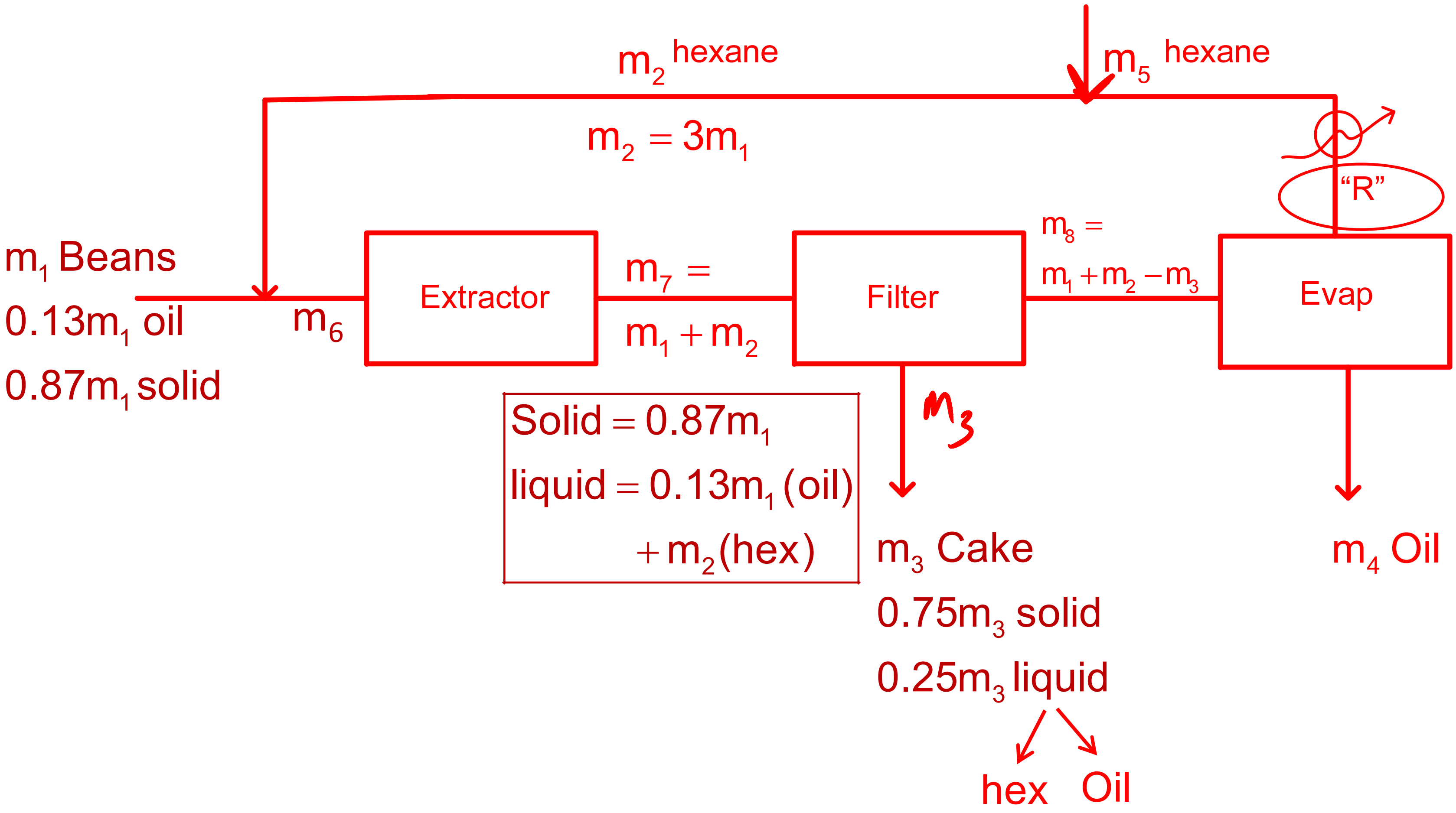
Prob 4.48

In the production of a bean oil, beans containing 13.0 wt% oil and 87.0% solids are ground and fed to a stirred tank (the *extractor*) along with a recycled stream of liquid *n*-hexane. The feed ratio is 3 kg hexane/kg beans. The ground beans are suspended in the liquid, and essentially all of the oil in the beans is extracted into the hexane. The extractor effluent passes to a filter. The filter cake contains 75.0 wt% bean solids and the balance bean oil and hexane, the latter two in the same ratio in which they emerge from the extractor. The filter cake is discarded and the liquid filtrate is fed to a heated evaporator in which the hexane is vaporized and the oil remains as a liquid. The oil is stored in drums and shipped. The hexane vapor is subsequently cooled and condensed, and the liquid hexane condensate is recycled to the extractor.

(a) Draw and label a flowchart of the process, do the degree-of-freedom analysis, and write in an efficient order the equations you would solve to determine all unknown stream variables, circling the variables for which you would solve.

(b) Calculate the yield of bean oil product (kg oil/kg beans fed), the required fresh hexane feed (kg C_6H_{14}/kg beans fed), and the recycle to fresh feed ratio (kg hexane recycled/kg fresh feed).



m_2 hexane

m_5 hexane

$m_2 = 3m_1$

"R"

