CHEMICAL PROCESS CALCULATIONS

(Chemical Reaction Stoichiometry)

Lecture # 12: October 05, 2023

Stoichiometry

- Proportion of chemical species that combine with one another
- Relative number of molecules/moles of reactants and products in a reaction
- Number of atoms of any atomic species on both sides of a reaction must be same
- Stoichiometric coefficients
- Stoichiometric ratio

Limiting & Excess Reactant

- Limiting reactant
- Excess reactant
- Fractional excess
- Percentage excess
- Fractional conversion

Limiting & Excess Reactant

$$C_2H_2 + 2H_2 \rightarrow C_2H_6$$

20 kmol acetylene
50 kmol hydrogen
50 kmol ethane

After some time
30 kmol hydrogen
reacted

$$n_{H_2} = (n_{H_2})_0 - 2\xi$$

$$n_{C_2H_2} = (n_{C_2H_2})_0 - \xi$$

$$n_{C_2H_6} = (n_{C_2H_6})_0 + \xi$$

$$\nu_{C_2H_2} = -1$$

$$\nu_{H_2} = -2$$

$$\nu_{C_2H_6} = +1$$

Limiting & Excess Reactant

$$n_{H_2} = (n_{H_2})_0 - 2\xi$$

$$n_{C_2H_2} = (n_{C_2H_2})_0 - \xi$$

$$n_{C_2H_6} = (n_{C_2H_6})_0 + \xi$$

$\nu_{C_2H_2} = -1$

$\nu_{H_2} = -2$

$\nu_{C_2H_6} = +1$

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

ξ = Extent of reaction

Limiting & Excess Reactant

$$C_3H_6 + NH_3 + \frac{3}{2}O_2 \rightarrow C_3H_3N + 3H_2O$$

Mole composition:

10% propylene, 12% amonia, 78% air

Fractional conversion:

