{/mol)} \]

\[ (1 - x_{5C} - x_{5H}) \text{(mol l/mol)} \]

\[ n_5 \text{(mol)} \]

\[ n_6 \text{(mol CO}_2\text{)} \]

\[ x_{5C} \text{(mol CO}_2\text{/mol)} \]

\[ x_{5H} \text{(mol H}_2\text{/mol)} \]

\[ (1 - x_{5C} - x_{5H}) \text{(mol l/mol)} \]

\[ n_6 \text{(mol)} \]

\[ n_{7\text{mol CO}} \]

\[ n_7 \text{(mol CO}_2\text{)} \]

\[ x_{5C} \text{(mol CO}_2\text{/mol)} \]

\[ x_{5H} \text{(mol H}_2\text{/mol)} \]

\[ (1 - x_{5C} - x_{5H}) \text{(mol l/mol)} \]

\[ n_7 \text{(mol)} \]

\[ n_{8\text{mol CO}} \]

\[ n_8 \text{(mol CO}_2\text{)} \]

\[ x_{5C} \text{(mol CO}_2\text{/mol)} \]

\[ x_{5H} \text{(mol H}_2\text{/mol)} \]

\[ (1 - x_{5C} - x_{5H}) \text{(mol l/mol)} \]

\[ n_8 \text{(mol)} \]

\[ n_{9\text{mol CO}} \]

\[ n_9 \text{(mol CO}_2\text{)} \]

\[ x_{5C} \text{(mol CO}_2\text{/mol)} \]

\[ x_{5H} \text{(mol H}_2\text{/mol)} \]

\[ (1 - x_{5C} - x_{5H}) \text{(mol l/mol)} \]

\[ n_9 \text{(mol)} \]

\[ n_{10\text{mol CO}} \]

\[ n_{10} \text{(mol CO}_2\text{)} \]

\[ x_{5C} \text{(mol CO}_2\text{/mol)} \]

\[ x_{5H} \text{(mol H}_2\text{/mol)} \]

\[ (1 - x_{5C} - x_{5H}) \text{(mol l/mol)} \]

\[ n_{10} \text{(mol)} \]
\[ n_{df} = 3 \text{ unknowns (} n_0, x_{0C}, n_r \text{)} \\
- 3 \text{ independent species balances} = 0 \]
\( n_{df} = 1 \) unknowns \( (n_p) \)

- 1 independent species balance

\( = 0 \)

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]

\[f_{\text{single-pass}} = 60\%\]

\( n_{p}(\text{mol}) \)

\( n_{i}(\text{mol}) \)

\( x_{5c}(\text{mol CO}_2/\text{mol}) \)

\( x_{5h}(\text{mol H}_2/\text{mol}) \)

\( (1 - x_{5c} - x_{5h}) \) (mol l/mol)

\( n_0(\text{mol}) \)

\( n_1(\text{mol CO}_2) \)

\( n_2(\text{mol H}_2) \)

\( n_3(\text{mol CH}_3\text{OH}) \)

\( n_4(\text{mol H}_2\text{O}) \)

\( n_{0c}(\text{mol CO}_2/\text{mol}) \)

\( x_{0c}(\text{mol CO}_2/\text{mol}) \) (mol l/mol)

\( 0.996 - x_{0c} \) (mol H\(_2\)/mol)

\( 0.00400 \) mol l/mol

\( 100 \) mol

\( 0.280 \) mol CO\(_2\)/mol

\( 0.700 \) mol H\(_2\)/mol

\( 0.020 \) mol l/mol

\( n_{5}(\text{mol}) \)

\( x_{5c}(\text{mol CO}_2/\text{mol}) \)

\( x_{5h}(\text{mol H}_2/\text{mol}) \)

\( (1 - x_{5c} - x_{5h}) \) (mol l/mol)

\( n_{3}(\text{mol CH}_3\text{OH}) \)

\( n_{4}(\text{mol H}_2\text{O}) \)
Combustion Reactions

- **Combustion** - rapid reaction of a fuel with oxygen.

- Valuable class of reactions due to the tremendous amount of heat liberated, subsequently used to produce steam used to drive turbines which generates most of the world’s electrical power.