m_1 Beans

$0.13m_1$ oil

$0.87m_1$ solid

m_6

Extractor

$m_7 = m_1 + m_2$

Filter

$m_8 = m_1 + m_2 - m_3$

Evap

$\text{Solid} = 0.87m_1$

$\text{liquid} = 0.13m_1\,(\text{oil})$

$+\,m_2(\text{hex})$

m_3

m_3 Cake

$0.75m_3$ solid

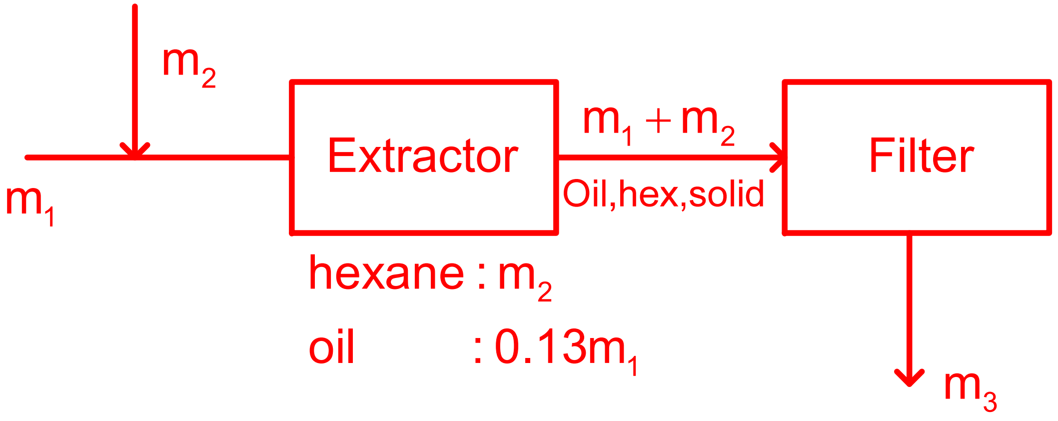
$0.25m_3$ liquid

hex Oil

m_4 Oil

<ins>Balances:</ins> oil, hexane, solid

* Assume Basis: $\boxed{100\text{ kg} = m_1}$



hexane : m_2

oil : $0.13m_1$

Reactions

Balanced reaction:

$$\begin{array}{ccccccc} \text{reactants} & & & & \text{products} & & \\ CH_4 & + & H_2O & \leftrightarrow & CO & + & 3H_2 \\ -1 & & -1 & & 1 & & 3 \end{array}$$

stoichiometric coefficients, ν_i

ν_i is positive for products and negative for reactants

Stoichiometric ratio: ratio of stoichiometric coeff., e.g., $CH_4/H_2O = 1$

Limiting reactant: the reactant that disappears first.

	CH_4	H_2O	CO	$3H_2$
Initial:	1	5	0	0
Final:	0	4	1	3

All quantities are in moles

Theoretical amount of reactant :

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

	CH_4	H_2O	CO	H_2
Initial:	1	5	0	0

Theoretical amount of H_2O = moles of H_2O needed for complete conversion of CH_4 = 1

Excess reactant :

$$\text{Excess } H_2O = \frac{H_2O\text{ fed} - \text{theoretical } H_2O}{\text{theoretical } H_2O} = \frac{5-1}{1} = 4$$
$$= 4 \times 100\%$$
$$= 400\%$$

Fractional excess of reactant "B"

$$= (n_{B,fed} - n_{B,stoich}) / n_{B,stoich}$$

Where $n_{B,stoich}$ is the amount of B required for complete stoichiometric conversion of B with the limiting reactant.

Fractional conversion: fraction of initial limiting reactant that reacted.

f_{CH4} (or x_{CH4}) = moles of CH_4 reacted/initial moles of CH_4

f_A (or x_A) = moles of A reacted/initial moles of A (n_{A0}) = $(n_{A0}-n_A)/n_{A0}$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

Initial:	1	5	0	0
Final:	0.5	4.5	0.5	1.5

$$f_{CH4} = 0.5/1.0 = 0.5 \text{ or } 50\%$$

Extent of reaction: moles of limiting reactant reacting divided by $|\nu_i|$
= ξ ("ksai")

$$\xi_A = \frac{n_{Ao} - n_A}{\mathbf{-(-1)}}$$

e.g. for the example above, ξ_{CH4} = 0.5 moles, and

$n_{CH4} = n_{CH4,o} - \xi_{CH4} = 1 - 0.5 = 0.5$ moles

$n_{H2O} = n_{H2O,o} - \xi_{CH4} = 5 - 0.5 = 4.5$ moles

$n_{CO} = n_{CO,o} + \xi_{CH4} = 0 + 0.5 = 0.5$ moles

$n_{H2} = n_{H2,o} + 3\xi_{CH4} = 0 + 1.5 = 1.5$ moles

What is the relation between f_A and ξ_A?

$$\xi_A = \frac{f_A n_{Ao}}{-\nu_A} = \frac{n_{Ao} - n_A}{-\nu_A}$$

In general :

$$n_i = n_{io} + \nu_i \xi \quad , \quad \dot{n}_i = \dot{n}_{io} + \nu_i \xi$$

For multiple “j” rxns”: $n_i = n_{io} + \Sigma \nu_{ij} \xi_j$

Generation of product = $n_i - n_{io}$

Consumption of reactant = $n_{io} - n_i$

ξ is always positive = $(n_i - n_{io})/\nu_i$

ξ is the same for all components in a reaction

Scaling and basis of calculation: (section 4.3b)

For rxn: $3A+2B \rightarrow 4C+D$

assuming A is limiting, & no C or D in feed:

Example 4.6-1

Reaction Stoichiometry

Acrylonitrile is produced in the reaction of propylene, ammonia, and oxygen:

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

The feed contains 10.0 mole% propylene, 12.0% ammonia, and 78.0% air. A fractional conversion of 30.0% of the limiting reactant is achieved. Taking 100 mol of feed as a basis, determine which reactant is limiting, the percentage by which each of the other reactants is in excess, and the molar amounts of all product gas constituents for a 30% conversion of the limiting reactant.

Basis: 100 mol Feed

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Basis: 100 mol Feed

Multiple reactions:

(1) $C_2H_6 = C_2H_4 + H_2$ desired

(2) $C_2H_6 + H_2 = 2CH_4$ undesired

fractional conversion, f_{C2H6}, includes both Reaction (1) and (2)

Selectivity:

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

Yield (3 ways)

$$Y(1) = \frac{\text{moles of desired product}}{\text{initial moles of reactant}}$$

$$Y(2) = \frac{\text{moles of desired product}}{\text{moles of reactant consumed}}$$

$$Y(3) = \frac{\text{moles of desired product}}{\left.\begin{array}{l}\text{moles of product formed if}\\ \text{complete conversion of limiting}\\ \text{reactant and no side reactions}\end{array}\right\}\text{Max possible amt of product}}$$

Use this unless otherwise stated →

Yield and Selectivity in a Dehydrogenation Reactor

$$\boxed{n_i = n_{io} + \Sigma\nu_{ij}\xi_j}$$

The reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2$$
$$C_2H_6 + H_2 \rightarrow 2\,CH_4$$

take place in a continuous reactor at steady state. The feed contains 85.0 mole% ethane (C_2H_6) and the balance inerts (I). The fractional conversion of ethane is 0.501, and the fractional yield of ethylene is 0.471. Calculate the molar composition of the product gas and the selectivity of ethylene to methane production.