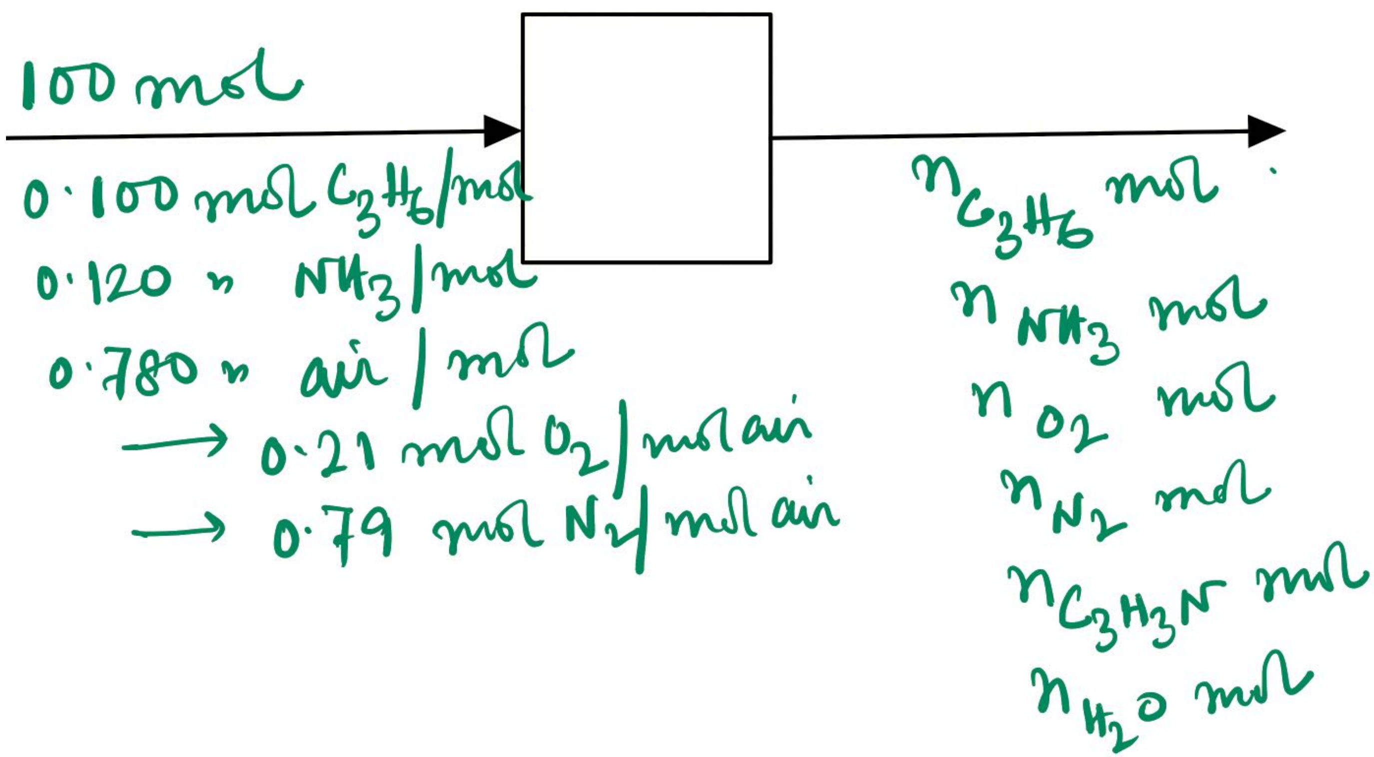
30% of the limiting reactant

% excess of other reactants

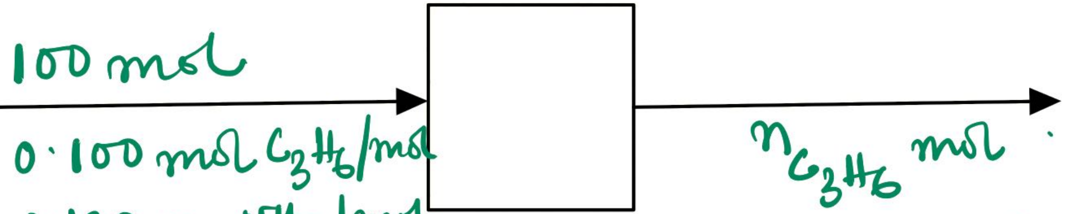
Molar composition of product gas

Limiting & Excess Reactant

$$C_3H_6 + NH_3 + \frac{3}{2}O_2 \rightarrow C_3H_3N + 3H_2O$$



100 mol



0.100 mol C_3H_6/mol
0.120 " NH_3/mol
0.780 " air/mol
→ 0.21 mol O_2/mol air
→ 0.79 mol N_2/mol air

$n_{C_3H_6}$ mol
n_{NH_3} mol
n_{O_2} mol
n_{N_2} mol
$n_{C_3H_3N}$ mol
n_{H_2O} mol

$(n_{C_3H_6})_0 = 10.0$ mol

$(n_{NH_3})_0 = 12.0$ mol

$(n_{O_2})_0 = 78.0 \times 0.210$
$= 16.4$ mol

$$(n_{NH_3}/n_{C_3H_6})_0 = \frac{12.0}{10.0} = 1.20$$

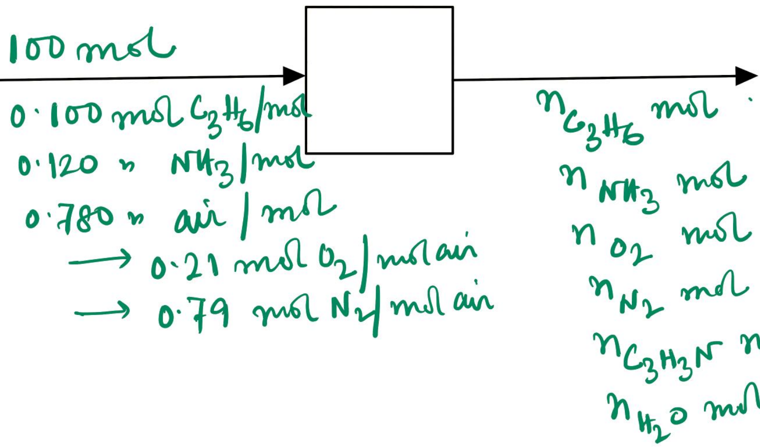
$$(n_{NH_3}/n_{C_3H_6})_{St} = 1/1 = 1$$

⇒ NH_3 is in excess.

$$(n_{O_2}/n_{C_3H_6})_0 = 16.4/10.0 = 1.64$$

$$(n_{O_2}/n_{C_3H_6})_{St} = 1.5/1 = 1.5$$

⇒ O_2 is in excess.



