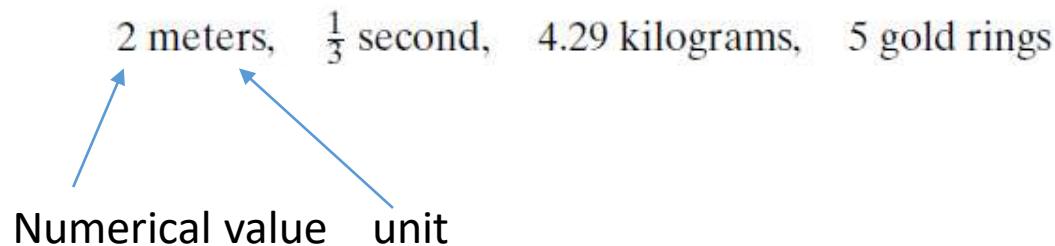


Lecture 4

Units and Dimensions



Dimensions

Addition/subtraction

$$3 \text{ cm} - 1 \text{ cm} = 2 \text{ cm} \quad (3x - x = 2x)$$

but

$$3 \text{ cm} - 1 \text{ mm} \text{ (or } 1 \text{ s)} = ? \quad (3x - y = ?)$$

Multiplication/division

$$3 \text{ N} \times 4 \text{ m} = 12 \text{ N}\cdot\text{m}$$

$$\frac{5.0 \text{ km}}{2.0 \text{ h}} = 2.5 \text{ km/h}$$

$$7.0 \frac{\text{km}}{\text{h}} \times 4 \text{ h} = 28 \text{ km}$$

$$3 \text{ m} \times 4 \text{ m} = 12 \text{ m}^2$$

Conversion of Units

$$\frac{1 \text{ cm}}{10 \text{ mm}} \quad (1 \text{ centimeter per 10 millimeters}) \quad (2.2-1)$$

$$\frac{10 \text{ mm}}{1 \text{ cm}} \quad (10 \text{ millimeters per centimeter}) \quad (2.2-2)$$

$$\left[\frac{10 \text{ mm}}{1 \text{ cm}} \right]^2 = \frac{100 \text{ mm}^2}{1 \text{ cm}^2} \quad (2.2-3)$$

Ratios of the form of Equations 2.2-1, 2.2-2, and 2.2-3 are known as **conversion factors**.

EXAMPLE 2.2-1

Conversion of Units

Convert an acceleration of 1 cm/s^2 to its equivalent in km/yr^2 .

SOLUTION

$$\begin{array}{c|c|c|c|c|c} 1 \text{ cm} & 3600^2 \text{ s}^2 & 24^2 \text{ h}^2 & 365^2 \text{ day}^2 & 1 \text{ m} & 1 \text{ km} \\ \hline \text{s}^2 & 1^2 \text{ h}^2 & 1^2 \text{ day}^2 & 1^2 \text{ yr}^2 & 10^2 \text{ cm} & 10^3 \text{ m} \\ \hline & (3600 \times 24 \times 365)^2 \text{ km} & & & & 9.95 \times 10^9 \text{ km/yr}^2 \end{array}$$

A principle illustrated in this example is that raising a quantity (in particular, a conversion factor) to a power raises its units to the same power. The conversion factor for h^2/day^2 is therefore the square of the factor for h/day :

$$\left(\frac{24 \text{ h}}{1 \text{ day}} \right)^2 = 24^2 \frac{\text{h}^2}{\text{day}^2}$$

System of Units

Base Units

Multiple Units

Derived Units

SI and CGS units

Table 2.3-1 SI and CGS Units

<i>Base Units</i>		
Quantity	Unit	Symbol
Length	meter (SI)	m
	centimeter (CGS)	cm
Mass	kilogram (SI)	kg
	gram (CGS)	g
Moles	gram-mole	mol or g-mole
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Light intensity	candela	cd

Multiple Unit Preferences

tera (T) = 10^{12}	centi (c) = 10^{-2}
giga (G) = 10^9	milli (m) = 10^{-3}
mega (M) = 10^6	micro (μ) = 10^{-6}
kilo (k) = 10^3	nano (n) = 10^{-9}

Derived Units

Quantity	Unit	Symbol	Equivalent in Terms of Base Units
Volume	liter	L	0.001 m^3 1000 cm^3
Force	newton (SI)	N	$1 \text{ kg} \cdot \text{m/s}^2$
	dyne (CGS)		$1 \text{ g} \cdot \text{cm/s}^2$
Pressure	pascal (SI)	Pa	1 N/m^2
Energy, work	joule (SI)	J	$1 \text{ N} \cdot \text{m} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$
	erg (CGS)		$1 \text{ dyne} \cdot \text{cm} = 1 \text{ g} \cdot \text{cm}^2/\text{s}^2$
	gram-calorie	cal	$4.184 \text{ J} = 4.184 \text{ kg} \cdot \text{m}^2/\text{s}^2$
Power	watt	W	$1 \text{ J/s} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^3$

Significant figures, precision

Significant figures

2300 or 2.3×10^3 has two significant figures.

2300. or 2.300×10^3 has four significant figures.

2300.0 or 2.3000×10^3 has five significant figures.

23,040 or 2.304×10^4 has four significant figures.

0.035 or 3.5×10^{-2} has two significant figures.

0.03500 or 3.500×10^{-2} has four significant figures.

Multiplication/division

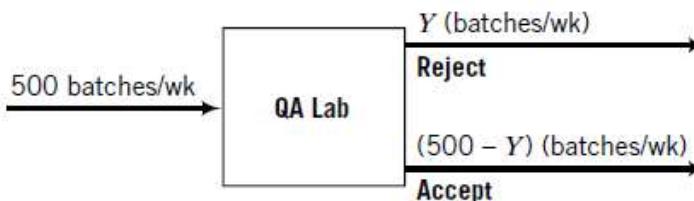
$$(3) \quad (4) \quad (7) \quad (3) \\ (3.57)(4.286) = 15.30102 \implies 15.3$$

$$(2) \quad (4) \quad (3) \quad (9) \quad (2) \quad (2) \\ (5.2 \times 10^{-4})(0.1635 \times 10^7)/(2.67) = 318.426966 \implies 3.2 \times 10^2 = 320$$

Sample variance of scattered data

EXAMPLE 2.5-2 Statistical Quality Control

Five hundred batches of a pigment are produced each week. In the plant's quality assurance (QA) program, each batch is subjected to a precise color analysis test. If a batch does not pass the test, it is rejected and sent back for reformulation.



Let Y be the number of bad batches produced per week, and suppose that QA test results for a 12-week base period are as follows:

Week	1	2	3	4	5	6	7	8	9	10	11	12
\bar{Y}	17	27	18	18	23	19	18	21	20	19	21	18

The company policy is to regard the process operation as normal as long as the number of bad batches produced in a week is no more than three standard deviations above the mean value for the base period (i.e., as long as $Y \leq \bar{Y} + 3s_Y$). If Y exceeds this value, the process is shut down for remedial maintenance (a long and costly procedure). Such large deviations from the mean might occur as part of the normal scatter of the process, but so infrequently that if it happens the existence of an abnormal problem in the process is considered the more likely explanation.

1. How many bad batches in a week would it take to shut down the process?
2. What would be the limiting value of Y if two standard deviations instead of three were used as the cutoff criterion? What would be the advantage and disadvantage of using this stricter criterion?

SOLUTION

1. From Equations 2.5-1, 2.5-3, and 2.5-4, the sample mean, sample variance, and sample standard deviation of Y during the base period are

$$\bar{Y} = \frac{1}{12} \sum_{j=1}^{12} (17 + 27 + \cdots + 18) = 19.9 \text{ batches/wk}$$

$$s_Y^2 = \frac{1}{11} [(17 - 19.9)^2 + (27 - 19.9)^2 + \cdots + (18 - 19.9)^2] = 7.9 \text{ (batches/wk)}^2$$

$$s_Y = \sqrt{7.9} = 2.8 \text{ batches/wk}$$

The maximum allowed value of Y is

$$\bar{Y} + 3s_Y = 19.9 + (3)(2.8) = \boxed{28.3}$$

If 29 or more bad batches are produced in a week, the process must be shut down for maintenance.

2. $\bar{Y} + 2s_Y = 19.9 + (2)(2.8) = \boxed{25.5}$. If this criterion were used, 26 bad batches in a week would be enough to shut down the process. The advantage is that if something *has* gone wrong with the process the problem will be corrected sooner and fewer bad batches will be made in the long run. The disadvantage is that more costly shutdowns may take place when nothing is wrong, the large number of bad batches simply reflecting normal scatter in the process.

EXAMPLE 3.3-1**Conversion Between Mass and Moles**

How many of each of the following are contained in 100.0 g of CO₂ ($M = 44.01$)? (1) mol CO₂; (2) lb-moles CO₂; (3) mol C; (4) mol O; (5) mol O₂; (6) g O; (7) g O₂; (8) molecules of CO₂.

SOLUTION

1.

$$\frac{100.0 \text{ g CO}_2}{44.01 \text{ g CO}_2} \left| \begin{array}{c} 1 \text{ mol CO}_2 \\ \hline \end{array} \right. = \boxed{2.273 \text{ mol CO}_2}$$

2.

$$\frac{2.273 \text{ mol CO}_2}{453.6 \text{ mol}} \left| \begin{array}{c} 1 \text{ lb-mol} \\ \hline \end{array} \right. = \boxed{5.011 \times 10^{-3} \text{ lb-mole CO}_2}$$

Each molecule of CO₂ contains one atom of C, one molecule of O₂, or two atoms of O. Therefore, each 6.02×10^{23} molecules of CO₂ (1 mol) contains 1 mol C, 1 mol O₂, or 2 mol O. Thus,

3.

$$\frac{2.273 \text{ mol CO}_2}{1 \text{ mol CO}_2} \left| \begin{array}{c} 1 \text{ mol C} \\ \hline \end{array} \right. = \boxed{2.273 \text{ mol C}}$$

4.

$$\frac{2.273 \text{ mol CO}_2}{1 \text{ mol CO}_2} \left| \begin{array}{c} 2 \text{ mol O} \\ \hline \end{array} \right. = \boxed{4.546 \text{ mol O}}$$

5.

$$\frac{2.273 \text{ mol CO}_2}{1 \text{ mol CO}_2} \left| \begin{array}{c} 1 \text{ mol O}_2 \\ \hline \end{array} \right. = \boxed{2.273 \text{ mol O}_2}$$

6.

$$\frac{4.546 \text{ mol O}}{1 \text{ mol O}} \left| \begin{array}{c} 16.0 \text{ g O} \\ \hline \end{array} \right. = \boxed{72.7 \text{ g O}}$$

7.

$$\frac{2.273 \text{ mol O}_2}{1 \text{ mol O}_2} \left| \begin{array}{c} 32.0 \text{ g O}_2 \\ \hline \end{array} \right. = \boxed{72.7 \text{ g O}_2}$$

8.

$$\frac{2.273 \text{ mol CO}_2}{1 \text{ mol}} \left| \begin{array}{c} 6.02 \times 10^{23} \text{ molecules} \\ \hline \end{array} \right. = \boxed{1.37 \times 10^{24} \text{ molecules}}$$

Note: Part 7 could also be done by observing from the molecular formula that each 44.0 g of CO₂ contains 32.0 g of O₂ or O, so that

$$\frac{100.0 \text{ g CO}_2}{44.0 \text{ g CO}_2} \left| \begin{array}{c} 32.0 \text{ g O}_2 \\ \hline \end{array} \right. = 72.7 \text{ g O}_2$$

EXAMPLE 3.3-2 *Conversions Using Mass and Mole Fractions*

A solution contains 15% A by mass ($x_A = 0.15$) and 20 mole % B ($y_B = 0.20$).

1. Calculate the mass of A in 175 kg of the solution.

$$\frac{175 \text{ kg solution}}{\text{kg solution}} \left| \begin{array}{c} 0.15 \text{ kg A} \\ \hline \end{array} \right. = \boxed{26 \text{ kg A}}$$

2. Calculate the mass flow rate of A in a stream of solution flowing at a rate of 53 lb_m/h.

$$\frac{53 \text{ lb}_m}{\text{h}} \left| \begin{array}{c} 0.15 \text{ lb}_m \text{ A} \\ \hline \text{lb}_m \end{array} \right. = \boxed{8.0 \frac{\text{lb}_m \text{ A}}{\text{h}}}$$

(If a mass or molar unit—such as lb_m in 53 lb_m/h—is not followed by the name of a species, the unit should be understood to refer to the total mixture or solution rather than to a specific component.)

3. Calculate the molar flow rate of B in a stream flowing at a rate of 1000 mol/min.

$$\frac{1000 \text{ mol}}{\text{min}} \left| \begin{array}{c} 0.20 \text{ mol B} \\ \hline \text{mol} \end{array} \right. = \boxed{200 \frac{\text{mol B}}{\text{min}}}$$

4. Calculate the total solution flow rate that corresponds to a molar flow rate of 28 kmol B/s.

$$\frac{28 \text{ kmol B}}{\text{s}} \left| \begin{array}{c} 1 \text{ kmol solution} \\ \hline 0.20 \text{ kmol B} \end{array} \right. = \boxed{140 \frac{\text{kmol solution}}{\text{s}}}$$

5. Calculate the mass of the solution that contains 300 lb_m of A.

$$\frac{300 \text{ lb}_m \text{ A}}{0.15 \text{ lb}_m \text{ A}} \left| \begin{array}{c} 1 \text{ lb}_m \text{ solution} \\ \hline \end{array} \right. = \boxed{2000 \text{ lb}_m \text{ solution}}$$

EXAMPLE 3.3-5**Conversion Between Mass, Molar, and Volumetric Flow Rates of a Solution**

A 0.50-molar aqueous solution of sulfuric acid flows into a process unit at a rate of 1.25 m³/min. The specific gravity of the solution is 1.03. Calculate (1) the mass concentration of H₂SO₄ in kg/m³, (2) the mass flow rate of H₂SO₄ in kg/s, and (3) the mass fraction of H₂SO₄.

SOLUTION**1.**

$$C_{H_2SO_4} \left(\frac{\text{kg H}_2\text{SO}_4}{\text{m}^3} \right) = \frac{0.50 \text{ mol H}_2\text{SO}_4}{\text{L}} \left| \begin{array}{c} 98 \text{ g} \\ \text{mol} \end{array} \right| \left| \begin{array}{c} 1 \text{ kg} \\ 10^3 \text{ g} \end{array} \right| \left| \begin{array}{c} 10^3 \text{ L} \\ 1 \text{ m}^3 \end{array} \right|$$
$$= \boxed{49 \frac{\text{kg H}_2\text{SO}_4}{\text{m}^3}}$$

2.

$$\dot{m}_{H_2SO_4} \left(\frac{\text{kg H}_2\text{SO}_4}{\text{s}} \right) = \frac{1.25 \text{ m}^3}{\text{min}} \left| \begin{array}{c} 49 \text{ kg H}_2\text{SO}_4 \\ \text{m}^3 \end{array} \right| \left| \begin{array}{c} 1 \text{ min} \\ 60 \text{ s} \end{array} \right| = \boxed{1.0 \frac{\text{kg H}_2\text{SO}_4}{\text{s}}}$$

3. The mass fraction of H₂SO₄ equals the ratio of the mass flow rate of H₂SO₄—which we know—to the total mass flow rate, which can be calculated from the total volumetric flow rate and the solution density.

$$\rho_{\text{solution}} = (1.03) \left(\frac{1000 \text{ kg}}{\text{m}^3} \right) = 1030 \frac{\text{kg}}{\text{m}^3}$$



$$\dot{m}_{\text{solution}} \left(\frac{\text{kg}}{\text{s}} \right) = \frac{1.25 \text{ m}^3 \text{ solution}}{\text{min}} \left| \begin{array}{c} 1030 \text{ kg} \\ \text{m}^3 \text{ solution} \end{array} \right| \left| \begin{array}{c} 1 \text{ min} \\ 60 \text{ s} \end{array} \right| = 21.46 \frac{\text{kg}}{\text{s}}$$



$$x_{H_2SO_4} = \frac{\dot{m}_{H_2SO_4}}{\dot{m}_{\text{solution}}} = \frac{1.0 \text{ kg H}_2\text{SO}_4/\text{s}}{21.46 \text{ kg solution/s}} = \boxed{0.048 \frac{\text{kg H}_2\text{SO}_4}{\text{kg solution}}}$$

Lecture 5

4.1 Process Classification

- Batch process
- Continuous process
- Semibatch process
- Steady state
- Unsteady or transient state

Classify the following processes as batch, continuous, or semibatch, and transient or steady-state.