- **Common fuels used in power plants:**
  - Coal
  - **Fuel oil (high MW hydrocarbons)**
  - Gaseous fuel (natural gas)
  - **Liquified petroleum gas (propane and/or butane)**
Combustion Chemistry

- When a fuel is burned
  - C forms CO$_2$ (complete) or CO (partial combustion)
  - H forms H$_2$O
  - S forms SO$_2$
  - N forms NO$_2$ (above 1800°C)

- Air is used as the source of oxygen. **DRY** air analysis:
  - 78.03 mol% N$_2$
  - 20.99 mol% O$_2$
  - 0.94 mol% Ar
  - 0.03 mol% CO$_2$
  - 0.01 mol% H$_2$, He, Ne, Kr, Xe

Usually safe to assume:
- 79 mol% N$_2$
- 21 mol% O$_2$
- Stack (flue) gas – product gas that leaves a furnace.

**Composition analysis:**
- wet basis – water is included in mole fractions
- dry basis – does not include water in mole fractions

**Stack gas contains (mol) on a wet basis:**
- 60.0% N$_2$, 15.0% CO$_2$, 10.0% O$_2$, 15.0% H$_2$O

**Dry basis analysis:**
- $\frac{60}{60+15+10} = 0.706$ mol N$_2$/mol
- $\frac{15}{60+15+10} = 0.176$ mol CO$_2$/mol
- $\frac{10}{60+15+10} = 0.118$ mol O$_2$/mol
Stack gas contains (mol) on a dry basis:

- 65% N₂, 14% CO₂, 10% O₂, 11% CO
- Assume 100 mole dry gas basis

- 7.53 mole H₂O
- 65 mole N₂
- 14 mole CO₂
- 10 mole O₂
- 11 mole CO

**total = 107.5 mole**

\[
x_{\text{H}_2\text{O}} = \frac{7.53}{107.5} = 0.0700 \\
x_{\text{N}_2} = \frac{65}{107.5} = 0.605 \\
x_{\text{CO}_2} = \frac{14}{107.5} = 0.130 \\
x_{\text{O}_2} = \frac{10}{107.5} = 0.0930 \\
x_{\text{CO}} = \frac{11}{107.5} = 0.102
\]
The less expensive reactant is commonly fed in excess of stoichiometric ratio relative to the more valuable reactant, thereby increasing conversion of the more expensive reactant at the expense of increased use of excess reactant.

In a combustion reaction, the less expensive reactant is oxygen, obtained from the air. Consequently, air is fed in excess to the fuel.

Theoretical oxygen is the exact amount of $O_2$ needed to completely combust the fuel to $CO_2$ and $H_2O$.

Theoretical air is that amount of air that contains the amount of theoretical oxygen.
**Excess air** is the amount by which the air fed to the reactor exceeds the theoretical air.

\[
\% \text{ excess air} = \frac{\text{moles air fed} - \text{moles air theoretical}}{\text{moles air theoretical}} \times 100\%
\]
Theoretical and Excess Air

\[ \text{C}_4\text{H}_{10} + \frac{13}{2} \text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O} \]

\[ n_{\text{C}_4\text{H}_{10}} = 100 \text{ mol/hr}; \quad n_{\text{air}} = 5000 \text{ mol/hr} \]

\[ (n_{\text{O}_2})_{\text{theoretical}} = \left( \frac{100 \text{ mol C}_4\text{H}_{10}}{\text{hr}} \right) \left( \frac{6.5 \text{ mol O}_2}{1 \text{ mol C}_4\text{H}_{10}} \right) = 650 \frac{\text{mol O}_2}{\text{hr}} \]

\[ (n_{\text{air}})_{\text{theoretical}} = \left( \frac{650 \text{ mol O}_2}{\text{hr}} \right) \left( \frac{4.76 \text{ mol air}}{1 \text{ mol O}_2} \right) = 3094 \frac{\text{mol air}}{\text{hr}} \]

\[ \% \text{ excess air} = \frac{5000 - 3094}{3094} \times 100\% = 61.6\% \]
Combustion Reactors

- Procedure for writing/solving material balances for a combustion reactor

1. When you draw and label the flowchart, be sure the outlet stream (the stack gas) includes:
   a. unreacted fuel (unless the fuel is completely consumed).
   b. unreacted oxygen.
   c. water and carbon dioxide (and CO if combustion is incomplete).
   d. nitrogen (if air is used as the oxygen source).