$$\% \text{ excess } NH_3 = \frac{(n_{NH_3})_0 - (n_{NH_3})_{st}}{(n_{NH_3})_{st}} \times 100\%$$

$$= \frac{12.0 - 10.0}{10.0} \times 100\% = 20\%$$

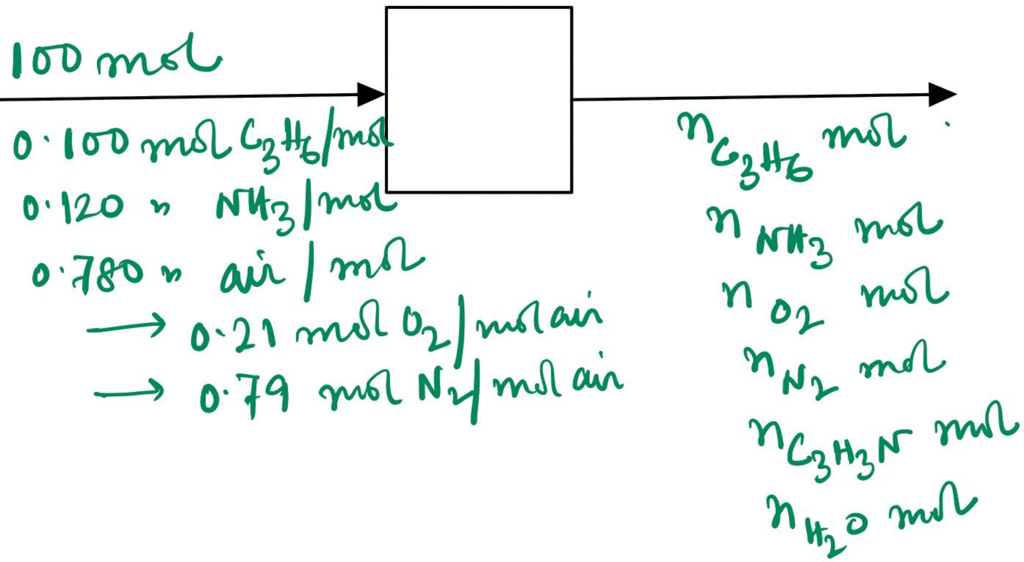
$$\% \text{ excess } O_2 = \frac{16.4 - 15.0}{15.0} \times 100\% = 9.33\%$$

$$(n_{NH_3})_{st} = 10.0 \text{ mol } C_3H_6 \times \frac{1 \text{ mol } NH_3}{1 \text{ mol } C_3H_6}$$

$$= 10.0 \text{ mol } NH_3$$

$$(n_{O_2})_{st} = 10.0 \text{ mol } C_3H_6 \times \frac{1.5 \text{ mol } O_2}{1 \text{ mol } C_3H_6}$$