1. A balloon is filled with air at a steady rate of 2 g/min.
2. A bottle of milk is taken from the refrigerator and left on the kitchen table.
3. Water is boiled in an open flask.
4. Carbon monoxide and steam are fed into a tubular reactor at a steady rate and react to form carbon dioxide and hydrogen. Products and unused reactants are withdrawn at the other end. The reactor contains air when the process is started up. The temperature of the reactor is constant, and the composition and flow rate of the entering reactant stream are also independent of time. Classify the process (a) initially and (b) after a long period of time has elapsed.

4.2 Balances

4.2a The General Balance Equation

Conservation

$$\begin{array}{l} \text{input} \\ (\text{enters} \\ \text{through} \\ \text{system} \\ \text{boundaries}) \end{array} + \begin{array}{l} \text{generation} \\ (\text{produced} \\ \text{within} \\ \text{system}) \end{array} - \begin{array}{l} \text{output} \\ (\text{leaves} \\ \text{through} \\ \text{system} \\ \text{boundaries}) \end{array} - \begin{array}{l} \text{consumption} \\ (\text{consumed} \\ \text{within} \\ \text{system}) \end{array} = \begin{array}{l} \text{accumulation} \\ (\text{buildup} \\ \text{within} \\ \text{system}) \end{array}$$

(4.2-1)

This course – mass

Subsequent courses – momentum, energy

EXAMPLE 4.2-1 *The General Balance Equation*

Each year 50,000 people move into a city, 75,000 people move out, 22,000 are born, and 19,000 die.
Write a balance on the population of the city.

SOLUTION

Let P denote people:

$$\text{input} + \text{generation} - \text{output} - \text{consumption} = \text{accumulation}$$

$$50,000 \frac{P}{\text{yr}} + 22,000 \frac{P}{\text{yr}} - 75,000 \frac{P}{\text{yr}} - 19,000 \frac{P}{\text{yr}} = A \left(\frac{P}{\text{yr}} \right)$$



$$A = -22,000 \frac{P}{\text{yr}}$$

Each year the city's population decreases by 22,000 people.

Two types of balances

1. Differential balances

Rate

Applied to continuous steady state systems

2. Integral balances

Amount

Applied to batch systems – between initial and final states

The following rules may be used to simplify the material balance equation:

- If the balanced quantity is total mass, set generation = 0 and consumption = 0. Except in nuclear reactions, mass can neither be created nor destroyed.
- If the balanced substance is a nonreactive species (neither a reactant nor a product), set generation = 0 and consumption = 0.
- If a system is at steady state, set accumulation = 0, regardless of what is being balanced. By definition, in a steady-state system nothing can change with time, including the amount of the balanced quantity.

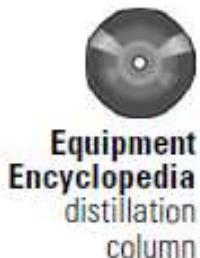
4.2b Balances on Continuous Steady State Processes

$$\text{input} + \text{generation} = \text{output} + \text{consumption} \quad (4.2-2)$$

If the balance is on a nonreactive species or on total mass, the generation and consumption terms equal zero and the equation reduces to *input* = *output*.

EXAMPLE 4.2-2

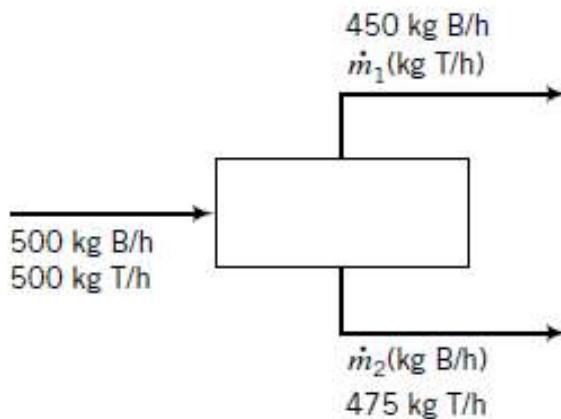
Material Balances on a Continuous Distillation Process



SOLUTION

One thousand kilograms per hour of a mixture of benzene (B) and toluene (T) containing 50% benzene by mass is separated by distillation into two fractions. The mass flow rate of benzene in the top stream is 450 kg B/h and that of toluene in the bottom stream is 475 kg T/h. The operation is at steady state. Write balances on benzene and toluene to calculate the unknown component flow rates in the output streams.

The process can be depicted schematically as follows:



Benzene Balance

$$500 \text{ kg B/h} = 450 \text{ kg B/h} + \dot{m}_2$$



$$\boxed{\dot{m}_2 = 50 \text{ kg B/h}}$$

Toluene Balance

$$500 \text{ kg T/h} = \dot{m}_1 + 475 \text{ kg T/h}$$



$$\boxed{\dot{m}_1 = 25 \text{ kg T/h}}$$

Check the calculation:

Total Mass Balance

$$1000 \text{ kg/h} = 450 + \dot{m}_1 + \dot{m}_2 + 475 \quad (\text{all kg/h})$$

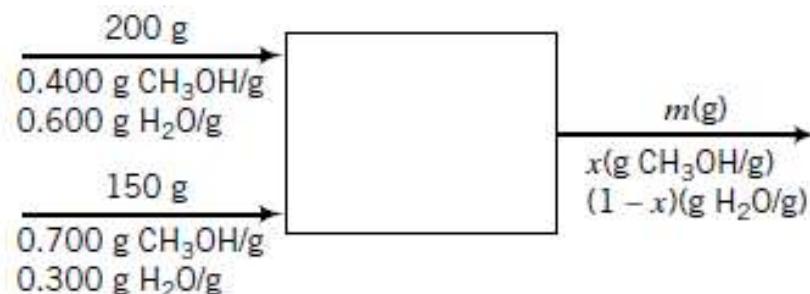
$$\downarrow \dot{m}_1 = 25 \text{ kg/h}, \dot{m}_2 = 50 \text{ kg/h}$$

$$1000 \text{ kg/h} = 1000 \text{ kg/h} \quad \checkmark$$

4.2c Integral Balances on Batch Processes

EXAMPLE 4.2-3 *Balances on a Batch Mixing Process*

Two methanol–water mixtures are contained in separate flasks. The first mixture contains 40.0 wt% methanol, and the second contains 70.0 wt% methanol. If 200 g of the first mixture is combined with 150 g of the second, what are the mass and composition of the product?



SOLUTION

Observe that the input and output “streams” shown on the chart denote the initial and final states for this batch process. Since no reactions are involved, the generation and consumption terms of Equation 4.2-3 may be omitted so that all balances have the simple form “*input = output*.”

Total Mass Balance

$$200 \text{ g} + 150 \text{ g} = m$$



$$m = 350 \text{ g}$$

Methanol Balance

$$\frac{200 \text{ g}}{\text{g}} \left| \begin{array}{c} 0.400 \text{ g CH}_3\text{OH} \\ \hline \end{array} \right. + \frac{150 \text{ g}}{\text{g}} \left| \begin{array}{c} 0.700 \text{ g CH}_3\text{OH} \\ \hline \end{array} \right. = \frac{m(\text{g})}{\text{(g)}} \left| \begin{array}{c} x(\text{g CH}_3\text{OH}) \\ \hline \end{array} \right.$$

$\downarrow m = 350 \text{ g}$

$$x = 0.529 \text{ g CH}_3\text{OH/g}$$

We now know everything about the product, including the mass fraction of water (what is it?). A water balance serves only to check the solution.

Water Balance (Verify that each additive term has the unit g H₂O.)

$$\text{input} = \text{output}$$

$$(200)(0.600) + (150)(0.300) = (350)(1 - 0.529) \quad (\text{Verify!})$$

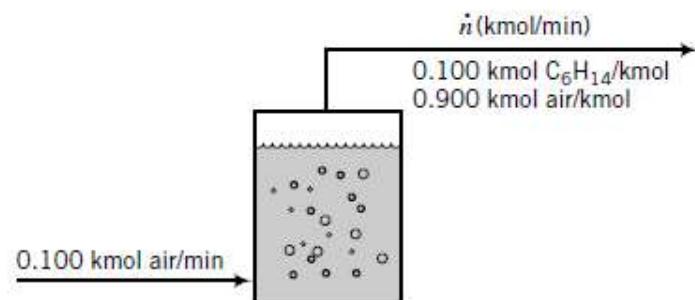
\downarrow

$$165 \text{ g H}_2\text{O} = 165 \text{ g H}_2\text{O} \checkmark$$

4.2c Integral Balances on Semi-Batch and Continuous Processes

EXAMPLE 4.2-4 Integral Balance on a Semibatch Process

Air is bubbled through a drum of liquid hexane at a rate of 0.100 kmol/min. The gas stream leaving the drum contains 10.0 mole% hexane vapor. Air may be considered insoluble in liquid hexane. Use an integral balance to estimate the time required to vaporize 10.0 m³ of the liquid.



SOLUTION

We begin with a differential balance on air. Since we assume that air neither dissolves in the liquid (*accumulation* = 0) nor reacts with hexane in the process unit (*generation* = *consumption* = 0), the balance reduces to *input* = *output*:

$$0.100 \frac{\text{kmol air}}{\text{min}} = \frac{0.900 \text{ kmol air}}{\text{kmol}} \left| \begin{array}{c} \dot{n}(\text{kmol}) \\ (\text{min}) \end{array} \right\| \implies \dot{n} = 0.111 \text{ kmol/min}$$

We next write an integral hexane balance, proceeding from time $t = 0$ to $t = t_f(\text{min})$, the time we seek to calculate. The balance has the form *accumulation* = $-output$ (*verify*). The accumulation term, which is the total change in the moles of liquid hexane in the system during time t_f , must be negative since hexane is being lost from the system. Since the total number of moles of hexane evaporated occupied a liquid volume of 10.0 cubic meters and (from Table B.1) the specific gravity of liquid hexane is 0.659, the accumulation term equals

$$\Delta n = \frac{-10.0 \text{ m}^3}{\text{L}} \left| \begin{array}{c} 0.659 \text{ kg} \\ \text{L} \end{array} \right| \frac{10^3 \text{ L}}{\text{m}^3} \left| \begin{array}{c} 1 \text{ kmol} \\ 86.2 \text{ kg} \end{array} \right\| = -76.45 \text{ kmol C}_6\text{H}_{14}$$

The output term in the balance is the rate at which hexane is leaving the system [$0.100\dot{n}$ (kmol C₆H₁₄/min)] times the total process time, $t_f(\text{min})$. The balance (*accumulation* = $-output$) is therefore

$$-76.45 \text{ kmol C}_6\text{H}_{14} = -0.100\dot{n}t_f$$

$$\downarrow \dot{n} = 0.111 \text{ kmol/min}$$

$$t_f = 6880 \text{ min}$$

Lecture 6

4.3 Material Balance Calculations

4.3a Flowcharts

The catalytic dehydrogenation of propane is carried out in a continuous packed-bed reactor. One thousand kilograms per hour of pure propane is preheated to a temperature of 670°C before it passes into the reactor. The reactor effluent gas, which includes propane, propylene, methane, and hydrogen, is cooled from 800°C to 110°C and fed to an absorption tower, where the propane and propylene are dissolved in oil. The oil then goes to a stripping tower in which it is heated, releasing the dissolved gases; these gases are recompressed and sent to a distillation column in which the propane and propylene are separated. The propane stream is recycled back to join the feed to the reactor preheater. The product stream from the distillation column contains 98% propylene, and the recycle stream is 97% propane. The stripped oil is recycled to the absorption tower.

For example, suppose a gas containing N₂ and O₂ is combined with propane in a batch combustion chamber in which some (but not all) of the O₂ and C₃H₈ react to form CO₂ and H₂O, and the product is then cooled, condensing the water. The flowchart of this two-unit process might appear as shown in Figure 4.3-1.

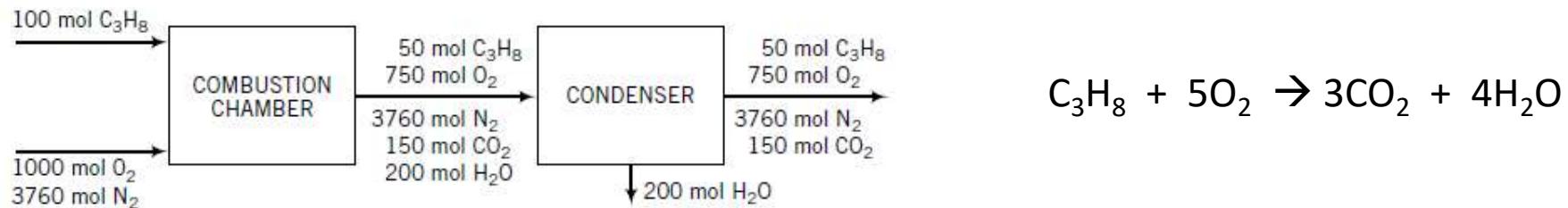


Figure 4.3-1 Flowchart of a combustion-condensation process.

- 1. Write the values and units of all known stream variables at the locations of the streams on the chart.** For example, a stream containing 21 mole% O₂ and 79% N₂ at 320°C and 1.4 atm flowing at a rate of 400 mol/h might be labeled

$\frac{400 \text{ mol/h}}{\longrightarrow}$
0.21 mol O₂/mol
0.79 mol N₂/mol
T = 320°C, P = 1.4 atm

When you have done this for every stream on the chart, you have a summary of the known information about the process, each item being conveniently associated with the part of the process to which it relates.

$\frac{60 \text{ kmol N}_2/\text{min}}{\longrightarrow} \Leftrightarrow \frac{100 \text{ kmol/min}}{\longrightarrow}$
0.6 kmol N₂/kmol
0.4 kmol O₂/kmol

- 2. Assign algebraic symbols to unknown stream variables [such as \dot{m} (kg solution/min), x (lb_m N₂/lb_m), and n (kmol C₃H₈)] and write these variable names and their associated units on the chart.** For example, if you did not know the flow rate of the stream described in the first illustration of step 1, you might label the stream

$\frac{\dot{n}(\text{mol/h})}{\longrightarrow}$
0.21 mol O₂/mol
0.79 mol N₂/mol
T = 320°C, P = 1.4 atm

while if the flow rate were known and the mole fractions were not, the stream might be labeled

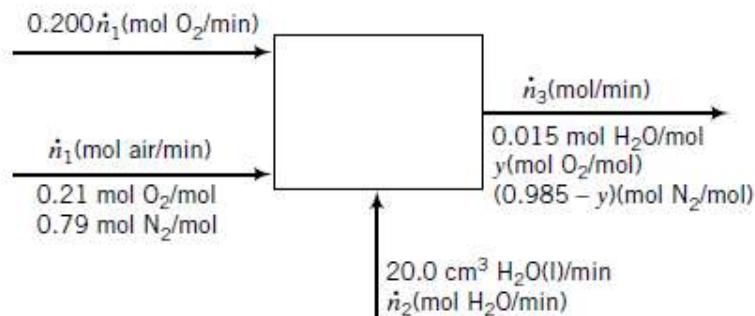
$\frac{400 \text{ mol/h}}{\longrightarrow}$
y(mol O₂/mol)
(1 - y)(mol N₂/mol)
T = 320°C, P = 1.4 atm

EXAMPLE 4.3-1**Flowchart of an Air Humidification and Oxygenation Process**

An experiment on the growth rate of certain organisms requires an environment of humid air enriched in oxygen. Three input streams are fed into an evaporation chamber to produce an output stream with the desired composition.

- A: Liquid water, fed at a rate of $20.0 \text{ cm}^3/\text{min}$
- B: Air (21 mole% O_2 , the balance N_2)
- C: Pure oxygen, with a molar flow rate one-fifth of the molar flow rate of stream B

The output gas is analyzed and is found to contain 1.5 mole% water. Draw and label a flowchart of the process, and calculate all unknown stream variables.

SOLUTION**Notes on the Labeling:**

1. Since the one known flow rate ($20 \text{ cm}^3 \text{ H}_2\text{O}/\text{min}$) is given on a per minute basis, it is most convenient to label all stream flow rates on this basis.
2. Once the variable name ($n̂_1$) is chosen for the air flow rate, the given information about the ratio of the air and O_2 flow rates may be used to label the O_2 flow rate $0.200 n̂_1$.
3. The mole fractions of the components of any stream must add up to 1. Since the mole fraction of H_2O in the outlet stream is known to be 0.015, once the mole fraction of O_2 is labeled y , that of N_2 must be $1 - (y + 0.015) = (0.985 - y) \text{ mol N}_2/\text{mol}$.

The quantity \dot{n}_2 may be calculated from the given volumetric flow rate and the density of liquid water:

$$\dot{n}_2 = \frac{20.0 \text{ cm}^3 \text{ H}_2\text{O}}{\text{min}} \left| \begin{array}{c} 1.00 \text{ g H}_2\text{O} \\ \text{cm}^3 \end{array} \right| \left| \begin{array}{c} 1 \text{ mol} \\ 18.02 \text{ g} \end{array} \right| \Rightarrow \boxed{\dot{n}_2 = 1.11 \frac{\text{mol H}_2\text{O}}{\text{min}}}$$

The three remaining unknowns (\dot{n}_1 , \dot{n}_3 , and y) may be determined from balances, all of which have the simple form *input* = *output* for this nonreactive steady-state process. The balances are easily written by referring to the flowchart.