Ethylene Yield

$$\text{maximum possible ethylene formed} = \frac{85.0\ \text{mol}\ C_2H_6\ \text{fed}}{} \left| \frac{1\ \text{mol}\ C_2H_4}{1\ \text{mol}\ C_2H_6} \right. = 85.0\ \text{mol}$$

$$\Downarrow$$

$$n_2 = 0.471(85.0\ \text{mol}\ C_2H_6) = 40.0\ \text{mol}\ C_2H_4 = \xi_1$$

Substituting 40.0 mol for ξ_1 in Equation 1 yields $\xi_2 = 2.6$ mol. Then

$$n_3 = \xi_1 - \xi_2 = 37.4\ \text{mol}\ H_2$$

$$n_4 = 2\xi_2 = 5.2\ \text{mol}\ CH_4$$

$$n_5 = 15.0\ \text{mol I}$$

$$n_{tot} = (42.4 + 40.0 + 37.4 + 5.2 + 15.0)\ \text{mol} = 140.0\ \text{mol}$$

$$\Downarrow$$

Product: $\boxed{30.3\%\ C_2H_6,\quad 28.6\%\ C_2H_4,\quad 26.7\%\ H_2,\quad 3.7\%\ CH_4,\quad 10.7\%\ \text{I}}$

$$\text{selectivity} = (40.0\ \text{mol}\ C_2H_4)/(5.2\ \text{mol}\ CH_4)$$

$$= \boxed{7.7\frac{\text{mol}\ C_2H_4}{\text{mol}\ CH_4}}$$

Chemical Equilibrium

- In reversible reactions, an equilibrium state is formed at which all reactants and products co-exist in some proportions. At equilibrium the rates of the forward and the reverse reactions are equal. The composition of the mixture is determined by the equilibrium constant K.

- The equilibrium constant is a function of a reaction temperature and is defined as follows:

- For the gas-phase reaction $aA+bB \longleftrightarrow cC$, at P_T **(total pressure in atm)**:

$$K= [(y_C)^c/(y_A)^a(y_B)^b]\cdot P_T^{(c-a-b)} \longleftarrow \mathbf{P_T^{\Sigma\nu}}$$

Where y_i is mole fraction of component i at equilibrium.

Note: Since mole fractions are dimensionless, the units of the equilibrium constant K are: $atm^{(c-a-b)}$

Chemical Equilibrium

- For the liquid-phase reaction $aA+bB \longleftrightarrow cC$. Pressure has no effect on the equilibrium constant, hence:

  $K= [(x_C)^c/(x_A)^a.(x_B)^b]$

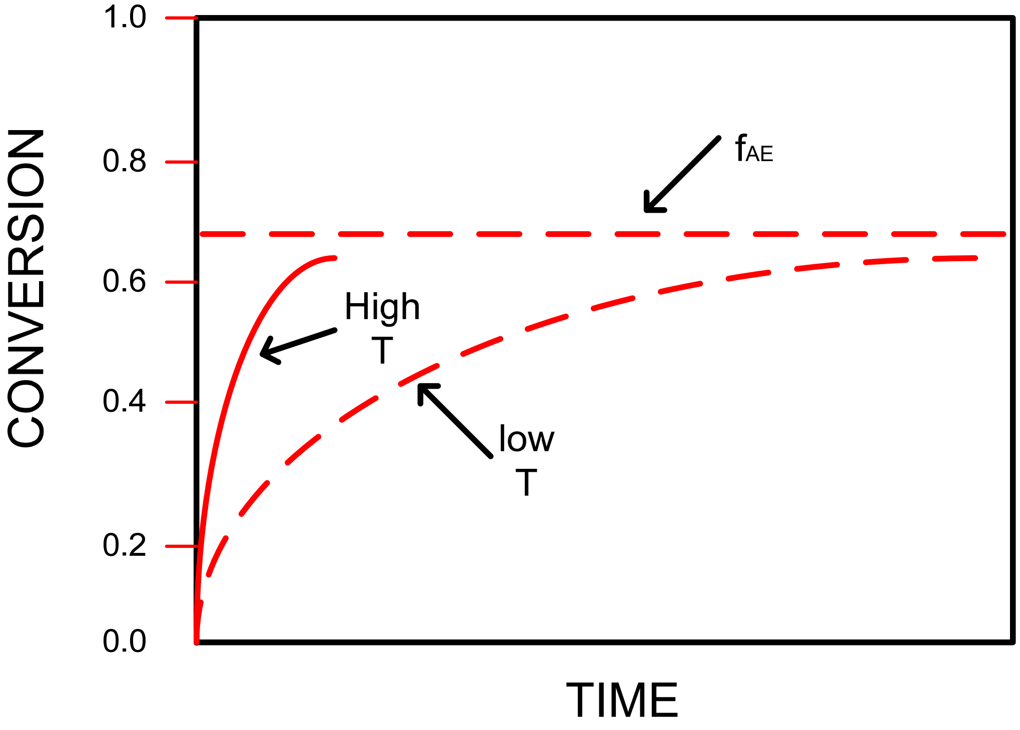
  Where x_i is mole fraction of liquid component i at equilibrium.

  Note: Since mole fractions are dimensionless, the equilibrium constant K is dimensionless.

Equilibrium reactions: reversible reactions

$CH_4 + H_2O \leftrightarrows CO + 3H_2$ (reversible)

Equilibrium constant $K(T) = [y_{CO}y_{H2}^3/y_{CH4}y_{H2O}]P^2$ (thermodynamics)