$$= 15.0 \text{ mol } O_2$$



$$(n_{C_3H_6})_{out} = 0.700 \times (n_{C_3H_6})_0 = 7.0 \text{ mol}$$

$$(n_{C_3H_6})_{out} = 10.0 - \xi$$

$$\Rightarrow \xi = 3.0 \text{ mol}$$

$$n_{NH_3} = 12.0 - \xi \qquad n_{C_3H_3N} = \xi$$

$$n_{O_2} = 16.4 - 1.5\xi \qquad n_{H_2O} = 3\xi$$

$$n_{N_2} = (n_{N_2})_0$$

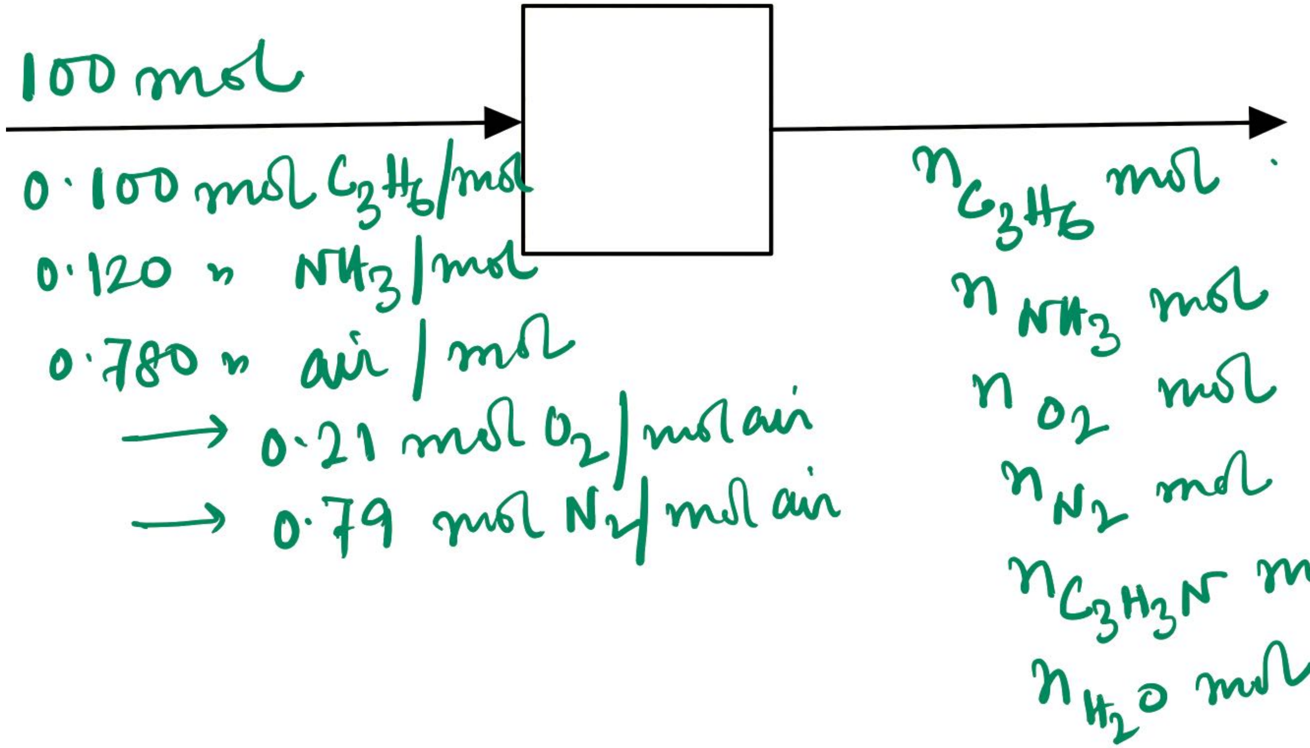
CHEMICAL PROCESS CALCULATIONS

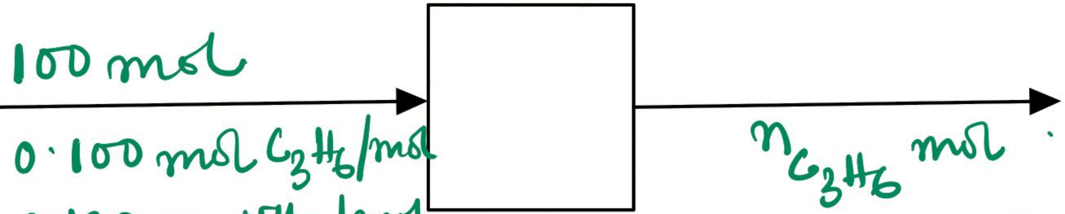
(Chemical Reaction Stoichiometry)