H₂O Balance

$$\dot{n}_2 \left(\frac{\text{mol H}_2\text{O}}{\text{min}} \right) = \dot{n}_3 \left(\frac{\text{mol}}{\text{min}} \right) \left| \begin{array}{c} 0.015 \text{ mol H}_2\text{O} \\ \text{mol} \end{array} \right.$$

$$\downarrow \dot{n}_2 = 1.11 \text{ mol/min}$$

$$\boxed{\dot{n}_3 = 74.1 \frac{\text{mol}}{\text{min}}}$$

Total Mole Balance

$$0.200\dot{n}_1 + \dot{n}_1 + \dot{n}_2 = \dot{n}_3$$

$$\downarrow \begin{array}{l} \dot{n}_2 = 1.11 \text{ mol/min} \\ \dot{n}_3 = 74.1 \text{ mol/min} \end{array}$$

$$\boxed{\dot{n}_1 = 60.8 \frac{\text{mol}}{\text{min}}}$$

N₂ Balance

$$\frac{\dot{n}_1(\text{mol})}{(\text{min})} \left| \begin{array}{c} 0.79 \text{ mol N}_2 \\ \text{mol} \end{array} \right| = \frac{\dot{n}_3(\text{mol})}{(\text{min})} \left| \begin{array}{c} (0.985 - y)(\text{mol N}_2) \\ (\text{mol}) \end{array} \right|$$

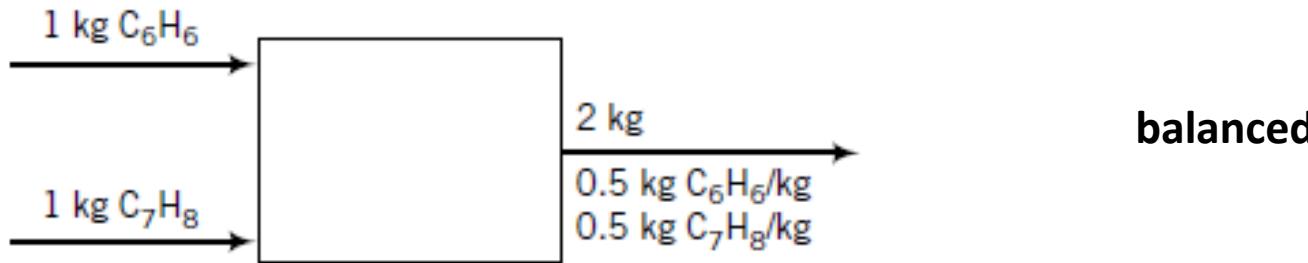
$$\downarrow$$

$$0.79\dot{n}_1 = \dot{n}_3(0.985 - y)$$

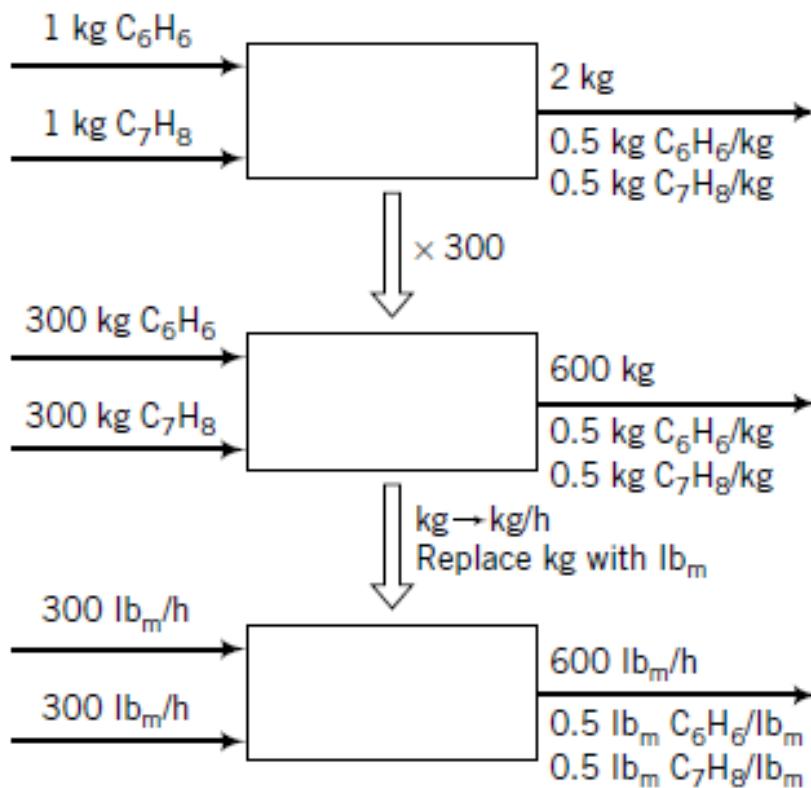
$$\downarrow \begin{array}{l} \dot{n}_1 = 60.8 \text{ mol/min} \\ \dot{n}_3 = 74.1 \text{ mol/min} \end{array}$$

$$\boxed{y = 0.337 \text{ mol O}_2/\text{mol}}$$

4.3b Flowchart Scaling and Basis of Calculations



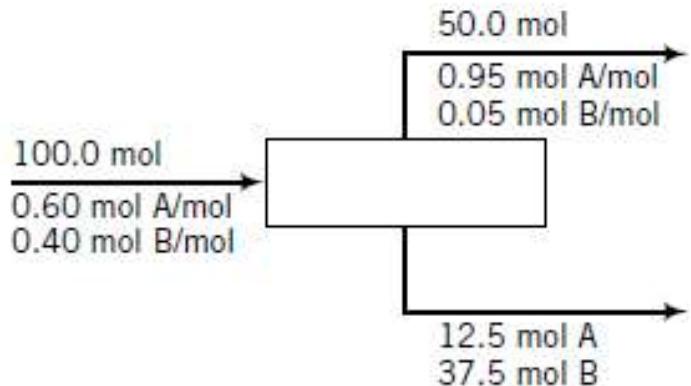
Scale-up



EXAMPLE 4.3-2

Scale-up of a Separation Process Flowchart

A 60–40 mixture (by moles) of A and B is separated into two fractions. A flowchart of the process is shown here.



It is desired to achieve the same separation with a continuous feed of 1250 lb-moles/h. Scale the flowchart accordingly.

The scale factor is

$$\frac{1250 \text{ lb-moles/h}}{100 \text{ mol}} = 12.5 \frac{\text{lb-moles/h}}{\text{mol}}$$

The masses of all streams in the batch process are converted to flow rates as follows:

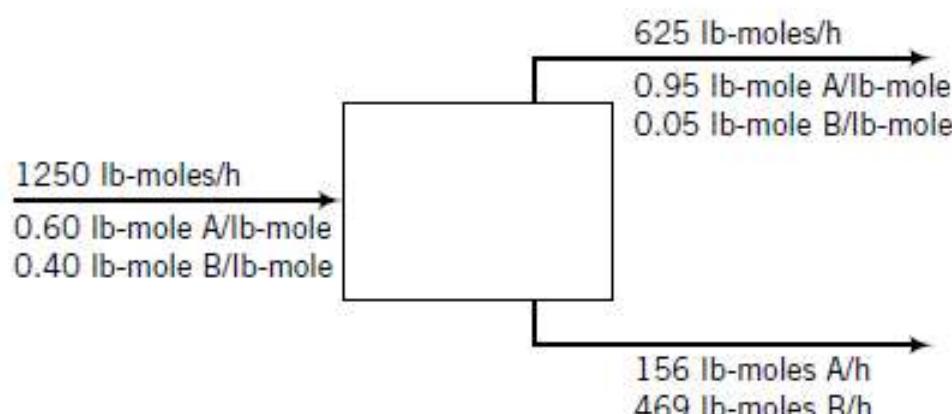
Feed: $\frac{100 \text{ mol}}{\text{mol}} \left| \begin{array}{c} 12.5 \text{ lb-moles/h} \\ \hline \end{array} \right. = 1250 \frac{\text{lb-moles}}{\text{h}} \quad (\text{as specified})$

Top product stream: $(50.0)(12.5) = 625 \text{ lb-moles/h}$

Bottom product stream: $(12.5)(12.5) = 156 \text{ lb-moles A/h}$

$(37.5)(12.5) = 469 \text{ lb-moles B/h}$

The units of the mole fractions in the top product stream may be changed from mol/mol to lb-mole/lb-mole, but their values remain the same. The flowchart for the scaled-up process follows.



4.3c Balancing a Process



Total Mass Balance:

$$3.0 \frac{\text{kg}}{\text{min}} + 1.0 \frac{\text{kg}}{\text{min}} = \dot{m} \implies \boxed{\dot{m} = 4.0 \text{ kg/min}}$$

Benzene Balance:

$$3.0 \frac{\text{kg C}_6\text{H}_6}{\text{min}} = \frac{\dot{m}(\text{kg})}{(\text{min})} \Big| \frac{x(\text{kg C}_6\text{H}_6)}{(\text{kg})}$$

$\Downarrow \dot{m} = 4.0 \text{ kg/min}$

$$\boxed{x = 0.75 \text{ kg C}_6\text{H}_6/\text{kg}}$$

Rules

1. *The maximum number of independent equations that can be derived by writing balances on a nonreactive system equals the number of chemical species in the input and output streams.*
2. *Write balances first that involve the fewest unknown variables.*

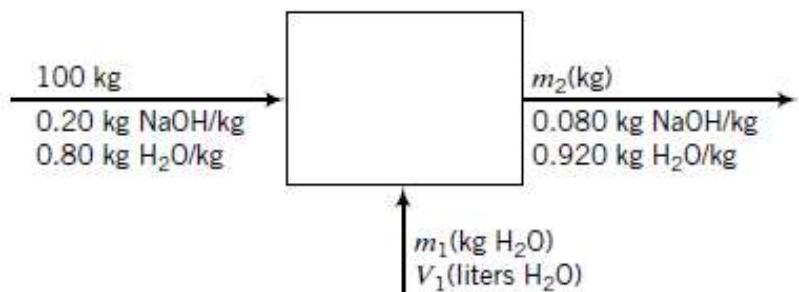
EXAMPLE 4.3-3

Balances on a Mixing Unit

An aqueous solution of sodium hydroxide contains 20.0% NaOH by mass. It is desired to produce an 8.0% NaOH solution by diluting a stream of the 20% solution with a stream of pure water. Calculate the ratios (liters H₂O/kg feed solution) and (kg product solution/kg feed solution).

- **Choose a basis of calculation**—an amount or flow rate of one of the feed or product streams—and then draw and label the flowchart.

We will arbitrarily choose a basis of 100 kg of the 20% feed solution. (We could also have chosen a flow rate of 100 lb_m/min of the 8% product solution or 10 tons of diluent water. The final results do not depend on the basis chosen since we are only asked to find ratios of stream amounts.) The flowchart appears as follows:



- **Express what the problem asks you to determine in terms of the labeled variables on the flowchart.**

The desired quantities are $V_1/100$ (liters H₂O/kg feed solution) and $m_2/100$ (kg product solution/kg feed solution). Our task is therefore to calculate the variables V_1 and m_2 .

- **Count unknown variables and equations relating them.**

If the number of unknowns equals the number of independent equations relating them, you will be able to solve the problem; otherwise, either you have forgotten some relations or the problem is not well defined. In the latter case, there is no point wasting your time by jumping into time-consuming calculations.

- (a) **Unknowns.** Examining the flowchart, we see three unknown variables— m_1 , m_2 , and V_1 .
- (b) **Equations.** *For a nonreactive process that involves N species, up to N independent material balance equations may be written.* Since there are two species in our process (sodium hydroxide and water), we can write two balances. We could write them on sodium hydroxide, water, total mass, atomic sodium, atomic hydrogen, and so on; the point is that once we have written any two, we can obtain no new information by writing a third one.

Since we may only write two material balances, we will need a third equation to solve for our three unknowns (m_1 , m_2 , and V). Fortunately, we have one: the mass and volume of the diluent water, m_1 and V_1 , are related by the density of liquid water, which we know. We thus have three equations in three unknowns and therefore a solvable problem.

- **Outline the solution procedure.**

All balances for this system have the form *input = output*. For example, a total mass balance is $100 \text{ kg} + m_1 = m_2$. Looking at the flowchart, we can see that balances on total mass and water each involve two unknowns (m_1 and m_2), a sodium hydroxide balance only involves one unknown (m_2), and the water density relationship involves two unknowns (m_1 and V_1). We would therefore begin the solution by writing and solving the NaOH balance for m_2 , then writing and solving a total mass or water balance for m_1 , and finally determining V_1 from m_1 and the density.

- **NaOH balance (input = output).**

$$(0.20 \text{ kg NaOH/kg})(100 \text{ kg}) = (0.080 \text{ kg NaOH/kg})m_2 \implies m_2 = 250 \text{ kg NaOH}$$

It is a good practice to write calculated variable values on the flowchart as soon as they are known for ease of use in later calculations. At this point, 250 would therefore be written in place of m_2 on the chart.

- **Total mass balance (input = output).**

$$100 \text{ kg} + m_1 = m_2 \xrightarrow{m_2 = 250 \text{ kg}} m_1 = 150 \text{ kg H}_2\text{O}$$

- **Diluent water volume.** Although we are not given the temperature or pressure at which the mixing is done, the density of liquid water is approximately constant at 1.00 kg/liter (see Equation 3.1-2). We may therefore calculate

$$V_1 = \frac{150 \text{ kg}}{\text{kg}} \times \frac{1.00 \text{ liter}}{\text{kg}} = 150 \text{ liters}$$

- **Ratios requested in problem statement.**

$$\frac{V_1}{100 \text{ kg}} = \boxed{1.50 \text{ liters H}_2\text{O/kg feed solution}}$$

$$\frac{m_2}{100 \text{ kg}} = \boxed{2.50 \text{ kg product solution/kg feed solution}}$$

Exercise: Prove to yourself that you would get the same results for a different basis of calculation.

Lecture 7

4.3d Degree-of-Freedom Analysis

n_{unknowns} = number of unknown variables

$n_{\text{indep eqns}}$ = number of independent equations

$$n_{\text{df}} = 0$$

$$n_{\text{df}} > 0$$

$$n_{\text{df}} < 0$$



$$n_{\text{df}} = n_{\text{unknowns}} - n_{\text{indep eqns}}$$

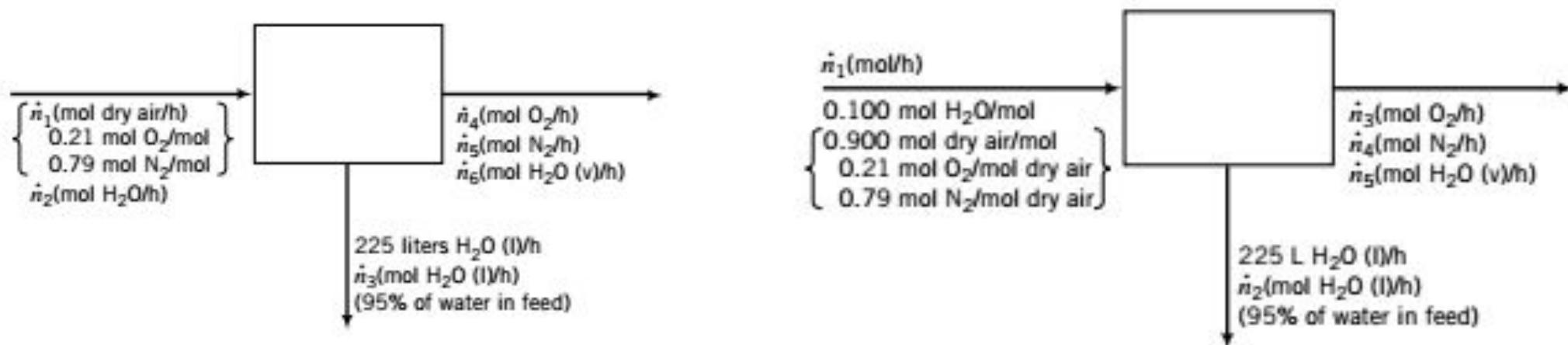
1. Materials balance
2. Energy balance
3. Process specifications
4. Physical properties and laws
5. Physical constraints
6. Stoichiometric relations

EXAMPLE 4.3-4**Degree-of-Freedom Analysis**

A stream of humid air enters a condenser in which 95% of the water vapor in the air is condensed. The flow rate of the condensate (the liquid leaving the condenser) is measured and found to be 225 L/h. Dry air may be taken to contain 21 mole% oxygen, with the balance nitrogen. Calculate the flow rate of the gas stream leaving the condenser and the mole fractions of oxygen, nitrogen, and water in this stream.