Calculation of an Equilibrium Composition

If the water–gas shift reaction,

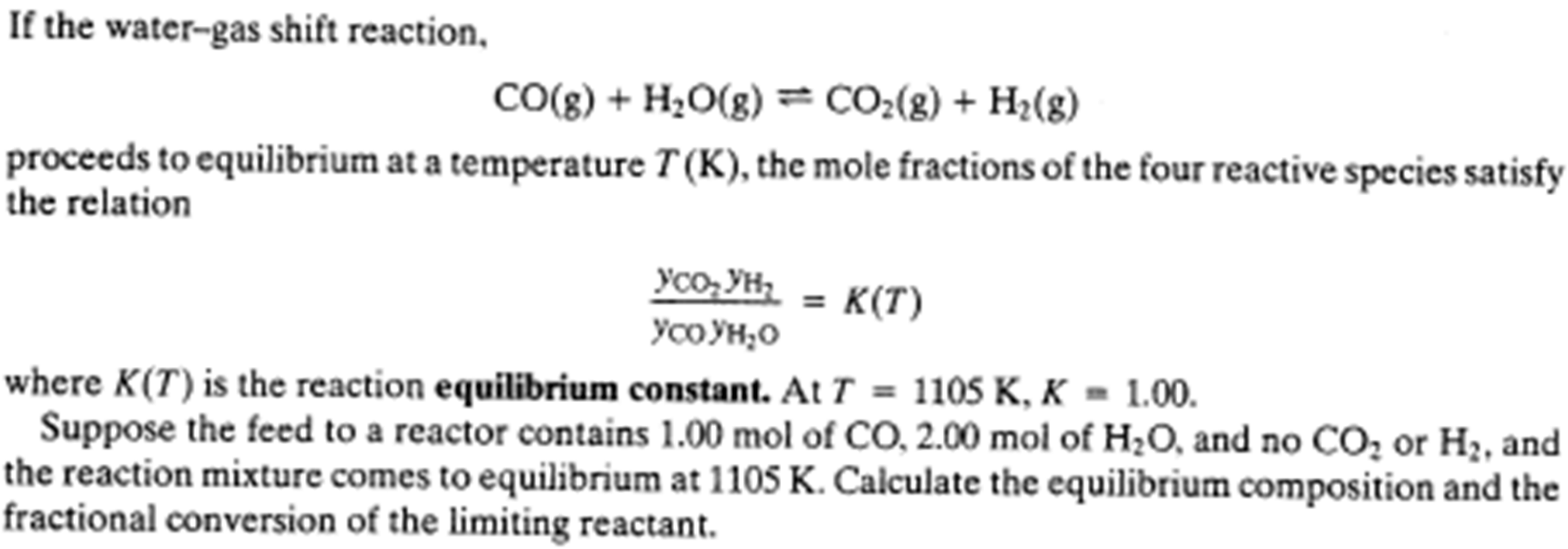
$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

proceeds to equilibrium at a temperature T (K), the mole fractions of the four reactive species satisfy the relation

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

where $K(T)$ is the reaction **equilibrium constant.** At $T = 1105$ K, $K = 1.00$.

Suppose the feed to a reactor contains 1.00 mol of CO, 2.00 mol of H_2O, and no CO_2 or H_2, and the reaction mixture comes to equilibrium at 1105 K. Calculate the equilibrium composition and the fractional conversion of the limiting reactant.



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Suppose the feed to a reactor contains 1.00 mol of CO, 2.00 mol of H_2O, and no CO_2 or H_2, and the reaction mixture comes to equilibrium at 1105 K. Calculate the equilibrium composition and the fractional conversion of the limiting reactant.

Methodology: Express mole fractions ("y"s) at equilibrium all in terms of the single variable ξ_e, the extent of rxn @ equilibrium, then solve for ξ_e using the equilibrium constant K.

Material balance for reacting systems:

(1) Molecular balance

General balance equation: input + generation = output + consumption + accum

(products) (reactants)

Degrees of freedom: $n_{df} = n_{uk} + n_{\text{ind reactions}} - n_{\text{ind molecule balances}} - n_{\text{other}}$

Simple for single reactions, Complex for multiple reactions

(2) Atomic balance

General balance equation: input = output + accumulation

Degrees of freedom: $n_{df} = \underline{n_{uk}} - n_{\text{ind atom bal}} - n_{\text{bal indep, non-reactive mol}} - n_{\text{other}}$

→ Simple for multiple reactions

(3) Extent of reaction (ξ) balance (version of molecular balance)

$n_i = n_{io} + \nu_i \xi$, or for multiple (j) rxns: $n_i = n_{io} + \Sigma \nu_{ij} \xi_j$

General balance equation: input + generation = output + consumption + accum

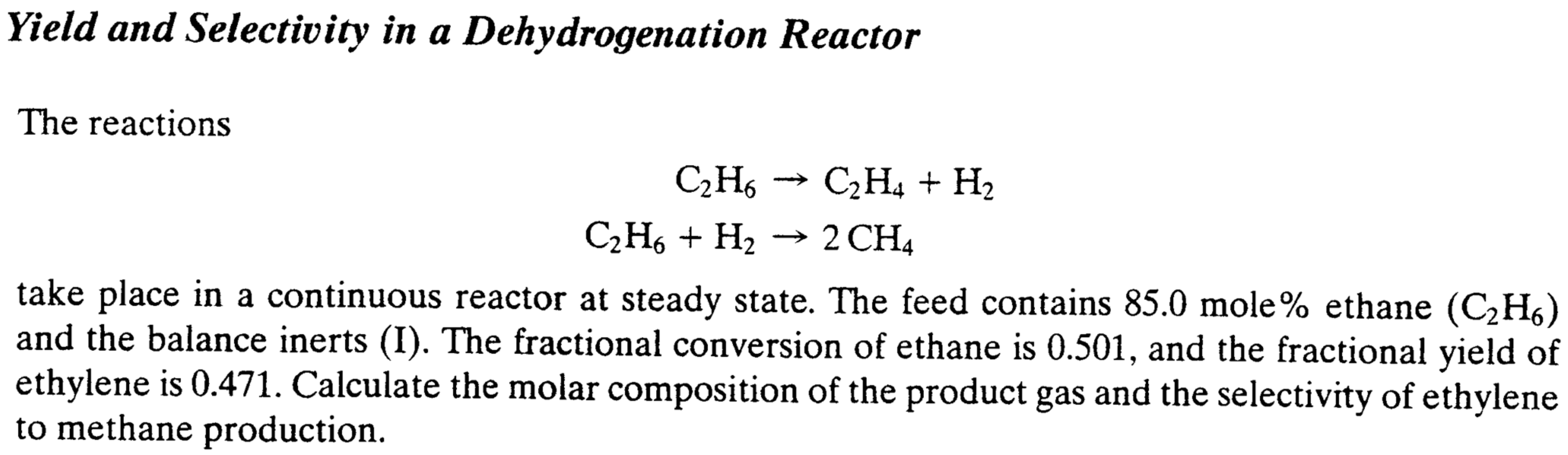
(products) (reactants)

Degrees of freedom:

$n_{df} = n_{uk} + n_{\text{ind reactions}} - n_{\text{ind reactive species } \xi \text{ balances}} - n_{\text{bal indep, non-reactive mol}} - n_{\text{other}}$

Useful for equilibrium systems, though not very different from Molecular Bal's!!