Lecture # 13: October 09, 2023

Limiting & Excess Reactant

$$C_3H_6 + NH_3 + \frac{3}{2}O_2 \rightarrow C_3H_3N + 3H_2O$$





100 mol

0.100 mol C_3H_6/mol

0.120 " NH_3/mol

0.780 " air/mol

$\longrightarrow$ 0.21 mol O_2/mol air

$\longrightarrow$ 0.79 mol N_2/mol air

$n_{C_3H_6}$ mol

n_{NH_3} mol

n_{O_2} mol

n_{N_2} mol

$n_{C_3H_3N}$ mol

n_{H_2O} mol

$$(n_{C_3H_6})_0 = 10.0 \text{ mol}$$

$$(n_{NH_3})_0 = 12.0 \text{ mol}$$

$$(n_{O_2})_0 = 78.0 \times 0.210 = 16.4 \text{ mol}$$

$$(n_{NH_3}/n_{C_3H_6})_0 = \frac{12.0}{10.0} = 1.20$$

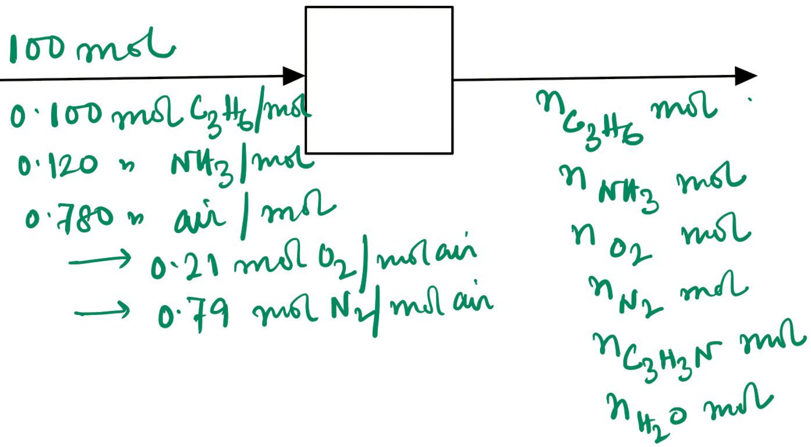
$$(n_{NH_3}/n_{C_3H_6})_{St} = 1/1 = 1$$

$\Rightarrow$ NH_3 is in excess.

$$(n_{O_2}/n_{C_3H_6})_0 = 16.4/10.0 = 1.64$$

$$(n_{O_2}/n_{C_3H_6})_{St} = 1.5/1 = 1.5$$

$\Rightarrow$ O_2 is in excess.



$$\% \text{ excess } NH_3 = \frac{(n_{NH_3})_0 - (n_{NH_3})_{st}}{(n_{NH_3})_{st}} \times 100\%$$

$$= \frac{12.0 - 10.0}{10.0} \times 100\% = 20\%$$

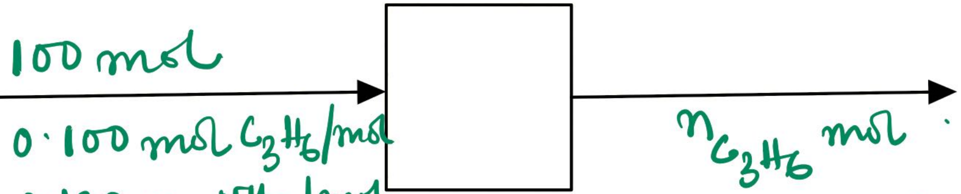
$$\% \text{ excess } O_2 = \frac{16.4 - 15.0}{15.0} \times 100\% = 9.33\%$$

$$(n_{NH_3})_{st} = 10.0 \text{ mol } C_3H_6 \times \frac{1 \text{ mol } NH_3}{1 \text{ mol } C_3H_6}$$

$$= 10.0 \text{ mol } NH_3$$

$$(n_{O_2})_{st} = 10.0 \text{ mol } C_3H_6 \times \frac{1.5 \text{ mol } O_2}{1 \text{ mol } C_3H_6}$$

$$= 15.0 \text{ mol } O_2$$



100 mol

0.100 mol C_3H_6/mol
0.120 " NH_3/mol
0.780 " air/mol
→ 0.21 mol O_2/mol air
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$n_{C_3H_6}$ mol
n_{NH_3} mol
n_{O_2} mol
n_{N_2} mol
$n_{C_3H_3N}$ mol
n_{H_2O} mol

$$(n_{C_3H_6})_{out} = 0.700 \times (n_{C_3H_6})_0 = 7.0 \text{ mol}$$

$$(n_{C_3H_6})_{out} = 10.0 - \xi$$

$$\Rightarrow \xi = 3.0 \text{ mol}$$

$$n_{NH_3} = 12.0 - \xi \qquad n_{C_3H_3N} = \xi$$

$$n_{O_2} = 16.4 - 1.5\,\xi \qquad n_{H_2O} = 3\,\xi$$

$$n_{N_2} = (n_{N_2})_0$$

Chemical Equilibrium

- Equilibrium composition of the reaction mixture
- Time to reach the onset of equilibrium
- Irreversible reaction
- Reversible reaction

$$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$$

Chemical Equilibrium

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

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

$\boxed{\begin{array}{l} \text{At } T = 1105\,K \\ \quad K = 1.00 \end{array}}$

Feed : $\begin{cases} 1 \text{ mol } CO \\ 2 \text{ mol } H_2O \end{cases}$

Calculate equilibrium composition.