SOLUTION

Basis: 225 L/h Condensate



- **Density relationship.**

$$\textcircled{\dot{n}_2} \left(\frac{\text{mol H}_2\text{O(l)}}{\text{h}} \right) = \frac{225 \text{ L H}_2\text{O(l)}}{\text{h}} \Bigg| \frac{1.00 \text{ kg H}_2\text{O(l)}}{\text{L}} \Bigg| \frac{1 \text{ mol H}_2\text{O}}{18.0 \times 10^{-3} \text{ kg}}$$

- **95% Condensation.** $\dot{n}_2 = 0.95 (0.100 \textcircled{\dot{n}_1})$

- **O_2 Balance.** $\dot{n}_1 (0.900)(0.21) = \textcircled{\dot{n}_3}$

- **N_2 Balance.** $\dot{n}_1 (0.900)(0.79) = \textcircled{\dot{n}_4}$

- **H_2O Balance.** $\dot{n}_1 (0.100) = \dot{n}_2 + \textcircled{\dot{n}_5}$

- **Total outlet gas flow rate.** $\textcircled{\dot{n}_{\text{total}}} = \dot{n}_3 + \dot{n}_4 + \dot{n}_5$

- **Outlet gas composition.** $y_{O_2} = \dot{n}_3 / \dot{n}_{\text{total}}, y_{N_2} = \dot{n}_4 / \dot{n}_{\text{total}}, y_{H_2O} = \dot{n}_5 / \dot{n}_{\text{total}}$

The algebra and arithmetic are left as an exercise.

4.3e General Procedure for Single-Unit Process Material Balance Calculations

1. Choose as a basis of calculation an amount or flow rate of one of the process streams.

- If an amount or flow rate of a stream is given in the problem statement, it is usually convenient to use it as the basis of calculation. Subsequently calculated quantities will then be correctly scaled.
- If several stream amounts or flow rates are given, always use them collectively as the basis.
- If no stream amount or flow rate is specified in the problem statement, take as a basis an arbitrary amount or flow rate of a stream with a known composition (e.g., 100 kg or 100 kg/h if all mass fractions are known, or 100 mol or 100 mol/h if all mole fractions are known).

2. Draw a flowchart and fill in all known variable values, including the basis of calculation. Then label unknown stream variables on the chart.

- The flowchart is completely labeled if you can express the mass or mass flow rate (or moles or molar flow rate) of each component of each stream in terms of labeled quantities. Labeled variables for each process stream should therefore include either
 - (a) the total mass [e.g., $m_1(\text{kg})$] or mass flow rate [$\dot{m}_1(\text{kg/s})$] and the mass fractions of all stream components [e.g., $y_{\text{CH}_4} (\text{kg CH}_4/\text{kg})$], or
 - (b) the total moles [e.g., $n_1(\text{kmol})$] or molar flow rate [$\dot{n}_1(\text{kmol/s})$] and the mole fractions of all stream components [e.g., $y_{\text{CH}_4} (\text{kmol CH}_4/\text{kmol})$], or
 - (c) for each stream component, the mass [e.g., $m_{\text{H}_2}(\text{kg H}_2)$], mass flow rate [$\dot{m}_{\text{H}_2}(\text{kg SO}_2/\text{s})$], moles [$n_{\text{CO}}(\text{kmol CO})$], or molar flow rate [$\dot{n}_{\text{CO}}(\text{kmol CO/s})$].

- If you are given (or you can easily determine) either the amount or flow rate or any of the component fractions for a stream, label the total stream quantity or flow rate and the component fractions (categories (a) and (b) in the preceding list). If you only know the species present but have no quantitative information, label component quantities or flow rates (category (c) in the preceding list). Any labeling system will work for any stream, but the algebra tends to be simpler if you follow these rules of thumb.
- Try to incorporate given relationships between unknown quantities in the labeling. For example, if you know that the molar flow rate of Stream 2 is double that of Stream 1, label the flow rates \dot{n}_1 and $2\dot{n}_1$ rather than \dot{n}_1 and \dot{n}_2 .
- *Label volumetric quantities only if they are given in the problem statement or you are asked to calculate them.* You will write mass or mole balances, but not volume balances.

3. Express what the problem statement asks you to determine in terms of the labeled variables. You will then know which unknowns you have to determine in order to solve the problem.

4. If you are given mixed mass and mole units for a stream (such as a total mass flow rate and component mole fractions or vice versa), **convert all quantities to one basis or the other using the methods of Section 3.3.**

5. Do the degree-of-freedom analysis. Count unknowns and identify equations that relate them. The equations may be any of the six types listed in Section 4.3d: material balances, an energy balance, process specifications, physical property relationships and laws, physical constraints, and stoichiometric relations. If you count more unknown variables than equations or vice versa, figure out what's wrong (e.g., the flowchart is not completely labeled, or an additional relation exists that was not counted, or one or more of your equations are not independent of the others, or the problem is underspecified or overspecified). If the number of unknowns does not equal the number of equations, there is no point wasting time trying to solve the problem.

6. *If the number of unknowns equals the number of equations relating them* (i.e., if the system has zero degrees of freedom), *write the equations in an efficient order (minimizing simultaneous equations) and circle the variables for which you will solve* (as in Example 4.3-4). Start with equations that only involve one unknown variable, then pairs of simultaneous equations containing two unknown variables, and so on. *Do no algebra or arithmetic in this step.*
7. *Solve the equations*, either manually or using equation-solving software. Manual solution should go smoothly since you have already worked out an efficient solution procedure.
8. *Calculate the quantities requested in the problem statement if they have not already been calculated.*
9. *If a stream quantity or flow rate n_g was given in the problem statement and another value n_c was either chosen as a basis or calculated for this stream, scale the balanced process by the ratio n_g/n_c to obtain the final result.*

EXAMPLE 4.3-5***Material Balances on a Distillation Column***

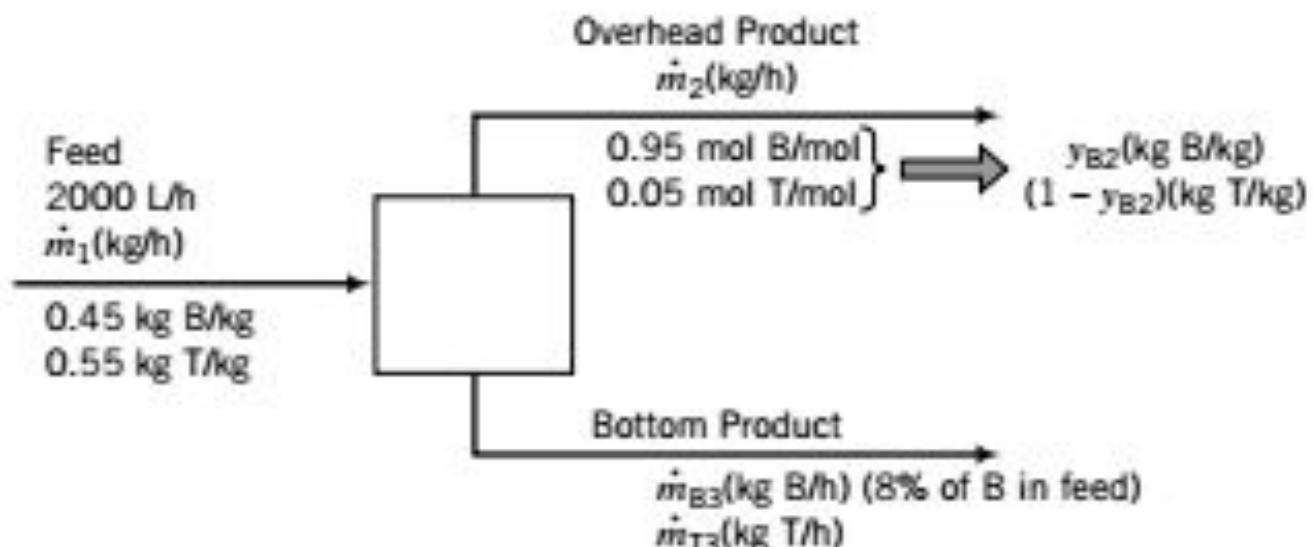
A liquid mixture containing 45.0% benzene (B) and 55.0% toluene (T) by mass is fed to a distillation column. A product stream leaving the top of the column (the *overhead product*) contains 95.0 mole % B, and a bottom product stream contains 8.0% of the benzene fed to the column (meaning that 92% of the benzene leaves with the overhead product). The volumetric flow rate of the feed stream is 2000 L/h and the specific gravity of the feed mixture is 0.872. Determine the mass flow rate of the overhead product stream and the mass flow rate and composition (mass fractions) of the bottom product stream.

SOLUTION

We will explicitly illustrate the implementation of the steps of the procedure just outlined.

1. ***Choose a basis.*** Having no reason to do otherwise, we choose the given feed stream flow rate (2000 L/h) as the basis of calculation.

2. Draw and label the flowchart.



3. Write expressions for the quantities requested in the problem statement. In terms of the quantities labeled on the flowchart, the quantities to be determined are \dot{m}_2 (the overhead product mass flow rate), $\dot{m}_3 = \dot{m}_{B3} + \dot{m}_{T3}$ (the bottom product mass flow rate), $x_B = \dot{m}_{B3}/\dot{m}_3$ (the benzene mass fraction in the bottom product), and $x_T = 1 - x_B$ (the toluene mass fraction). Once we determine \dot{m}_2 , \dot{m}_{B3} , and \dot{m}_{T3} , the problem is essentially solved.

4. Convert mixed units in overhead product stream (see procedure preceding Example 3.3-3).

Basis: 100 kmol overhead \Rightarrow 95.0 kmol B, 5.00 kmol T

$$\Rightarrow (95.0 \text{ kmol B}) \times (78.11 \text{ kg B/kmol B}) = 7420 \text{ kg B}, \quad (5.00 \times 92.13) = 461 \text{ kg T}$$

$$\Rightarrow (7420 \text{ kg B}) + (461 \text{ kg T}) = 7881 \text{ kg mixture}$$

$$\Rightarrow y_{B2} = (7420 \text{ kg B}) / (7881 \text{ kg mixture}) = 0.942 \text{ kg B/kg} \quad (\text{write on chart})$$

The molecular weights of benzene (78.11) and toluene (92.13) were looked up in Table B.1.

5. Perform degree-of-freedom analysis.

- 4 unknowns (\dot{m}_1 , \dot{m}_2 , \dot{m}_{B3} , \dot{m}_{T3})
 - 2 material balances (since there are two molecular species in this nonreactive process)
 - 1 density relationship (relating the mass flow rate to the given volumetric flow rate of the feed)
 - 1 specified benzene split (8% in bottom–92% in overhead)
-

0 degrees of freedom

The problem is therefore solvable.

6. Write system equations and outline a solution procedure. The variables for which each equation will be solved are circled.

- **Volumetric flow rate conversion.** From the given specific gravity, the density of the feed stream is 0.872 kg/L. (Verify.) Therefore,

$$\textcircled{\dot{m}_1} = \left(2000 \frac{\text{L}}{\text{h}}\right) \left(0.872 \frac{\text{kg}}{\text{L}}\right)$$

- **Benzene split fraction.** The benzene in the bottom product stream is 8% of the benzene in the feed stream. This statement translates directly into the equation

$$\textcircled{\dot{m}_{B3}} = 0.08(0.45\dot{m}_1)$$

There are two unknowns remaining on the flowchart (\dot{m}_2 and \dot{m}_{T3}), and we are allowed to write two balances. Balances on total mass and on toluene each involve both unknowns, but a benzene balance only involves \dot{m}_2 (convince yourself, remembering that \dot{m}_{B3} is now known), so we begin with that one.

- **Benzene balance** $0.45\dot{m}_1 = (\dot{m}_2)y_{B2} + \dot{m}_{B3}$
- **Toluene balance** $0.55\dot{m}_1 = (1 - y_{B2})\dot{m}_2 + \dot{m}_{T3}$

7. Do the algebra. The four equations may be solved manually or with equation-solving software. If a manual solution is performed, each newly calculated variable value should be written on the flowchart for ease of reference in the remainder of the solution. The results are $\dot{m}_1 = 1744 \text{ kg/h}$, $\dot{m}_{B3} = 62.8 \text{ kg benzene/h}$, $\boxed{\dot{m}_2 = 766 \text{ kg/h}}$, and $\dot{m}_{T3} = 915 \text{ kg toluene/h}$. (*Verify.*) A total mass balance (which is the sum of the benzene and toluene balances) may be written as a check on this solution:

$$\dot{m}_1 = \dot{m}_2 + \dot{m}_{B3} + \dot{m}_{T3} \implies 1744 \text{ kg/h} = (766 + 62.8 + 915) \text{ kg/h} = 1744 \text{ kg/h}$$

8. Calculate additional quantities requested in the problem statement.

$$\dot{m}_3 = \dot{m}_{B3} + \dot{m}_{T3} = 62.8 \text{ kg/h} + 915 \text{ kg/h} = \boxed{978 \text{ kg/h}}$$

$$y_{B3} = \frac{\dot{m}_{B3}}{\dot{m}_3} = \frac{62.8 \text{ kg B}}{978 \text{ kg/h}} = \boxed{0.064 \text{ kg B/kg}}$$

$$y_{T3} = 1 - y_{B3} = \boxed{0.936 \text{ kg T/kg}}$$

Lecture 8

4.4 Balances on Multiple-Unit Processes

Most industrial processes – multiple-unit processes

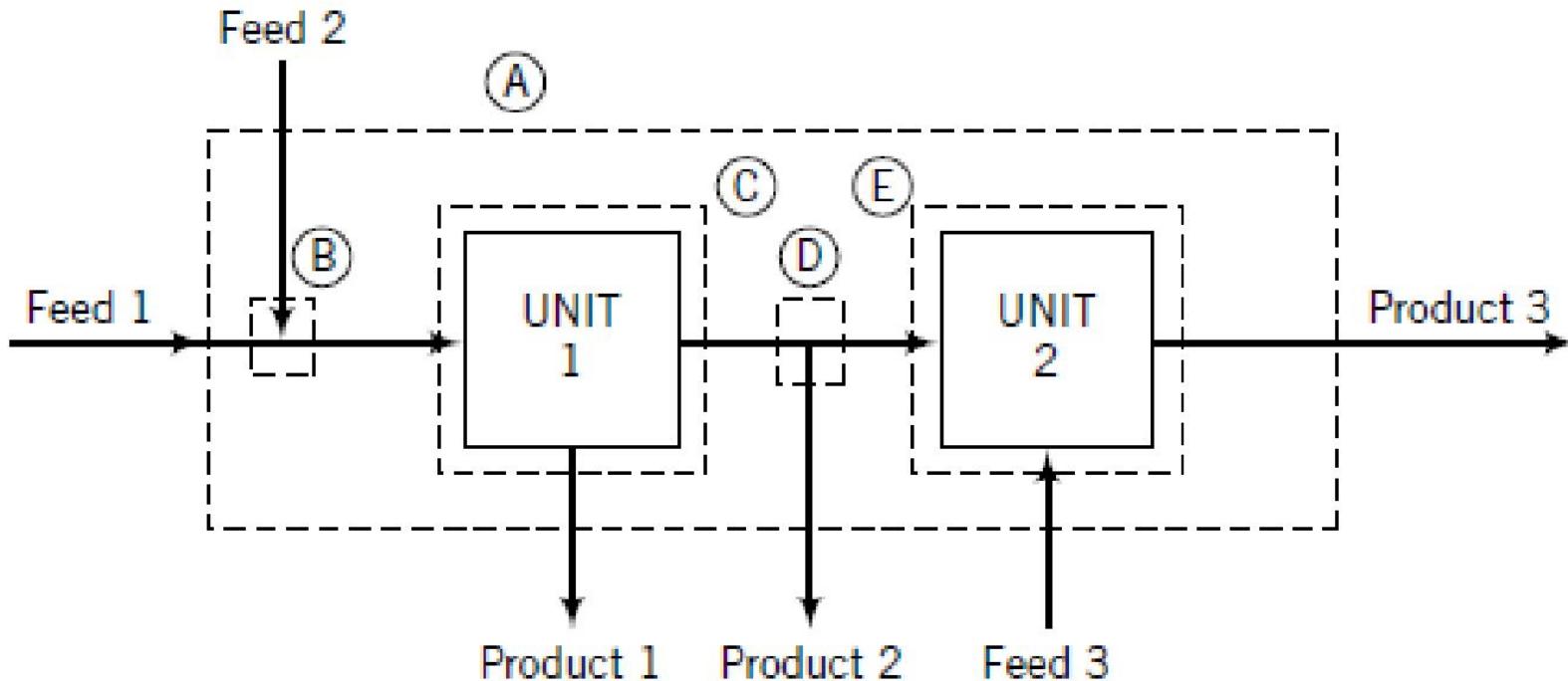
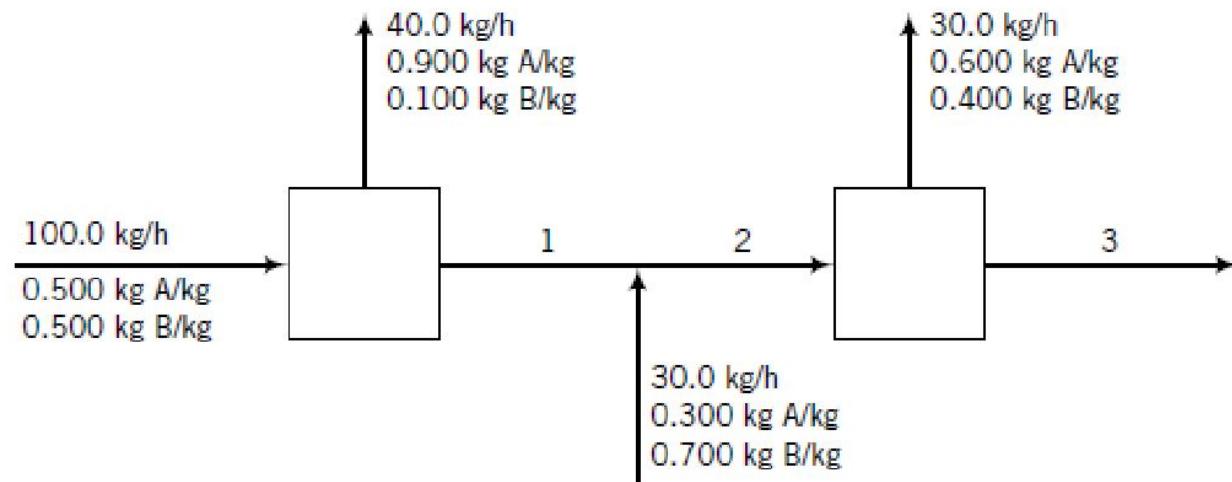


Figure 4.4-1 Flowchart of a two-unit process. Dashed lines denote boundaries of systems about which balances can be written.