Recall this problem…   We used extent of reaction balance



Yield and Selectivity in a Dehydrogenation Reactor

The reactions

$$C_2H_6 \rightarrow C_2H_4 + H_2$$
$$C_2H_6 + H_2 \rightarrow 2\,CH_4$$

take place in a continuous reactor at steady state. The feed contains 85.0 mole% ethane (C_2H_6) and the balance inerts (I). The fractional conversion of ethane is 0.501, and the fractional yield of ethylene is 0.471. Calculate the molar composition of the product gas and the selectivity of ethylene to methane production.

$$C_2H_6 \rightarrow C_2H_4 + H_2$$
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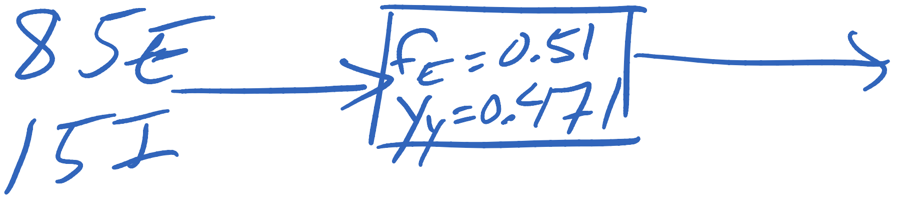
take place in a continuous reactor at steady state. The feed contains 85.0 mole% ethane (C_2H_6) and the balance inerts (I). The fractional conversion of ethane is 0.501, and the fractional yield of ethylene is 0.471. Calculate the molar composition of the product gas and the selectivity of ethylene to methane production.

*** Can alternately use atomic balances:**



$n_E = (1-f_E)(n_{E0}) = 42.4$
n_Y
n_H
n_M

$$\boxed{\begin{array}{l} y = 0.471 = \dfrac{n_Y}{85} \\ \therefore\ n_Y = 40 \end{array}}$$

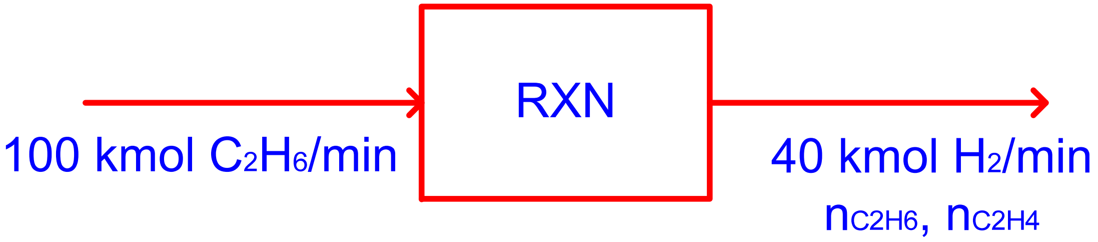
Two unknowns…

C-balance: $85 \times 2 = 42.2 \times 2 + n_M + 2n_Y$

H-balance: $85 \times 6 = 42.2 \times 6 + 2n_H + 4(n_Y + n_M)$

Example: Dehydrogenation of Ethane to Ethylene

$$C_2H_6 \rightarrow C_2H_4 + H_2$$



RXN

100 kmol C_2H_6/min

40 kmol H_2/min

n_{C2H6}, n_{C2H4}

Molecular species balance:

2 unknowns + 1 indep chem rxn – 3 indep molec species = 0

Atomic species balance:

2 unknowns – 2 indep atomic species = 0

Extent of Reaction balance: $n_i = n_{io} + \nu_i \xi$

2 unknowns + 1 indep chem rxn – 3 indep reactive species = 0

H_2: $\nu = 1$, $40 = 0 + \xi$ → $\xi = 40$ kmol/min

C_2H_6: $\nu = -1$, $n_{C2H6} = 100 - \xi$ → $n_{C2H6} = 60$ kmol/min

C_2H_4: $\nu = 1$, $n_{C2H4} = 0 + \xi$ → $n_{C2H4} = 40$ kmol/min

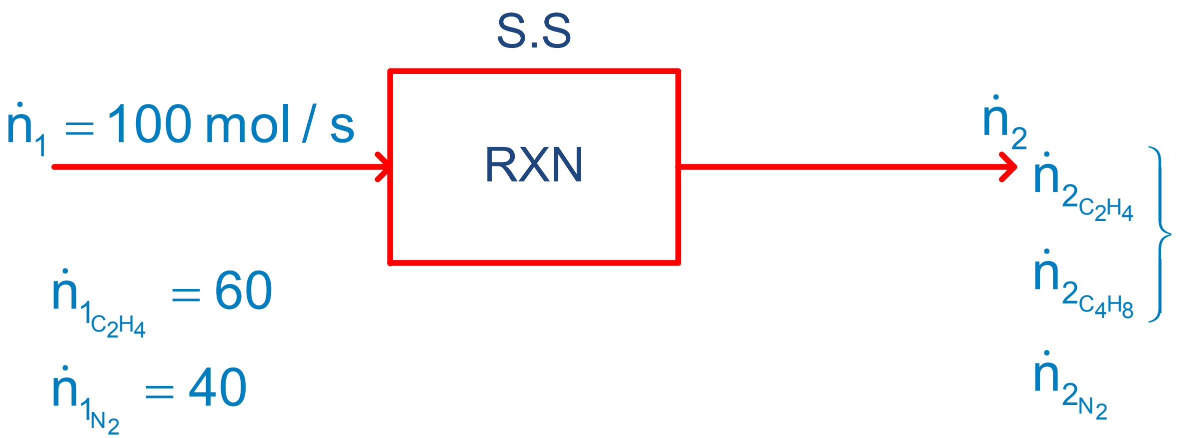
Material balance for reactors (including total process):

- Only balance Independent molecular or atomic species, and Independent reactions

- If two molecular or atomic species are in the same ratio to each other wherever they appear in a process, balances on those species are not independent equations.