fractional conversion

Chemical Equilibrium

$$n_{CO} = 1.00 - \xi_e$$
$$n_{H_2O} = 2.00 - \xi_e$$
$$n_{CO_2} = \xi_e$$
$$n_{H_2} = \xi_e$$
$$n_t = 3.00$$

$$y_{CO} = (1.00 - \xi_e)/3.00$$
$$y_{H_2O} = (2.00 - \xi_e)/3.00$$
$$y_{CO_2} = \xi_e/3.00$$
$$y_{H_2} = \xi_e/3.00$$

Chemical Equilibrium

$$\frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = \frac{\xi_e^2}{(1.00-\xi_e)(2.00-\xi_e)} = 1.00$$

$$\Rightarrow \quad \xi_e = 0.667$$

$y_{CO} = 0.111$ $\qquad$ $y_{CO_2} = 0.222$

$y_{H_2O} = 0.444$ $\qquad$ $y_{H_2} = 0.222$

Chemical Equilibrium

$$n_{CO} = (1.00 - 0.667)\text{ mol} = 0.333\text{ mol}$$

$$f_{CO} = \frac{(1.00 - 0.333)\text{ CO reacted}}{1.00\text{ mol CO fed}} = 0.667$$

The reaction between ethylene and hydrogen bromide to form ethyl bromide is carried out in a continuous reactor. The product stream is analyzed and found to contain 51.7 mole% C_2H_5Br and 17.3% HBr. The feed to the reactor contains only ethylene and hydrogen bromide. Calculate the fractional conversion of the limiting reactant and the percentage by which the other reactant is in excess. If the molar flow rate of the feed stream is 165 mol/s, what is the extent of reaction?

CHEMICAL PROCESS CALCULATIONS

(Chemical Reaction Stoichiometry)

Lecture # 14: October 12, 2023

Multiple Reactions, Yield, and Selectivity

- Desired product yield
- Desired product purity
- Yield and Selectivity

$$\text{Yield} = \frac{\text{moles of desired product formed}}{\begin{array}{c}\text{moles that would be formed if there were no side reactions}\\ \text{and the limiting reactant were consumed completely}\end{array}} \times 100\%$$

$$\text{Selectivity} = \frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}}$$

Multiple Reactions, Yield, and Selectivity

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$C_2H_6 + H_2 \rightarrow 2CH_4$$

$$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$$

$$\text{Yield} = \frac{(n_{C_2H_4})_{gen}}{(\nu_{C_2H_4}/\nu_{C_2H_6})(n_{C_2H_6})_{input}} \times 100\%$$

$$\text{Selectivity} = \frac{(n_{C_2H_4})_{gen}}{(n_{CH_4})_{gen}}$$

Yield ⇒ moles of desired product divided by either moles of reactant fed or moles of reactant consumed in the reactor

Multiple Reactions, Yield, and Selectivity

Single reaction : $n_i = n_{io} + \nu_i \xi$

Multiple reaction: $n_i = n_{io} + \sum_j \nu_{ij} \xi_j$

$$C_2H_4 + \frac{1}{2}O_2 \longrightarrow C_2H_4O$$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

Multiple Reactions, Yield, and Selectivity

$$(n_{C_2H_4})_{out} = (n_{C_2H_4})_0 - \xi_1 - \xi_2$$

$$(n_{O_2})_{out} = (n_{O_2})_0 - 0.5\,\xi_1 - 3\,\xi_2$$

$$(n_{C_2H_4O})_{out} = (n_{C_2H_4O})_0 + \xi_1$$

$$(n_{CO_2})_{out} = (n_{CO_2})_0 + 2\,\xi_2$$

$$(n_{H_2O})_{out} = (n_{H_2O})_0 + 2\,\xi_2$$

$$C_2H_4 + \tfrac{1}{2}O_2 \longrightarrow C_2H_4O$$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

Multiple Reactions, Yield, and Selectivity

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$C_2H_6 + H_2 \rightarrow 2CH_4$$