EXAMPLE 4.4-1

Two-Unit Process

A labeled flowchart of a continuous steady-state two-unit process is shown below. Each stream contains two components, A and B, in different proportions. Three streams whose flow rates and/or compositions are not known are labeled 1, 2, and 3.

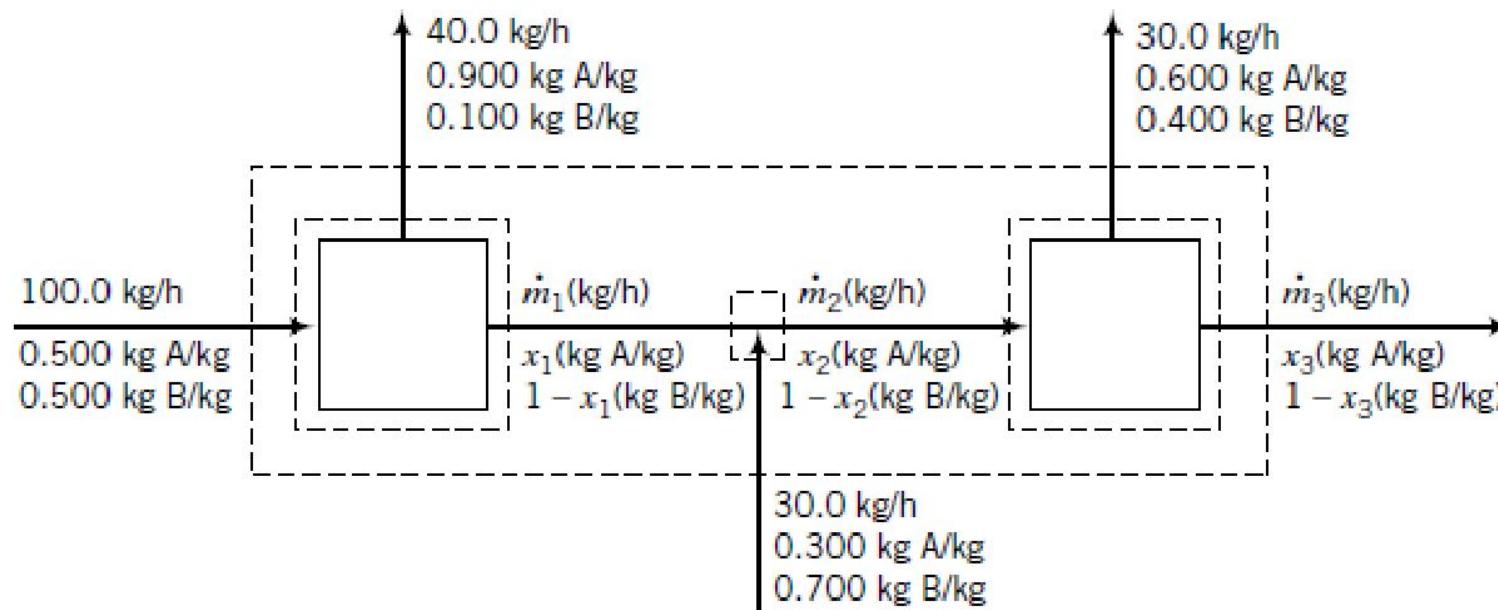


Calculate the unknown flow rates and compositions of streams 1, 2, and 3.

SOLUTION

Basis—Given Flow Rates

The systems about which balances might be written are shown on the following representation of the flowchart:



Degree-of-Freedom Analysis

We first outline the solution procedure by performing degree-of-freedom analyses on different systems. Remember that only variables associated with streams intersecting a system boundary are counted in the analysis of that system.

Overall system (outer dashed boundary):

$$\begin{aligned} 2 \text{ unknowns } (\dot{m}_3, x_3) - 2 \text{ balances (2 species)} &= 0 \text{ degrees of freedom} \\ \implies \underline{\text{Determine } \dot{m}_3 \text{ and } x_3} \end{aligned}$$

In subsequent analyses, we may consider these two variables as known. Suppose we decide to consider the intermediate stream mixing point as the next system.

Mixing point:

$$4 \text{ unknowns } (\dot{m}_1, x_1, \dot{m}_2, x_2) - 2 \text{ balances (2 species)} = 2 \text{ degrees of freedom}$$

We have too many unknowns for the number of available equations. Let us try Unit 1.

Unit 1:

$$\begin{aligned} 2 \text{ unknowns } (\dot{m}_1, x_1) - 2 \text{ balances (2 species)} &= 0 \text{ degrees of freedom} \\ \implies \underline{\text{Determine } \dot{m}_1 \text{ and } x_1} \end{aligned}$$

We may now analyze either the mixing point or Unit 2, each of which has two unknown variables associated with it.

Mixing point:

$$\begin{aligned} 2 \text{ unknowns } (\dot{m}_2, x_2) - 2 \text{ balances (2 species)} &= 0 \text{ degrees of freedom} \\ \implies \underline{\text{Determine } \dot{m}_2 \text{ and } x_2} \end{aligned}$$

Calculations

Overall Mass Balance:

$$(100.0 + 30.0) \frac{\text{kg}}{\text{h}} = (40.0 + 30.0) \frac{\text{kg}}{\text{h}} + \dot{m}_3 \implies \boxed{\dot{m}_3 = 60.0 \text{ kg/h}}$$

Overall Balance on A: (Verify that each additive term has the units kg A/h.)

$$\begin{aligned} (0.500)(100.0) + (0.300)(30.0) &= (0.900)(40.0) + (0.600)(30.0) + x_3(60.0) \\ \implies \boxed{x_3 = 0.0833 \text{ kg A/kg}} \end{aligned}$$

Mass Balance on Unit 1: (each term has the units kg/h)

$$100 = 40 + \dot{m}_1 \implies \boxed{\dot{m}_1 = 60.0 \text{ kg/h}}$$

A Balance on Unit 1: (each additive term has the units kg A/h)

$$(0.500)(100.0) = (0.900)(40.0) + x_1(60.0) \implies \boxed{x_1 = 0.233 \text{ kg A/kg}}$$

Mass Balance on Stream Mixing Point: (Each term has the units kg/h.)

$$\dot{m}_1 + 30.0 = \dot{m}_2 \xrightarrow{\dot{m}_1 = 60.0 \text{ kg/h}} \boxed{\dot{m}_2 = 90.0 \text{ kg/h}}$$

A Balance on Stream Mixing Point: (Each additive term has the units kg A/h.)

$$x_1\dot{m}_1 + (0.300)(30.0) = x_2\dot{m}_2$$

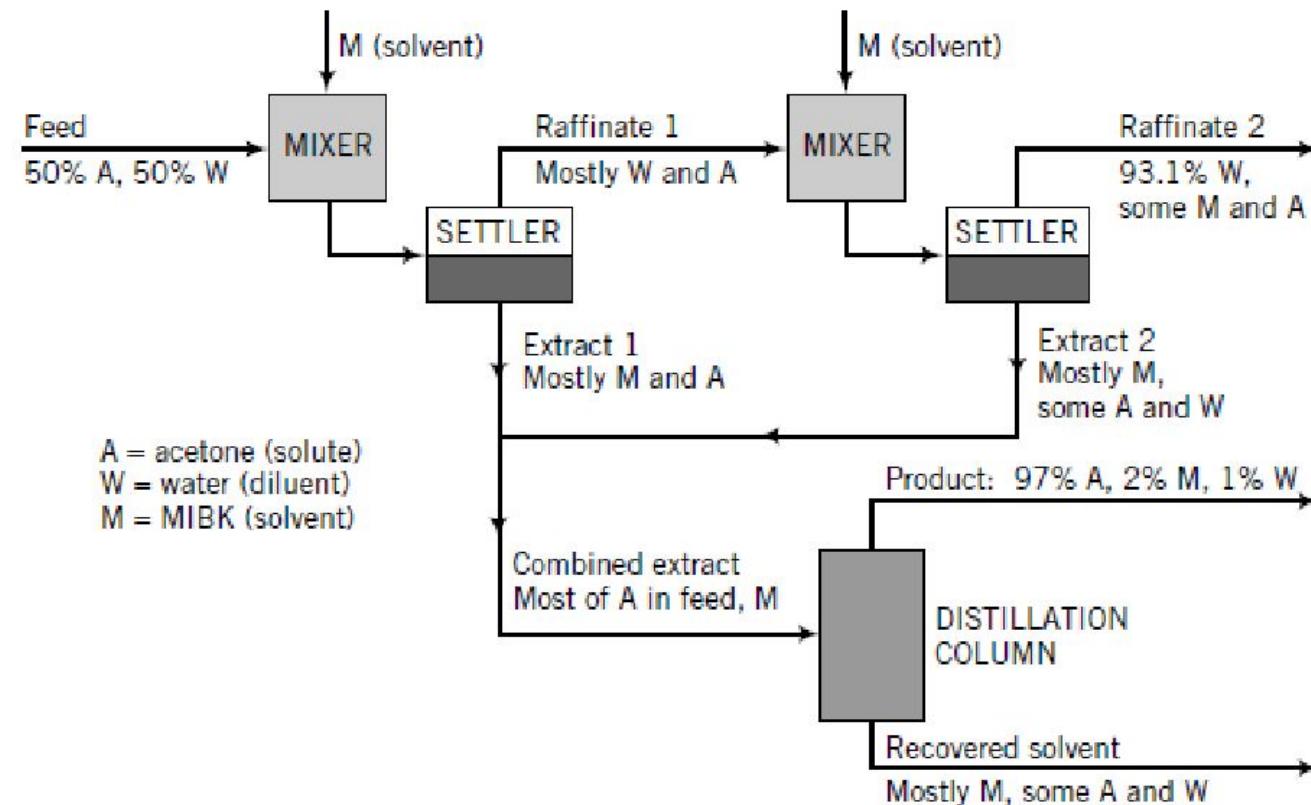
$$\begin{array}{c} \downarrow \\ \dot{m}_1 = 60.0 \text{ kg/h} \\ x_1 = 0.233 \text{ kg/kg} \\ \downarrow \\ \dot{m}_2 = 90.0 \text{ kg/h} \end{array}$$

$$\boxed{x_2 = 0.255 \text{ kg A/kg}}$$

EXAMPLE 4.4-2

An Extraction-Distillation Process

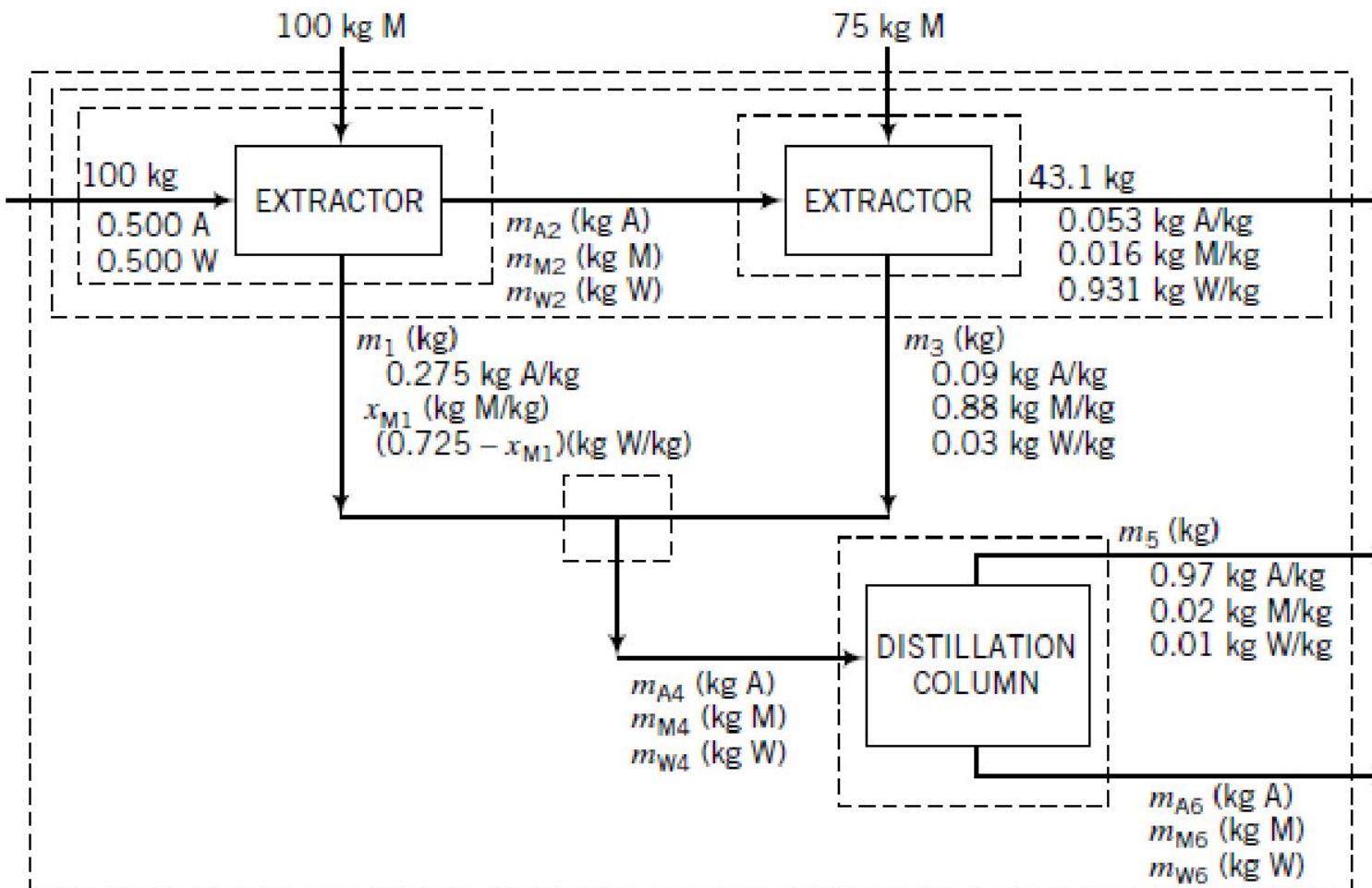
A mixture containing 50.0 wt% acetone and 50.0 wt% water is to be separated into two streams—one enriched in acetone, the other in water. The separation process consists of extraction of the acetone from the water into methyl isobutyl ketone (MIBK), which dissolves acetone but is nearly immiscible with water. The description that follows introduces some of the terms commonly used in reference to liquid extraction processes. The process is shown schematically below.



In a pilot-plant study, for every 100 kg of acetone–water fed to the first extraction stage, 100 kg of MIBK is fed to the first stage and 75 kg is fed to the second stage. The extract from the first stage is found to contain 27.5 wt% acetone. (All percentages in the remainder of this paragraph are weight percents.) The second-stage raffinate has a mass of 43.1 kg and contains 5.3% acetone, 1.6% MIBK, and 93.1% water, and the second-stage extract contains 9.0% acetone, 88.0% MIBK, and 3.0% water. The overhead product from the distillation column contains 2.0% MIBK, 1.0% water, and the balance acetone.