2. Calculate the $O_2$ feed rate from the specified percent excess oxygen or air.

3. If multiple reactions, use atomic balances.
Example

Ethane is burned with 50% excess air. The percentage conversion of the ethane is 90% of the Ethane burned, 25% reacts to form CO and the balance reacts to form CO₂. Calculate the molar composition of the stack gas on a dry basis and the mole ratio of water to dry stack gas.

\[
\begin{align*}
C_2H_6 + \frac{7}{2}O_2 & \rightarrow 2CO_2 + 3H_2O \\
C_2H_6 + \frac{5}{2}O_2 & \rightarrow 2CO + 3H_2O
\end{align*}
\]
Combustion of Ethane

\[ C_2H_6 + \frac{7}{2} O_2 \rightarrow 2CO_2 + 3H_2O \]

\[ C_2H_6 + \frac{5}{2} O_2 \rightarrow 2CO + 3H_2O \]

Degree-Of-Freedom analysis:

- 7 unknowns
- 3 atomic balances
- 1 nitrogen balance
- 1 excess air specification
- 1 ethane conversion specification
- 1 CO/CO_2 ratio specification

\[ n_{df} = 0 \]

25% of the ethane burned forms CO
**Excess air specification**

\[ C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O \]
\[ C_2H_6 + \frac{5}{2}O_2 \rightarrow 2CO + 3H_2O \]

\[ f_{C_2H_6} = 0.9 \]

- \( n_0(\text{mol}) \)
  - 0.21 mol O\(_2\)/mol
  - 0.79 mol N\(_2\)/mol

- 50% excess air

\( (n_{O_2})_{\text{theoretical}} = \left( \frac{100 \text{ mol } C_2H_6}{\text{mol } C_2H_6} \right) \left( \frac{3.5 \text{ mol } O_2}{\text{mol } C_2H_6} \right) = 350 \text{ mol } O_2 \)

- 0.21\(n_0 = 1.5(350\text{ mol } O_2) \)

\( n_0 = 2500 \text{ mol air} \)

25% of the ethane burned forms CO

**Ethane conversion specification**

\( n_1 = (1 - 0.90)(100\text{ mol } C_2H_6) = 10.0\text{ mol } C_2H_6 \)
**CO/CO₂ ratio specification**

\[ C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O \]

\[ C_2H_6 + \frac{5}{2}O_2 \rightarrow 2CO + 3H_2O \]

\[ n_1 = 10.0 \text{ mol } C_2H_6 \]

\[ n_2(\text{mol } O_2) \]

\[ n_3(\text{mol } N_2) \]

\[ n_4(\text{mol } CO) \]

\[ n_5(\text{mol } CO_2) \]

\[ n_6(\text{mol } H_2O) \]

50% excess air

\[ n_0(\text{mol}) \]

\[ 0.21 \text{ mol } O_2/\text{mol} \]

\[ 0.79 \text{ mol } N_2/\text{mol} \]

25% of the ethane burned forms CO

\[ n_4 = (0.25)(0.9)(100\text{mol } C_2H_6) \left( \frac{2\text{mol CO gen}}{1\text{mol } C_2H_6 \text{ react}} \right) = 45.0 \text{ mol CO} \]

\[ n_3 = (0.79)(2500 \text{ mol air}) = 1975 \text{ mol } N_2 \]

**Nitrogen balance**

**Atomic C balance**

\[ (100 \text{ mol } C_2H_6) \left( \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right) = n_1 \left( \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right) + n_4 \left( \frac{1 \text{ mol C}}{1 \text{ mol } CO} \right) + n_5 \left( \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} \right) \]

\[ (100 \text{ mol } C_2H_6) \left( \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right) = 100 \left( \frac{2 \text{ mol C}}{1 \text{ mol } C_2H_6} \right) + 45 \left( \frac{1 \text{ mol C}}{1 \text{ mol } CO} \right) + n_5 \left( \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} \right) \]

\[ n_5 = 135 \text{ mol } CO_2 \]
\[ C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O \]
\[ C_2H_6 + \frac{5}{2}O_2 \rightarrow 2CO + 3H_2O \]

\[ f_{C_2H_6} = 0.9 \]

\[ n_1 = 10.0 \text{ mol } C_2H_6 \]
\[ n_2 = 1975 \text{ mol } N_2 \]
\[ n_3 = 45.0 \text{ mol } CO \]
\[ n_4 = 135 \text{ mol } CO_2 \]