- Example: dimerization of ethylene in presence of nitrogen

$$C_2H_4 \rightarrow C_4H_8$$



S.S

RXN

$\dot{n}_1 = 100\ \text{mol/s}$

$\dot{n}_{1_{C_2H_4}} = 60$

$\dot{n}_{1_{N_2}} = 40$

$\dot{n}_2$

$\dot{n}_{2_{C_2H_4}}$

$\dot{n}_{2_{C_4H_8}}$

$\dot{n}_{2_{N_2}}$

- 3 independent molecular species (N_2, C_2H_4,C_4H_8)
- 2 independent atomic species N & C or H

$$\text{N balance}: 2\dot{n}_{1_{N_2}} = 2\dot{n}_{2_{N_2}} = 80$$

$$\text{C balance}: 2\dot{n}_{2_{C_2H_4}} + 4\dot{n}_{2_{C_4H_8}} = 2\dot{n}_{1_{C_2H_4}} = 120$$

$$\text{H balance}: 4(\quad) + 8(\quad) = 4(\quad) = 240$$

$$\text{H} - \text{balance} = 2(\text{C} - \text{balance}) \rightarrow \text{not independent}$$

$$\rightarrow \text{Can't} \quad \text{Solve!}$$

Problem 4.56

$\dot{n}_1 = 165\,\text{mol/s}$

$\dot{n}_{1E}$

$\dot{n}_{1HB}$

$C_2H_4 + HBr = C_2H_5Br$

E HB EB

$\dot{n}_2$

$y_{2HB} = 0.173$

$y_{2EB} = 0.517$

$y_{2E} = 1 - 0.173 - 0.517$

$= 0.310$

Flow, mol/s	1	2
Total n_i	165	
Comp, n_{ij} n_{iE} n_{iHB} n_{iEB}		

one reaction: molecular balance

$n_{df} = n_{uk} + n_{indrx} - n_{mol\ bal} - n_{other}$

$2 + 1 - 3 - 0 = 0$ ✓

Other methods are similar… (maybe atomic is easiest here…)

Dehydrogenation of Propane

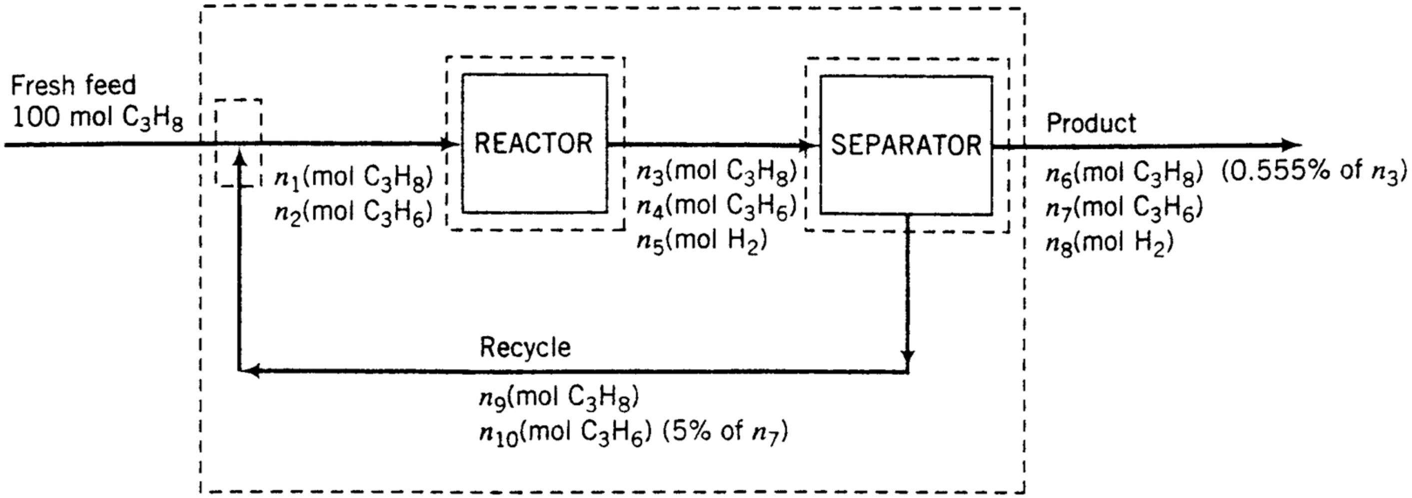
Propane is dehydrogenated to form propylene in a catalytic reactor:

Example 4.7-2

$$C_3H_8 \rightarrow C_3H_6 + H_2$$

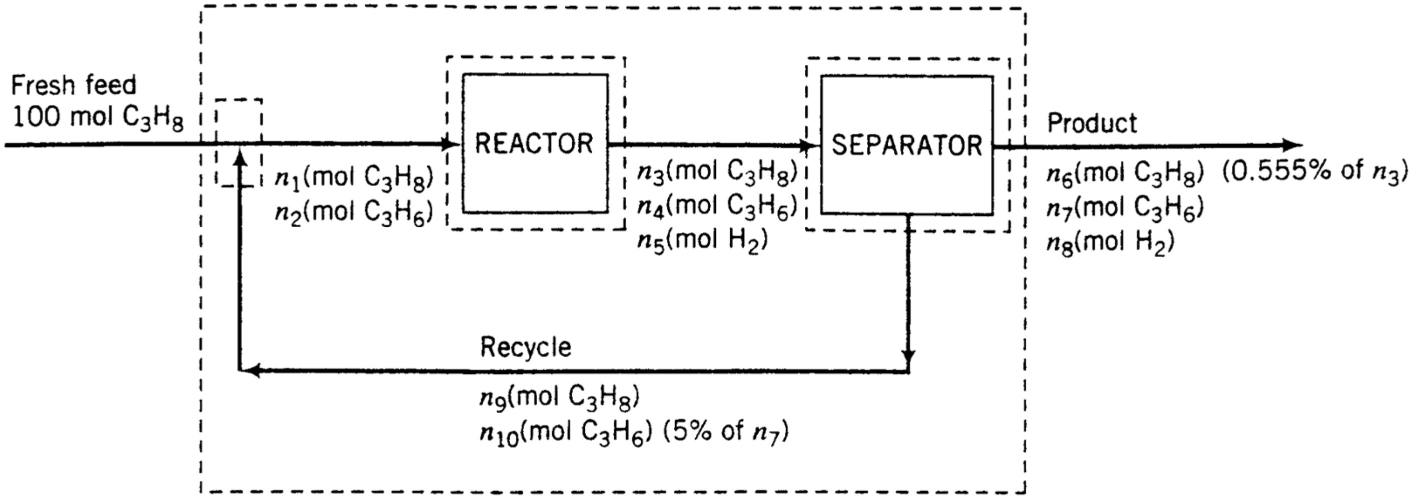
The process is to be designed for a 95% overall conversion of propane. The reaction products are separated into two streams: the first, which contains H_2, C_3H_6, and 0.555% of the propane that leaves the reactor, is taken off as product; the second stream, which contains the balance of the unreacted propane and 5% of the propylene in the first stream, is recycled to the reactor. Calculate the composition of the product, the ratio (moles recycled)/(mole fresh feed), and the single-pass conversion.