Taking a basis of calculation of 100 kg acetone–water feed, calculate the masses and compositions (component weight percentages) of the Stage 1 raffinate and extract, the Stage 2 extract, the combined extract, and the distillation overhead and bottoms products.

SOLUTION



- **Analyze two-extractor subsystem.** Write a total mass balance and an acetone balance; solve simultaneously to determine m_1 and m_3 . Write an MIBK balance to determine x_{M1} .
- **Analyze extract mixing point.** Write acetone, MIBK, and water balances; solve to determine m_{A4} , m_{M4} , and m_{W4} , respectively.
- **Analyze first (or second) extractor.** Write acetone, MIBK, and water balances; solve to determine m_{A2} , m_{M2} , and m_{W2} .

Balances Around Two-Extractor Subsystem

$$\text{Total mass: } (100 + 100 + 75)\text{kg} = 43.1 \text{ kg} + m_1 + m_3$$

$$\text{A: } 100(0.500) \text{ kg A} = (43.1)(0.053) \text{ kg A} + m_1(0.275) + m_3(0.09)$$

\downarrow Solve simultaneously

$$m_1 = 145 \text{ kg}, m_3 = 86.8 \text{ kg}$$

$$\text{M: } (100 + 75) \text{ kg M} = (43.1)(0.016) \text{ kg M} + m_1 x_{M1} + m_3(0.88)$$

\downarrow $m_1 = 145 \text{ kg}, m_3 = 86.8 \text{ kg}$

$$x_{M1} = 0.675 \text{ kg MIBK/kg}$$

Balances Around Extract Mixing Point

$$\text{A: } m_1(0.275) + m_3(0.09) = m_{A4}$$

\downarrow $m_1 = 145 \text{ kg}, m_3 = 86.8 \text{ kg}$

$$m_{A4} = 47.7 \text{ kg acetone}$$

$$\text{M: } m_1 x_{M1} + m_3(0.88) = m_{M4}$$

\downarrow $m_1 = 145 \text{ kg}, m_3 = 86.8 \text{ kg}, x_{M1} = 0.675 \text{ kg M/kg}$

$$m_{M4} = 174 \text{ kg MIBK}$$

$$\text{W: } m_1(0.725 - x_{M1}) + m_3(0.03) = m_{W4}$$

\downarrow $m_1 = 145 \text{ kg}, m_3 = 86.8 \text{ kg}, x_{M1} = 0.675 \text{ kg M/kg}$

$$m_{W4} = 9.9 \text{ kg water}$$

Balances Around First Extractor

$$\text{A: } 100(0.500) \text{ kg A} = m_{A2} + m_1(0.275)$$

\downarrow $m_1 = 145 \text{ kg}$

$$m_{A2} = 10.1 \text{ kg acetone}$$

$$\text{M: } 100 \text{ kg M} = m_{M2} + m_1 x_{M1}$$

\downarrow $m_1 = 145 \text{ kg}, x_{M1} = 0.675 \text{ kg M/kg}$

$$m_{M2} = 2.3 \text{ kg MIBK}$$

$$\text{W: } (100)(0.500) = m_{W2} + m_1(0.725 - x_{M1})$$

\downarrow $m_1 = 145 \text{ kg}, x_{M1} = 0.675 \text{ kg M/kg}$

$$m_{W2} = 42.6 \text{ kg water}$$

If we knew (or could independently determine) any one of the variables m_5 , m_{A6} , m_{M6} , or m_{W6} , we could calculate the remaining three. Since we do not, we must terminate the calculations at this point.

Lecture 9

4.5 Recycle and Bypass

A □ B

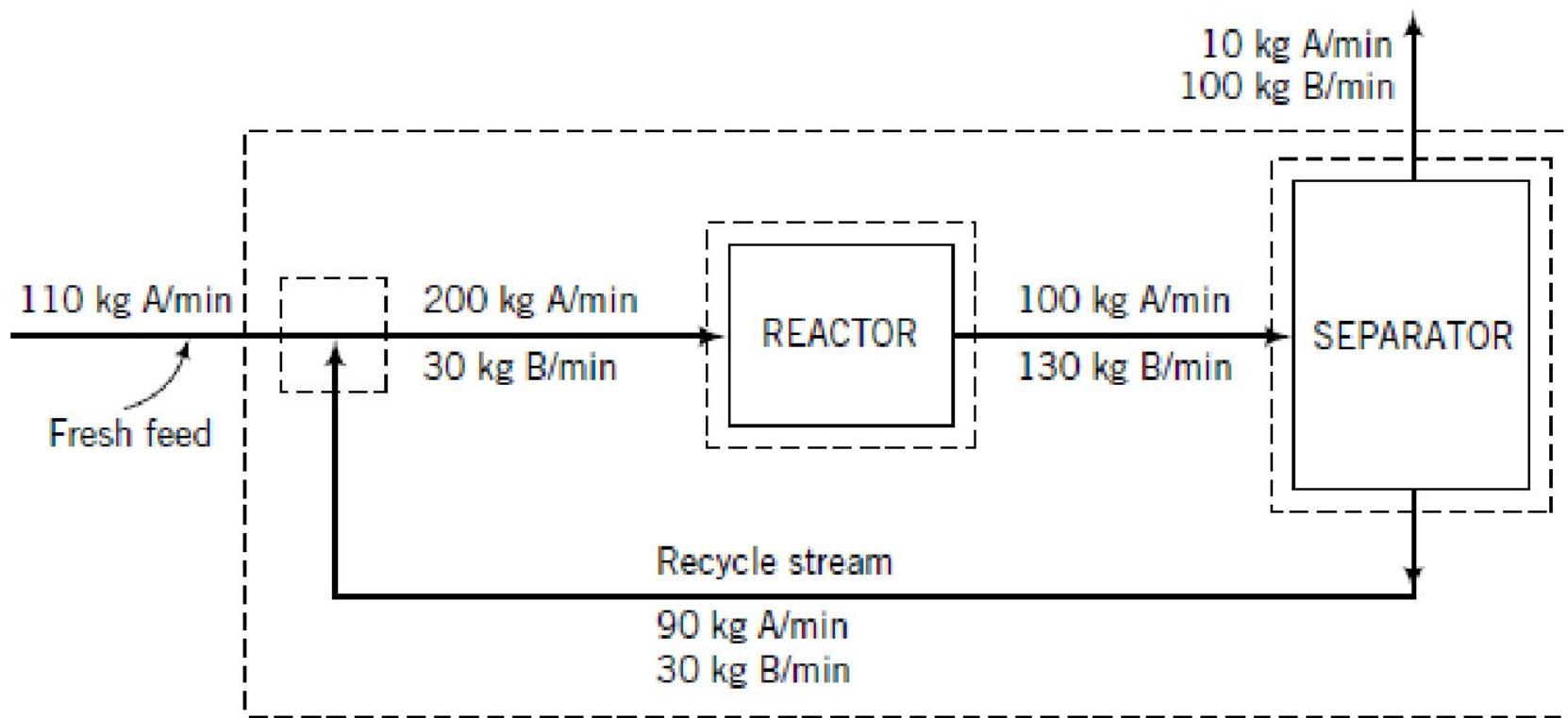


Figure 4.5-1 Flowchart of a reactor with separation and recycle of unconsumed reactant.

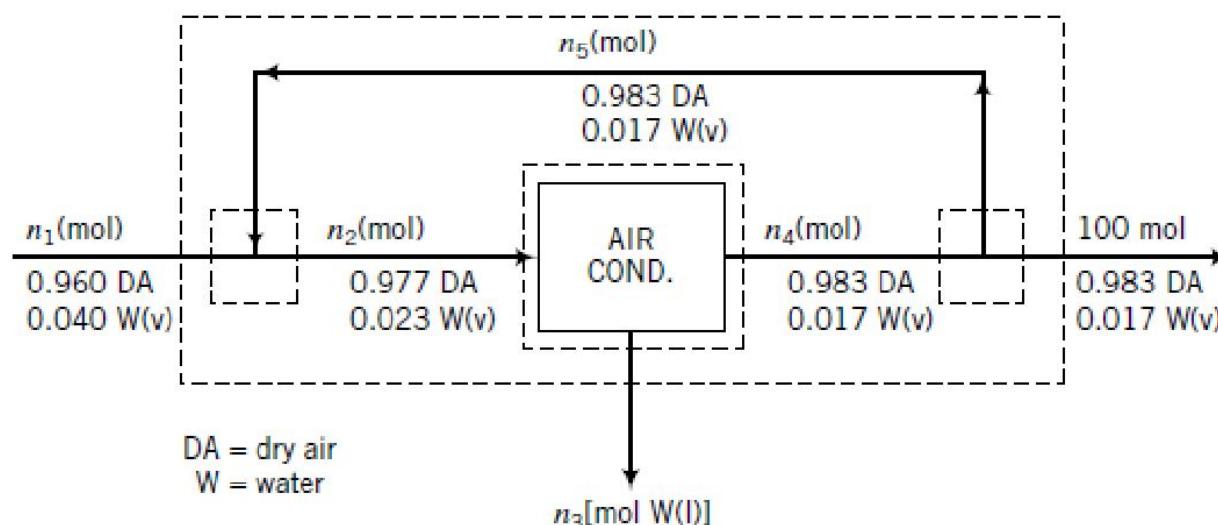
EXAMPLE 4.5-1

Material and Energy Balances on an Air Conditioner

Fresh air containing 4.00 mole % water vapor is to be cooled and dehumidified to a water content of 1.70 mole % H₂O. A stream of fresh air is combined with a recycle stream of previously dehumidified air and passed through the cooler. The blended stream entering the unit contains 2.30 mole % H₂O. In the air conditioner, some of the water in the feed stream is condensed and removed as liquid. A fraction of the dehumidified air leaving the cooler is recycled and the remainder is delivered to a room. Taking 100 mol of dehumidified air delivered to the room as a basis of calculation, calculate the moles of fresh feed, moles of water condensed, and moles of dehumidified air recycled.

SOLUTION

The labeled flowchart for this process, including the assumed basis of calculation, is shown below. Dashed lines depict the four subsystems about which balances might be written—the overall process, the recycle–fresh feed mixing point, the air conditioner, and the recycle–product gas splitting point. The quantities to be determined are n_1 , n_3 , and n_5 .



Overall System

2 variables (n_1, n_3)	(Only consider streams that intersect the system boundary.)
<u>-2 balance equations</u>	(Two species—dry air and water—are in the streams.)
0 degrees of freedom	

Mixing Point

2 variables (n_2, n_5)
<u>-2 balances</u>
0 degrees of freedom

Cooler

2 variables (n_2, n_4)
<u>-2 balances</u>
0 degrees of freedom

Splitting Point

2 variables (n_4, n_5)
<u>-1 balance (see below)</u>
1 degree of freedom

Overall dry air balance: $0.960n_1 = 0.983(100 \text{ mol}) \Rightarrow n_1 = 102.4 \text{ mol fresh feed}$

Overall mole balance: $n_1 = n_3 + 100 \text{ mol} \xrightarrow{n_1 = 102.4 \text{ mol}} n_3 = 2.4 \text{ mol H}_2\text{O condensed}$

Mole balance on mixing point: $n_1 + n_5 = n_2$

Water balance on mixing point: $0.04n_1 + 0.017n_5 = 0.023n_2$

↓

$n_1 = 102.4 \text{ mol}$

Solve simultaneously

$n_2 = 392.5 \text{ mol}$

$n_5 = 290 \text{ mol recycled}$

1. *Recovery of catalyst.*

2. *Dilution of a process stream.*

3. *Control of a process variable.*

4. *Circulation of a working fluid.*

Almost three moles are recycled for every mole of air delivered to the room.

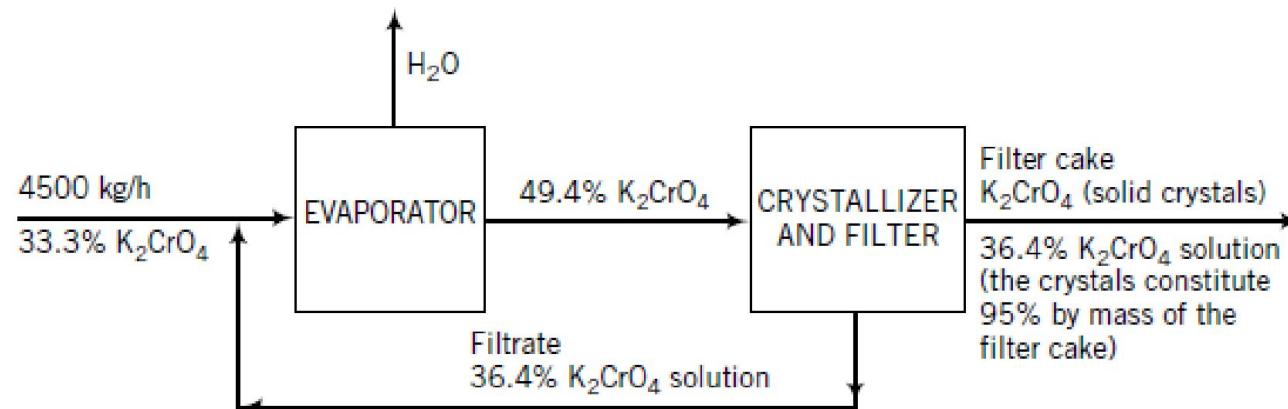
EXAMPLE 4.5-2

An Evaporative Crystallization Process

The flowchart of a steady-state process to recover crystalline potassium chromate (K_2CrO_4) from an aqueous solution of this salt is shown below.

Forty-five hundred kilograms per hour of a solution that is one-third K_2CrO_4 by mass is joined by a recycle stream containing 36.4% K_2CrO_4 , and the combined stream is fed into an evaporator. The concentrated stream leaving the evaporator contains 49.4% K_2CrO_4 ; this stream is fed into a crystallizer in which it is cooled (causing crystals of K_2CrO_4 to come out of solution) and then filtered. The filter cake consists of K_2CrO_4 crystals and a solution that contains 36.4% K_2CrO_4 by mass; the crystals account for 95% of the total mass of the filter cake. The solution that passes through the filter, also 36.4% K_2CrO_4 , is the recycle stream.

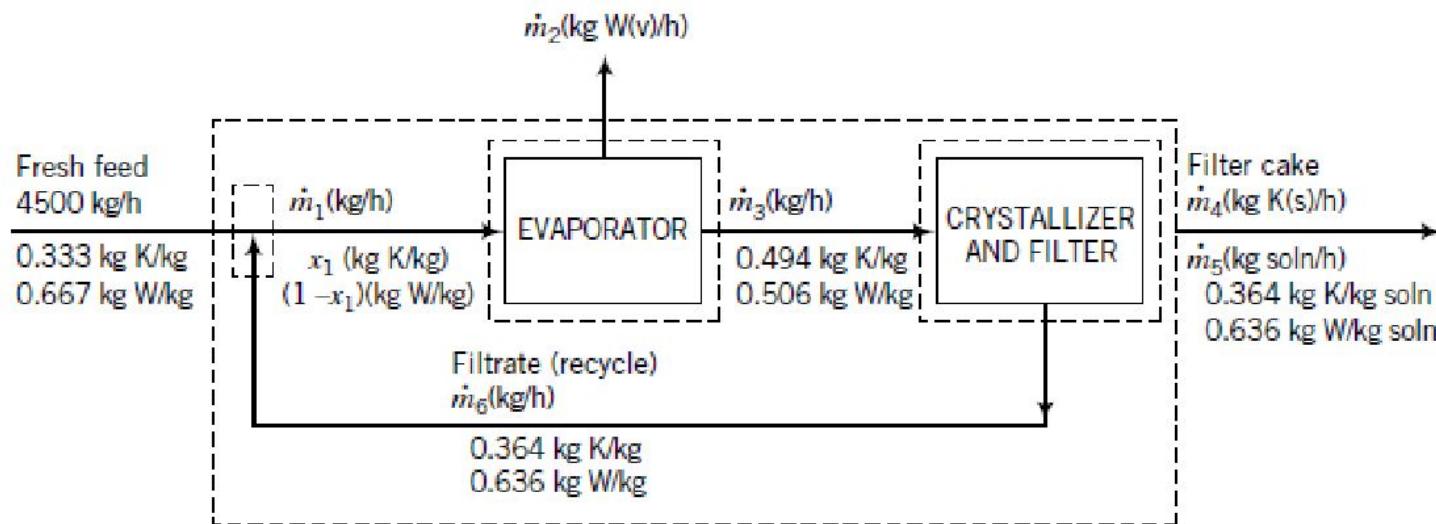
1. Calculate the rate of evaporation, the rate of production of crystalline K_2CrO_4 , the feed rates that the evaporator and the crystallizer must be designed to handle, and the *recycle ratio* (mass of recycle)/(mass of fresh feed).
2. Suppose that the filtrate were discarded instead of being recycled. Calculate the production rate of crystals. What are the benefits and costs of the recycling?