**atomic H balance**

\[
(100 \text{ mol } C_2H_6) \left( \frac{6 \text{ mol } H}{1 \text{ mol } C_2H_6} \right) = (n_1 \text{ mol } C_2H_6) \left( \frac{6 \text{ mol } H}{1 \text{ mol } C_2H_6} \right) + n_6 \left( \frac{2 \text{ mol } H}{1 \text{ mol } H_2O} \right)
\]

\[
(100 \text{ mol } C_2H_6) \left( \frac{6 \text{ mol } H}{1 \text{ mol } C_2H_6} \right) = (10 \text{ mol } C_2H_6) \left( \frac{6 \text{ mol } H}{1 \text{ mol } C_2H_6} \right) + n_6 \left( \frac{2 \text{ mol } H}{1 \text{ mol } H_2O} \right)
\]

\[ n_6 = 270 \text{ mol } H_2O \]
C₂H₆ + \( \frac{7}{2} \) O₂ → 2CO₂ + 3H₂O
C₂H₆ + \( \frac{5}{2} \) O₂ → 2CO + 3H₂O

100 mol C₂H₆

50% excess air

\( n_0 = 2500 \) mol air

0.21 mol O₂/mol
0.79 mol N₂/mol

\( f_{C2H6} = 0.9 \)

\[ n_1 = 10.0 \text{ mol C}_2\text{H}_6 \]
\[ n_2 = \text{mol(O}_2 \text{)} \]
\[ n_3 = 1975 \text{ mol N}_2 \]
\[ n_4 = 45.0 \text{ mol CO} \]
\[ n_5 = 135 \text{ mol CO}_2 \]
\[ n_6 = 270 \text{ mol H}_2\text{O} \]

25% of the ethane burned forms CO

\[ (0.21 \times 2500) \left(\frac{2 \text{ mol O}}{1 \text{ mol O}_2}\right) = n_2 \left(\frac{2 \text{ mol O}}{1 \text{ mol O}_2}\right) + n_4 \left(\frac{1 \text{ mol O}}{1 \text{ mol CO}}\right) + n_5 \left(\frac{2 \text{ mol O}}{1 \text{ mol CO}_2}\right) + n_6 \left(\frac{1 \text{ mol O}}{1 \text{ mol H}_2\text{O}}\right) \]

\[ (525 \text{ mol O}_2) \left(\frac{2 \text{ mol O}}{1 \text{ mol O}_2}\right) = n_2 \left(\frac{2 \text{ mol O}}{1 \text{ mol O}_2}\right) + (45 \text{ mol CO}) \left(\frac{1 \text{ mol O}}{1 \text{ mol CO}}\right) + (135 \text{ mol CO}_2) \left(\frac{2 \text{ mol O}}{1 \text{ mol CO}_2}\right) + (270 \text{ mol H}_2\text{O}) \left(\frac{1 \text{ mol O}}{1 \text{ mol H}_2\text{O}}\right) \]

\[ n_2 = 232 \text{ mol O}_2 \]
\[
\begin{align*}
\text{C}_2\text{H}_6 + \frac{7}{2} \text{O}_2 & \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \\
\text{C}_2\text{H}_6 + \frac{5}{2} \text{O}_2 & \rightarrow 2\text{CO} + 3\text{H}_2\text{O}
\end{align*}
\]

50% excess air

\[n_0 = 2500 \text{ mol air}\]

\[0.21 \text{ mol O}_2/\text{mol}\]

\[0.79 \text{ mol N}_2/\text{mol}\]

\[f_{\text{C}_2\text{H}_6} = 0.9\]

\[25\% \text{ of the ethane burned forms CO}\]

**Stack gas composition (dry basis)**

\[\text{sum} = 10 + 232 + 1975 + 45 + 135 = 2396\]

\[y_1 = 10/2396 = 0.00417 \text{ mol } \text{C}_2\text{H}_6/\text{mol}\]

\[y_2 = 232/2396 = 0.0970 \text{ mol } \text{O}_2/\text{mol}\]

\[y_3 = 1975/2396 = 0.824 \text{ mol } \text{N}_2/\text{mol}\]

\[y_4 = 45/2396 = 0.019 \text{ mol } \text{CO}/\text{mol}\]

\[y_5 = 135/2396 = 0.0563 \text{ mol } \text{CO}_2/\text{mol}\]

\[\frac{270 \text{ mol } \text{H}_2\text{O}}{2396 \text{ mol dry stack gas}} = 0.113 \frac{\text{mol } \text{H}_2\text{O}}{\text{mol dry stack gas}}\]