Basis: 100 mol Fresh Feed



Example 4.7-2

Basis: 100 mol Fresh Feed



Example 4.7-3

Recycle and Purge in the Synthesis of Methanol

Methanol is produced in the reaction of carbon dioxide and hydrogen:

$$CO_2 + 3\,H_2 \longrightarrow CH_3OH + H_2O$$

The fresh feed to the process contains hydrogen, carbon dioxide, and 0.400 mole% inerts (I). The reactor effluent passes to a condenser that removes essentially all of the methanol and water formed and none of the reactants or inerts. The latter substances are recycled to the reactor. To avoid buildup of the inerts in the system, a purge stream is withdrawn from the recycle.

The feed to the *reactor* (not the fresh feed to the process) contains 28.0 mole% CO_2, 70.0 mole% H_2, and 2.00 mole% inerts. The single-pass conversion of hydrogen is 60.0%. Calculate the molar flow rates and molar compositions of the fresh feed, the total feed to the reactor, the recycle stream, and the purge stream for a methanol production rate of 155 kmol CH_3OH/h.

Combustion

Produce energy from fuel.

Complete combustion = full oxidation to CO_2, H_2O, SO_2, etc

Partial/incomplete combustion yields some CO.

Air is common source of O_2. Typically ~ 50% excess air

**Air: 21% oxygen → 4.76 mole air / mole O_2

$\& \; 3.76 \frac{\text{mole } N_2}{\text{mole } O_2}$

"Stack Gas" or "Flue Gas" = product leaving combustion chamber.

Theoretical Oxygen: moles or molar flow rate of O_2 needed for complete combustion of all fuel to $CO_2 + H_2O + SO_2$

Theoretical Air: the amount of air needed to satisfy theoretical O_2

**Air: 21% oxygen → 4.76 mole air / mole O_2

Excess Air: the amount of air that exceeds theoretical air

Percent Excess Air

= 100x(moles fed – moles theoretical)/(moles theoretical)

Balances on Combustion Reactions:

- theoretical oxygen is calculated from stoichiometry based on complete oxidation (combustion) of all reactants– regardless of how much is really reacted, or whether it is actually completely oxidized.

- Any of the balance methods can be used, but atomic balances are preferred / typically the easiest.

Composition on a dry basis: the composition of a gas that contains water, but calculated with the water taken out.

$$\left.\begin{aligned}\text{Wet Gas}: y_{N_2} &= 0.5\\ y_{CO_2} &= 0.3\\ y_{O_2} &= 0.1\\ y_{H_2O} &= 0.1\end{aligned}\right\}$$

↑

10% water, 90% dry gas

$$\text{Dry Basis} \Rightarrow y_{N_2} = \frac{0.5}{0.9} = 0.56$$

$$y_{CO_2} = \frac{0.3}{0.9} = 0.33$$

$$y_{O_2} = \frac{0.1}{0.9} = \frac{0.11}{1.00}$$

If y_{N2} = 0.6 on dry basis, but gas has 15% humidity:

Page 164 test yourself

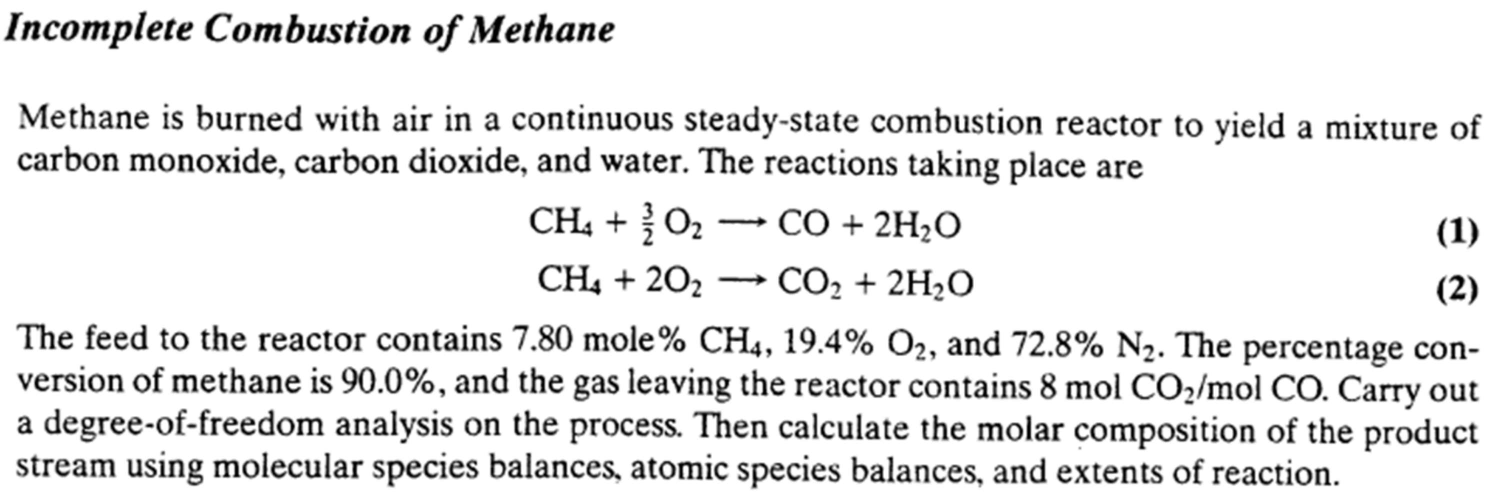
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

$CH_4 + 3/2\ O_2 \rightarrow CO + 2\ H_2O$

100 mol/h CH_4

1) 2x100 = 200 mol/h
2) Still 200 mol/h !!!
3) 200 mol/h x 4.76 mole air / mole O2 = 952 mole air/h
4) 100 = 100*(n – 952)/952 → n = 1904 mole/h (= 2x952)
5) % excess = 100*(300-200)/200 = 50%

Example 4.7-1



Incomplete Combustion of Methane

Methane is burned with air in a continuous steady-state combustion reactor to yield a mixture of carbon monoxide, carbon dioxide, and water. The reactions taking place are

$$CH_4 + \frac{3}{2}O_2 \longrightarrow CO + 2H_2O \qquad \textbf{(1)}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \textbf{(2)}$$

The feed to the reactor contains 7.80 mole% CH_4, 19.4% O_2, and 72.8% N_2. The percentage conversion of methane is 90.0%, and the gas leaving the reactor contains 8 mol CO_2/mol CO. Carry out a degree-of-freedom analysis on the process. Then calculate the molar composition of the product stream using molecular species balances, atomic species balances, and extents of reaction.