SOLUTION

1. Basis: 4500 kg/h Fresh Feed.

Let K denote K_2CrO_4 and W denote water. The flowchart is shown below; included on it are dashed boxes denoting the overall system and subsystems about which balances may be written.



In terms of labeled variables, the quantities requested in the problem statement are \dot{m}_2 (kg W evaporated/h), \dot{m}_4 [kg K(s)/h], \dot{m}_1 (kg/h fed to evaporator), \dot{m}_3 (kg/h fed to crystallizer), and $(\dot{m}_6/4500)$ (kg recycle/kg fresh feed).

Degree-of-Freedom Analysis

The degree-of-freedom analysis begins with the overall system and proceeds as follows:

- *Overall system*

3 unknown variables ($\dot{m}_2, \dot{m}_4, \dot{m}_5$)
–2 balances (2 species involved)
–1 additional relation ($\dot{m}_4 = 95\%$ of the total filter cake mass)

0 degrees of freedom

We will therefore be able to determine \dot{m}_2 , \dot{m}_4 , and \dot{m}_5 by analyzing the overall system.

- *Recycle-fresh food mixing point*

3 unknown variables ($\dot{m}_6, \dot{m}_1, x_1$)
–2 balances

1 degree of freedom

- *Evaporator*

3 unknown variables ($\dot{m}_1, x_1, \dot{m}_3$)
–2 balances

1 degree of freedom

- *Crystallizer/filter*

2 unknown variables (\dot{m}_3, \dot{m}_6)
–2 balances

0 degrees of freedom

- A total mass balance involves all three system variables— \dot{m}_2 , \dot{m}_4 , and \dot{m}_5 .
- A K balance involves \dot{m}_4 and \dot{m}_5 —the same two variables that occur in Equation 1.
- A W balance involves \dot{m}_2 and \dot{m}_5 .

Overall K_2CrO_4 Balance

$$(0.333)(4500) \text{ kg K/h} = \dot{m}_4 + 0.364\dot{m}_5$$

\downarrow Solve simultaneously with Equation 1

$$\dot{m}_4 = \boxed{1470 \text{ kg } K_2CrO_4 \text{ crystals/h}}$$

$$\dot{m}_5 = 77.5 \text{ kg entrained solution/h}$$

Overall Total Mass Balance

$$4500 \text{ kg/h} = \dot{m}_2 + \dot{m}_4 + \dot{m}_5$$

$\downarrow \dot{m}_4 = 1470 \text{ kg/h}, \dot{m}_5 = 77.5 \text{ kg/h}$

$$\dot{m}_2 = \boxed{2950 \text{ kg H}_2\text{O evaporated/h}}$$

Mass Balance Around Crystallizer

$$\dot{m}_3 = \dot{m}_4 + \dot{m}_5 + \dot{m}_6$$

$\downarrow \dot{m}_4 = 1470 \text{ kg/h}, \dot{m}_5 = 77.5 \text{ kg/h}$

$$\dot{m}_3 = 1550 \text{ kg/h} + \dot{m}_6$$

Water Balance Around Crystallizer

$$0.506\dot{m}_3 = 0.636\dot{m}_5 + 0.636\dot{m}_6$$

$\downarrow \dot{m}_5 = 77.5 \text{ kg/h}$

$$\dot{m}_3 = 97.4 \text{ kg/h} + 1.257\dot{m}_6$$

Solving Equations 2 and 3 simultaneously yields

$$\dot{m}_3 = 7200 \text{ kg/h fed to crystallizer}$$

$$\dot{m}_6 = 5650 \text{ kg/h}$$

and hence

$$\frac{\dot{m}_6 (\text{kg recycle/h})}{4500 \text{ kg fresh feed/h}} = \frac{5650}{4500} = \boxed{1.26 \frac{\text{kg recycle}}{\text{kg fresh feed}}}$$

Mass Balance Around Recycle-Fresh Feed Mixing Point

$$4500 \text{ kg/h} + \dot{m}_6 = \dot{m}_1$$

$$\downarrow \dot{m}_6 = 5650 \text{ kg/h}$$

$$\dot{m}_1 = \boxed{10,150 \text{ kg/h feed to evaporator}}$$

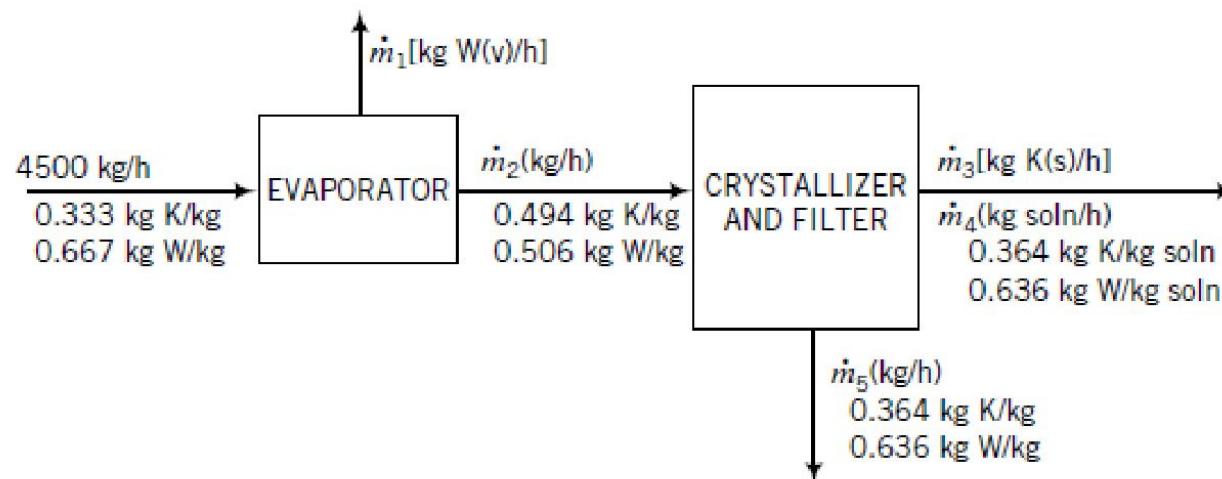
Check: A mass balance about the evaporator yields

$$\dot{m}_1 = \dot{m}_2 + \dot{m}_3$$

$$\implies 10,150 \text{ kg/h entering evaporator} = (2950 + 7200) \text{ kg/h} = 10,150 \text{ kg/h leaving evaporator.}$$

2. Basis: 4500 kg/h Fresh Feed.

The flowchart for the system without recycle appears as shown below.



$$\dot{m}_3 = 622 \text{ kg K(s)/h}$$

With recycle it was 1470 kg/h,

$$\dot{m}_5 = 2380 \text{ kg/h}$$

The filtrate (which is discarded) contains $0.364 \times 2380 = 866 \text{ kg/h}$ of potassium chromate, more than the filter cake contains. Recycling the filtrate enables us to recover most of this salt. The obvious benefit of recycling is the revenue from selling the additional potassium chromate. The costs include the purchase and installation costs for the recycle piping and pump and the cost of power consumed by the pump. It would probably not take long for the benefit to equal the cost, and thereafter the recycling would continue to increase the process profitability.

Lecture 10

4.6 Chemical Reaction Stoichiometry

4.6a Stoichiometry

Stoichiometry is the theory of the proportions in which chemical species combine with one another. The **stoichiometric equation** of a chemical reaction is a statement of the relative number of molecules or moles of reactants and products that participate in the reaction. For example, the stoichiometric equation



indicates that for every two molecules (g-moles, lb-moles) of SO_2 that react, one molecule (g-mole, lb-mole) of O_2 reacts to produce two molecules (g-moles, lb-moles) of SO_3 . The numbers that precede the formulas for each species are the stoichiometric coefficients of the reaction components.

The **stoichiometric ratio** of two molecular species participating in a reaction is the ratio of their stoichiometric coefficients in the balanced reaction equation. This ratio can be used as a conversion factor to calculate the amount of a particular reactant (or product) that was consumed (or produced), given a quantity of another reactant of product that participated in the reaction. For the reaction



you can write the stoichiometric ratios

$$\frac{2 \text{ mol SO}_3 \text{ generated}}{1 \text{ mol O}_2 \text{ consumed}}, \quad \frac{2 \text{ lb-moles SO}_2 \text{ consumed}}{2 \text{ lb-moles SO}_3 \text{ generated}}$$

and so on. If you know, for example, that 1600 kg/h of SO_3 is to be produced, you can calculate the amount of oxygen required as

$$\begin{array}{c} \frac{1600 \text{ kg SO}_3 \text{ generated}}{\text{h}} \left| \begin{array}{c} 1 \text{ kmol SO}_3 \\ 80 \text{ kg SO}_3 \end{array} \right| \frac{1 \text{ kmol O}_2 \text{ consumed}}{2 \text{ kmol SO}_3 \text{ generated}} = 10 \frac{\text{kmol O}_2}{\text{h}} \\ \implies 10 \frac{\text{kmol O}_2}{\text{h}} \left| \begin{array}{c} 32 \text{ kg O}_2 \\ 1 \text{ kmol O}_2 \end{array} \right| = 320 \text{ kg O}_2/\text{h} \end{array}$$

4.6b Limiting and excess reactants, fractional conversion, and extent of reaction

For the reactants in the reaction



to be present in stoichiometric proportion, there must be 2 moles of SO_2 for every mole of O_2 (so that $n_{\text{SO}_2}/n_{\text{O}_2} = 2:1$) present in the feed to the reactor.

The reactant that would run out if a reaction proceeded to completion is called the **limiting reactant**, and the other reactants are termed **excess reactants**. A reactant is limiting if it is present in less than its stoichiometric proportion relative to every other reactant. If all reactants are present in stoichiometric proportion, then no reactant is limiting (or they all are, depending on how you choose to look at it).

Suppose $(n_A)_{\text{feed}}$ is the number of moles of an excess reactant, A, present in the feed to a reactor and that $(n_A)_{\text{stoich}}$ is the **stoichiometric requirement** of A, or the amount needed to react completely with the limiting reactant. Then $(n_A)_{\text{feed}} - (n_A)_{\text{stoich}}$ is the amount by which the A in the feed exceeds the amount needed to react completely if the reaction goes to completion. The **fractional excess** of the reactant is the ratio of the excess to the stoichiometric requirement:

$$\text{fractional excess of A} = \frac{(n_A)_{\text{feed}} - (n_A)_{\text{stoich}}}{(n_A)_{\text{stoich}}} \quad (4.6-1)$$

The **percentage excess of A** is 100 times the fractional excess.

Consider, for example, the hydrogenation of acetylene to form ethane:



and suppose that 20.0 kmol/h of acetylene and 50.0 kmol/h of hydrogen are fed to a reactor. The stoichiometric ratio of hydrogen to acetylene is 2:1 (the ratio of coefficients in the stoichiometric equation), and since the ratio of H_2 to C_2H_2 in the feed is 2.5:1 (50:20), hydrogen is fed in a greater-than-stoichiometric proportion to acetylene. Acetylene is therefore the limiting reactant. (Convince yourself.) Since it would take 40.0 kmol H_2/h to react completely with all the acetylene fed to the reactor, $(n_{\text{H}_2})_{\text{stoich}} = 40.0 \text{ kmol/h}$, and from Equation 4.6-1,

$$\text{fractional excess of H}_2 = \frac{(50.0 - 40.0)\text{kmol/h}}{40.0 \text{ kmol/h}} = 0.25$$

We say that there is 25% *excess hydrogen* in the feed.

Chemical reactions do not take place instantaneously, and indeed often proceed rather slowly. In such cases, it is not practical to design the reactor for complete conversion of the limiting reactant; instead, the reactor effluent emerges with some of the limiting reactant still present and is then usually subjected to a separation process to remove the unconverted reactant from the product. The separated reactant is then recycled to the reactor inlet. The **fractional conversion** of a reactant is the ratio

$$f = \frac{\text{moles reacted}}{\text{moles fed}} \quad (4.6-2)$$

The fraction unreacted is accordingly $1 - f$. If 100 moles of a reactant are fed and 90 moles react, the fractional conversion is 0.90 (the **percentage conversion** is 90%) and the fraction unreacted is 0.10. If 20 mol/min of a reactant is fed and the percentage conversion is 80%, then $(20)(0.80) = 16 \text{ mol/min}$ has reacted and $(20)(1 - 0.80) = 4 \text{ mol/min}$ remains unreacted.

Considering the reaction discussed above ($C_2H_2 + 2H_2 \rightarrow C_2H_6$), suppose 20.0 kmol of acetylene, 50.0 kmol of hydrogen, and 50.0 kmol of ethane are charged into a batch reactor. Furthermore, suppose that after some time 30.0 kmol of hydrogen has reacted. How much of each species will be present in the reactor at the moment?

Clearly, if you start with 50.0 kmol of H_2 and 30.0 kmol reacts, you will be left with 20.0 kmol H_2 . Also, if 30.0 kmol of H_2 reacts, 15.0 kmol of C_2H_2 also reacts (Why?), leaving you with $(20.0 - 15.0)$ kmol $C_2H_2 = 5.0$ kmol C_2H_2 . Finally, the 30.0 kmol of H_2 that reacts forms 15.0 kmol of C_2H_6 , which when added to the 50.0 kmol you started with gives you 65.0 kmol C_2H_6 .

More generally, if 2ξ (kmol of H_2) react (where 2 is the stoichiometric coefficient of H_2), we may follow the same reasoning and write

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

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

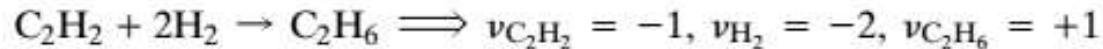
$$n_{C_2H_6} = (n_{C_2H_6})_0 + \xi$$

Once you know how much hydrogen (or acetylene) reacts or how much ethane is formed, you can determine ξ from one of these equations and then determine the remaining component amounts from the other two equations.

In → 120

Out → 90

Next, we may generalize this result to any chemical reaction. To begin with, let us define a quantity v_i to be the stoichiometric coefficient of the i th species in a chemical reaction, making it negative for reactants and positive for products. For example,

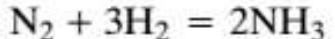


Then if n_{i0} (or \dot{n}_{i0}) is the moles (batch) or molar flow rate (continuous) of species i in the feed to a batch or continuous steady-state process,

$$n_i = n_{i0} + v_i \xi \quad \text{or} \quad \dot{n}_i = \dot{n}_{i0} + v_i \dot{\xi} \quad (4.6-3)$$

(Verify that this expression yields the previously given formulas for the acetylene reaction.) The quantity ξ (or $\dot{\xi}$), which has the same units as n (or \dot{n}), is called the **extent of reaction**. If you know the feed quantities (n_{i0} for all i) and you also know any one of the n_i values, you can calculate ξ by applying Equation 4.6-3 to the component for which n_i is known. You can then calculate the remaining n_i values by applying Equation 4.6-3 to the other species, substituting the known values of ξ .

For example, consider the ammonia formation reaction:



Suppose the feed to a continuous reactor consists of 100 mol/s of nitrogen, 300 mol/s of hydrogen, and 1 mol/s of argon (an inert gas). From Equation 4.6-3, we may write for the reactor outlet flow rates

$$\dot{n}_{\text{N}_2} = 100 \text{ mol/s} - \dot{\xi}$$

$$\dot{n}_{\text{H}_2} = 300 \text{ mol/s} - 3\dot{\xi}$$

$$\dot{n}_{\text{NH}_3} = 2\dot{\xi}$$

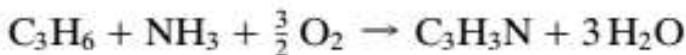
$$\dot{n}_{\text{A}} = 1 \text{ mol/s}$$

Extent of reaction

Stoichiometric coefficient

EXAMPLE 4.6-1**Reaction Stoichiometry**

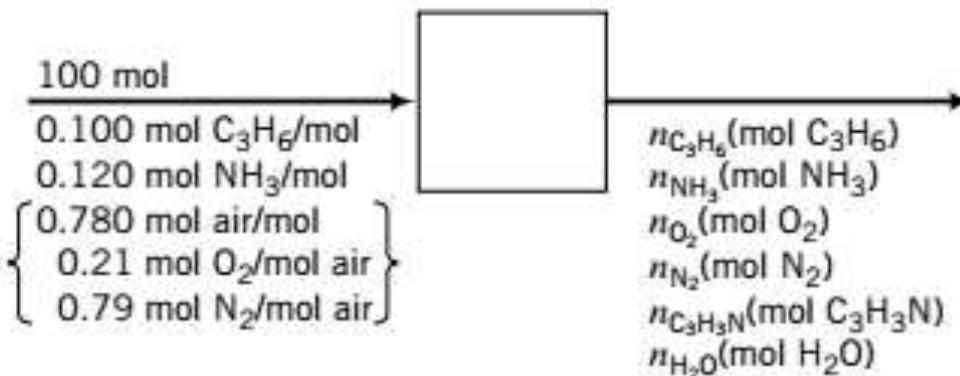
Acrylonitrile is produced in the reaction of propylene, ammonia, and oxygen:



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.