Feed: 85.0 mole% ethane and the balance inert

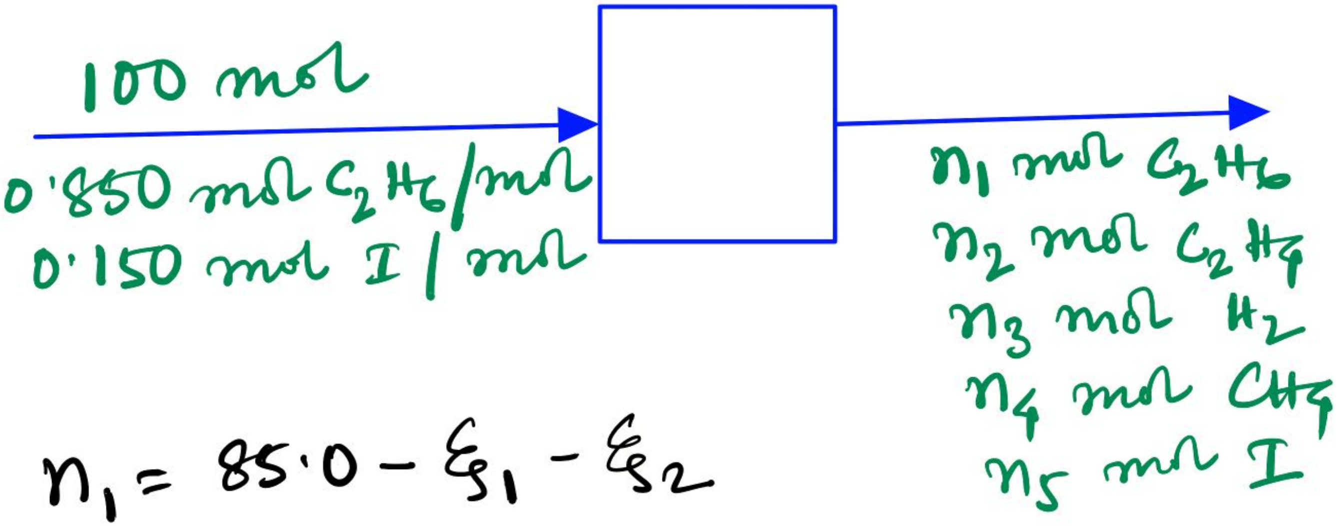
Fractional conversion of ethane = 0.501

Fractional yield of ethylene = 0.471

Calculate

- molar composition of the product gas
- selectivity of ethylene to methane production

Multiple Reactions, Yield, and Selectivity



$$n_1 = 85.0 - \xi_1 - \xi_2$$

$$n_2 = \xi_1$$

$$n_3 = \xi_1 - \xi_2$$

$$n_4 = 2\xi_2$$

$$n_5 = 15.0$$

Multiple Reactions, Yield, and Selectivity

$\underline{\underline{C_2H_6}}$:

fractional conversion : 0.501

$(1-0.501) \times 85.0 = n_1$

$\Rightarrow \boxed{n_1 = 42.4 = 85.0 - \xi_1 - \xi_2}$

$\underline{\underline{C_2H_4}}$:

fractional yield : 0.471

$0.471 \times 85.0 = n_2$

$\boxed{\Rightarrow \; n_2 = 40.0 = \xi_1}$ $\Rightarrow \boxed{\xi_2 = 2.6}$

Multiple Reactions, Yield, and Selectivity

$n_3 = \xi_{s1} - \xi_{s2} = 37.4$

$n_4 = 2\xi_{s2} = 5.2$

$n_5 = 15.0$

$n_1 = 42.4$

$n_2 = 40.0$

$n_t = 140.0$

Product

C_2H_6 – 30.3%

C_2H_4 – 28.6%

H_2 – 26.7%

CH_4 – 3.7%

I – 10.7%

$\boxed{\text{Selectivity}}$

$$= \frac{40.0 \text{ mol } C_2H_4}{5.2 \text{ mol } CH_4} = 7.69 \text{ mol } C_2H_4/\text{mol } CH_4$$

Reactive system balance

(a) molecular species balances (similar to nonreactive systems)

(b) atomic species balances

(c) extents of reaction

- independent equations
- independent species
- independent chemical reactions