Flow, mol/s		
Total n_i		
Comp, n_{ij} nM nO nN2 nC nD nW		
n_{uk}	0	6

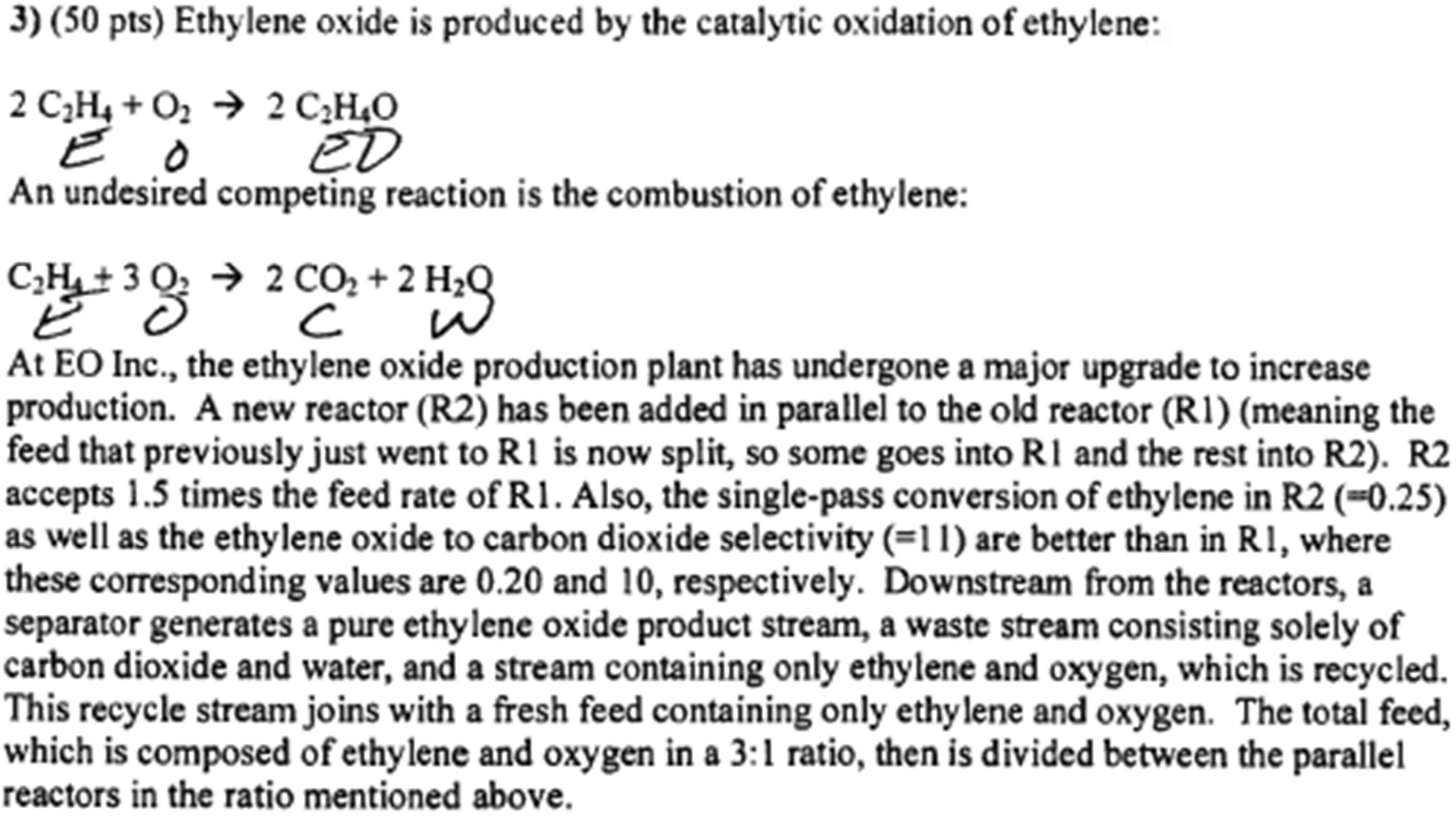
$$n_{df} = n_{uk} - n_{at\ bal} - n_{mol\ bal} - n_{other}$$

$$6 \ - \ 3 \ - \ 1\ (N_2) \ - \ 2 \ = \ 0$$ ✓

input = output

Example: Ethane burned with 50% excess air, to 90% conversion. 25% of the ethane burned forms CO, and the balance CO_2. Calculate composition of the stack gas ***on a dry basis***, and the mole ratio of water to dry stack gas.

Old exam question…



3) (50 pts) Ethylene oxide is produced by the catalytic oxidation of ethylene:

$$\underset{E}{2\,C_2H_4} + \underset{O}{O_2} \rightarrow \underset{EO}{2\,C_2H_4O}$$

An undesired competing reaction is the combustion of ethylene:

$$\underset{E}{C_2H_4} + \underset{O}{3\,O_2} \rightarrow \underset{C}{2\,CO_2} + \underset{W}{2\,H_2O}$$

At EO Inc., the ethylene oxide production plant has undergone a major upgrade to increase production. A new reactor (R2) has been added in parallel to the old reactor (R1) (meaning the feed that previously just went to R1 is now split, so some goes into R1 and the rest into R2). R2 accepts 1.5 times the feed rate of R1. Also, the single-pass conversion of ethylene in R2 (=0.25) as well as the ethylene oxide to carbon dioxide selectivity (=11) are better than in R1, where these corresponding values are 0.20 and 10, respectively. Downstream from the reactors, a separator generates a pure ethylene oxide product stream, a waste stream consisting solely of carbon dioxide and water, and a stream containing only ethylene and oxygen, which is recycled. This recycle stream joins with a fresh feed containing only ethylene and oxygen. The total feed, which is composed of ethylene and oxygen in a 3:1 ratio, then is divided between the parallel reactors in the ratio mentioned above.