SOLUTION

Basis: 100 mol Feed



The feed to the reactor contains

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

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

$$(n_{O_2})_0 = \frac{78.0 \text{ mol air}}{\text{mol air}} \left| \frac{0.210 \text{ mol O}_2}{\text{mol air}} \right. = 16.4 \text{ mol}$$



$$\begin{aligned} (n_{NH_3}/n_{C_3H_6})_0 &= 12.0/10.0 = 1.20 \\ (n_{NH_3}/n_{C_3H_6})_{\text{stoich}} &= 1/1 = 1 \end{aligned} \} \implies NH_3 \text{ is in excess } (1.20 > 1)$$

$$\begin{aligned} (n_{O_2}/n_{C_3H_6})_0 &= 16.4/10.0 = 1.64 \\ (n_{O_2}/n_{C_3H_6})_{\text{stoich}} &= 1.5/1 = 1.5 \end{aligned} \} \implies O_2 \text{ is in excess } (1.64 > 1.5)$$

Since propylene is fed in less than stoichiometric proportion relative to the two other reactants, *propylene is the limiting reactant*.

To determine the percentages by which ammonia and oxygen are in excess, we must first determine the stoichiometric amounts of these reactants corresponding to the amount of propylene in the feed (10 mol) and then apply Equation 4.6-1.

$$(n_{\text{NH}_3})_{\text{stoich}} = \frac{10.0 \text{ mol C}_3\text{H}_6}{1 \text{ mol C}_3\text{H}_6} \left| \frac{1 \text{ mol NH}_3}{1 \text{ mol C}_3\text{H}_6} \right. = 10.0 \text{ mol NH}_3$$

$$(n_{\text{O}_2})_{\text{stoich}} = \frac{10.0 \text{ mol C}_3\text{H}_6}{1 \text{ mol C}_3\text{H}_6} \left| \frac{1.5 \text{ mol O}_2}{1 \text{ mol C}_3\text{H}_6} \right. = 15.0 \text{ mol O}_2$$

$$\begin{aligned} (\% \text{ excess})_{\text{NH}_3} &= \frac{(\text{NH}_3)_0 - (\text{NH}_3)_{\text{stoich}}}{(\text{NH}_3)_{\text{stoich}}} \times 100\% \\ &= (12.0 - 10.0)/10.0 \times 100\% = \boxed{20\% \text{ excess NH}_3} \end{aligned}$$

$$(\% \text{ excess})_{\text{O}_2} = (16.4 - 15.0)/15.0 \times 100\% = \boxed{9.3\% \text{ excess O}_2}$$

If the fractional conversion of C_3H_6 is 30%, then

$$(n_{\text{C}_3\text{H}_6})_{\text{out}} = 0.700(n_{\text{C}_3\text{H}_6})_0 = \boxed{7.0 \text{ mol C}_3\text{H}_6}$$

But from Equation 4.6-3, $n_{\text{C}_3\text{H}_6} = 10.0 \text{ mol C}_3\text{H}_6 - \xi$. The extent of reaction is therefore $\xi = 3.0 \text{ mol}$. Then, also from equation 4.6-3,

$$\begin{aligned} n_{\text{NH}_3} &= 12.0 \text{ mol NH}_3 - \xi = \boxed{9.0 \text{ mol NH}_3} \\ n_{\text{O}_2} &= 16.4 \text{ mol O}_2 - 1.5\xi = \boxed{11.9 \text{ mol O}_2} \\ n_{\text{C}_3\text{H}_3\text{N}} &= \xi = \boxed{3.00 \text{ mol C}_3\text{H}_3\text{N}} \\ n_{\text{N}_2} &= (n_{\text{N}_2})_0 = \boxed{61.6 \text{ mol N}_2} \\ n_{\text{H}_2\text{O}} &= 3\xi = \boxed{9.0 \text{ mol H}_2\text{O}} \end{aligned}$$

4.6c Chemical Equilibrium

Two of the fundamental questions of chemical reaction engineering are, given a set of reactive species and reaction conditions, (a) what will be the final (equilibrium) composition of the reaction mixture, and (b) how long will the system take to reach a specified state short of equilibrium? The field of **chemical equilibrium thermodynamics** concerns itself with the first question, and **chemical kinetics** deals with the second.

Reversible
Irreversible

EXAMPLE 4.6-2

Calculation of an Equilibrium Composition

If the water-gas shift reaction,



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

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

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 H₂O, and no CO₂ or H₂, and the reaction mixture comes to equilibrium at 1105 K. Calculate the equilibrium composition and the fractional conversion of the limiting reactant.

SOLUTION

The strategy is to express all mole fractions in terms of a single variable (ξ_c , the extent of reaction at equilibrium), substitute in the equilibrium relation, solve for ξ_c , and back-substitute to calculate the mole fractions and any other desired quantity.

From Equation 4.6-3,

$$n_{CO} = 1.00 \text{ mol} - \xi_c \quad (\text{number of gram-moles of CO present at equilibrium})$$

$$n_{H_2O} = 2.00 \text{ mol} - \xi_c$$

$$n_{CO_2} = \xi_c$$

$$n_{H_2} = \xi_c$$

$$\underline{n_{\text{total}} = 3.00 \text{ mol}}$$

from which

$$y_{CO} = (1.00 \text{ mol} - \xi_c)/3.00 \text{ mol}$$

$$y_{H_2O} = (2.00 \text{ mol} - \xi_c)/3.00 \text{ mol}$$

$$y_{CO_2} = \xi_c/3.00 \text{ mol}$$

$$y_{H_2} = \xi_c/3.00 \text{ mol}$$

Substitution of these expressions into the equilibrium relation (with $K = 1.00$) yields

$$\frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} = \frac{\xi_c^2}{(1.00 \text{ mol} - \xi_c)(2.00 \text{ mol} - \xi_c)} = 1.00$$

This may be rewritten as a standard quadratic equation (*verify*) and solved to yield $\xi_c = 0.667 \text{ mol}$. This quantity may in turn be substituted back into the expression for y_i to yield

$$y_{CO} = 0.111, \quad y_{H_2O} = 0.444, \quad y_{CO_2} = 0.222, \quad y_{H_2} = 0.222$$

The limiting reactant in this case is CO (*verify*). At equilibrium,

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

The fractional conversion of CO at equilibrium is therefore

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

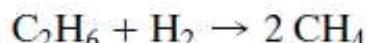
Lecture 11

4.6d Multiple Reactions, Yield, and Selectivity

For example, ethylene can be produced by the dehydrogenation of ethane:



Once some hydrogen is produced, it can react with ethane to produce methane:



Moreover, ethylene can react with ethane to form propylene and methane:



Since the object of the process is to produce ethylene, only the first of these reactions may be regarded as desirable; the second one consumes the reactant without yielding the desired product and the third consumes both the reactant and the desired product. The engineer designing the reactor and specifying operating conditions for it must consider not only how to maximize the production of the desired product (C_2H_4), but also how to minimize the production of undesired by-products (CH_4 , C_3H_6).

The terms **yield** and **selectivity** are used to describe the degree to which a desired reaction predominates over competing side reactions.

Yield:
$$\frac{\text{moles of desired product formed}}{\text{moles that would have been formed if there were no side reactions and the limiting reactant had reacted completely}} \quad (4.6-4)$$

Selectivity:
$$\frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}} \quad (4.6-5)$$

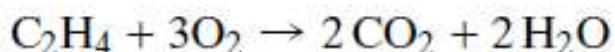
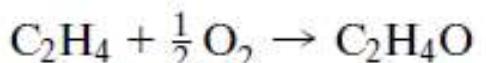
The yield defined by Equation 4.6-4 is always a fraction; it may also be expressed as a percentage by multiplying by 100%. If A is the desired product and B is an undesired product, one then refers to the *selectivity of A relative to B*. High values of the yield and selectivity signify that the undesired side reactions have been successfully suppressed relative to the desired reaction.

The concept of extent of reaction can be extended to multiple reactions, only now each independent reaction has its own extent. If a set of reactions takes place in a batch or continuous steady-state reactor and ν_{ij} is the stoichiometric coefficient of substance i in reaction j (negative for reactants, positive for products), we may then write

$$n_i = n_{i0} + \sum_j \nu_{ij} \xi_j \quad (4.6-6)$$

For a single reaction, this equation reduces to Equation 4.6-3.

For example, consider the pair of reactions in which ethylene is oxidized either to ethylene oxide (desired) or to carbon dioxide (undesired):



The moles (or molar flow rates) of each of the five species involved in these reactions can be expressed in terms of the feed values and extents of reaction using Equation 4.6-6:

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

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

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

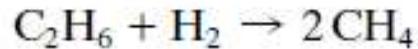
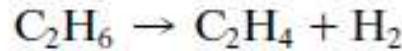
$$(n_{CO_2})_{out} = (n_{CO_2})_0 + 2\xi_2$$

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

EXAMPLE 4.6-3

Yield and Selectivity in a Dehydrogenation Reactor

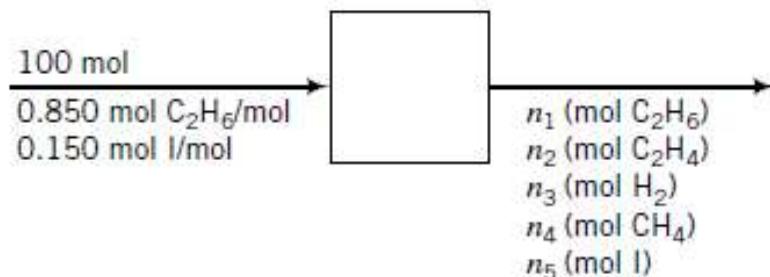
The reactions



take place in a continuous reactor at steady state. The feed contains 85.0 mole% ethane (C_2H_6) and the balance inert (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.

SOLUTION

Basis: 100 mol Feed



From Equation 4.6-6, the outlet component amounts in terms of extents of reaction are as follows:

$$n_1(\text{mol C}_2\text{H}_6) = 85.0 \text{ mol C}_2\text{H}_6 - \xi_1 - \xi_2$$

$$n_2(\text{mol C}_2\text{H}_4) = \xi_1$$

$$n_3(\text{mol H}_2) = \xi_1 - \xi_2$$

$$n_4(\text{mol CH}_4) = 2\xi_2$$

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

Ethane Conversion

If the fractional conversion of ethane is 0.501, the fraction unconverted (and hence leaving the reactor) must be (1 - 0.501).

$$\begin{aligned} n_1 &= \frac{(1 - 0.501) \text{ mol C}_2\text{H}_6 \text{ unreacted}}{\text{mol C}_2\text{H}_6 \text{ fed}} \Bigg| \frac{85.0 \text{ mol C}_2\text{H}_6 \text{ fed}}{} \\ &= 42.4 \text{ mol C}_2\text{H}_6 = 85.0 \text{ mol C}_2\text{H}_6 - \xi_1 - \xi_2 \end{aligned} \tag{1}$$

Ethylene Yield

$$\text{maximum possible ethylene formed} = \frac{85.0 \text{ mol C}_2\text{H}_6 \text{ fed}}{1 \text{ mol C}_2\text{H}_6} \times 1 \text{ mol C}_2\text{H}_4 = 85.0 \text{ mol}$$



$$n_2 = 0.471(85.0 \text{ mol C}_2\text{H}_6) = 40.0 \text{ mol C}_2\text{H}_4 = \xi_1$$

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

$$n_3 = \xi_1 - \xi_2 = 37.4 \text{ mol H}_2$$

$$n_4 = 2\xi_2 = 5.2 \text{ mol CH}_4$$

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

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



Product:

30.3% C ₂ H ₆ , 28.6% C ₂ H ₄ , 26.7% H ₂ , 3.7% CH ₄ , 10.7% I

$$\text{selectivity} = (40.0 \text{ mol C}_2\text{H}_4)/(5.2 \text{ mol CH}_4)$$

$$= 7.7 \frac{\text{mol C}_2\text{H}_4}{\text{mol CH}_4}$$

4.7 Balance on Reactive Processes

4.7a balances on Molecular and Atomic Species

Figure 4.7-1 shows a flowchart for the dehydrogenation of ethane in a steady-state continuous reactor. The reaction is

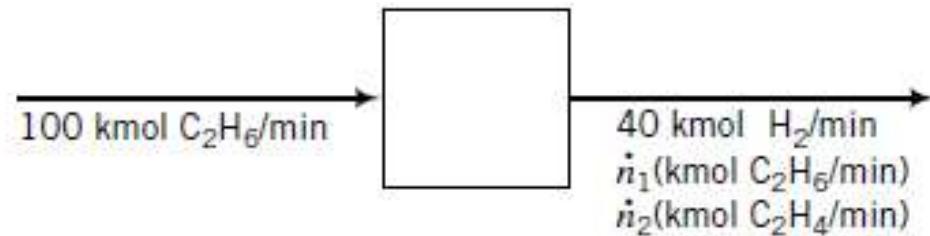
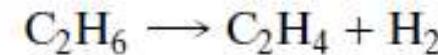


Figure 4.7-1 Dehydrogenation of ethane.

Some of the balances that can be written for the process shown in Figure 4.7-1 are as follows. (Recall that the general balance equation for a steady-state process is input + generation = output + consumption.)

Molecular H₂ Balance: generation = output

$$\text{Gen}_{\text{H}_2} \left(\frac{\text{mol H}_2 \text{ generated}}{\text{min}} \right) = 40 \text{ mol H}_2/\text{min}$$

C₂H₆ Balance: input = output + consumption

$$\frac{100 \text{ mol C}_2\text{H}_6}{\text{min}} = \dot{n}_1 \left(\frac{\text{mol C}_2\text{H}_6}{\text{min}} \right) + \text{Cons}_{\text{C}_2\text{H}_6} \left(\frac{\text{mol C}_2\text{H}_6 \text{ consumed}}{\text{min}} \right)$$

C₂H₄ Balance: generation = output

$$\text{Gen}_{\text{C}_2\text{H}_4} \left(\frac{\text{mol C}_2\text{H}_4 \text{ generated}}{\text{min}} \right) = \dot{n}_2 \left(\frac{\text{mol C}_2\text{H}_4}{\text{min}} \right)$$

Atomic C Balance: input = output

$$\frac{100 \text{ mol C}_2\text{H}_6}{\text{min}} \left| \begin{array}{c} 2 \text{ mol C} \\ 1 \text{ mol C}_2\text{H}_6 \end{array} \right. = \dot{n}_1 \frac{\text{mol C}_2\text{H}_6}{\text{min}} \left| \begin{array}{c} 2 \text{ mol C} \\ 1 \text{ mol C}_2\text{H}_6 \end{array} \right. + \dot{n}_2 \frac{\text{mol C}_2\text{H}_4}{\text{min}} \left| \begin{array}{c} 2 \text{ mol C} \\ 1 \text{ mol C}_2\text{H}_4 \end{array} \right.$$



$$100 \text{ mol C/min} = \dot{n}_1 + \dot{n}_2$$

Atomic H Balance: input = output

$$\frac{100 \text{ mol C}_2\text{H}_6}{\text{min}} \left| \begin{array}{c} 6 \text{ mol H} \\ 1 \text{ mol C}_2\text{H}_6 \end{array} \right. = \frac{40 \text{ mol H}_2}{\text{min}} \left| \begin{array}{c} 2 \text{ mol H} \\ 1 \text{ mol H}_2 \end{array} \right. + \dot{n}_1 \frac{\text{mol C}_2\text{H}_6}{\text{min}} \left| \begin{array}{c} 6 \text{ mol H} \\ 1 \text{ mol C}_2\text{H}_6 \end{array} \right. + \dot{n}_2 \frac{\text{mol C}_2\text{H}_4}{\text{min}} \left| \begin{array}{c} 4 \text{ mol H} \\ 1 \text{ mol C}_2\text{H}_4 \end{array} \right.$$



$$600 \text{ mol H/min} = 80 \text{ mol H/min} + 6\dot{n}_1 + 4\dot{n}_2$$

4.7b Independent Equations, Independent Species, and Independent Reactions

The key concept is that of *independent equations*. Algebraic equations are independent if you cannot obtain any one of them by adding and subtracting multiples of any of the others. For example, the equations

$$[1] \quad x + 2y = 4$$

$$[2] \quad 3x + 6y = 12$$

are not independent, because $[2] = 3 \times [1]$. In effect, they are really the same equation. (Convince yourself by seeing what happens if you try to solve the two equations for x and y .) Similarly, the equations

$$[1] \quad x + 2y = 4$$

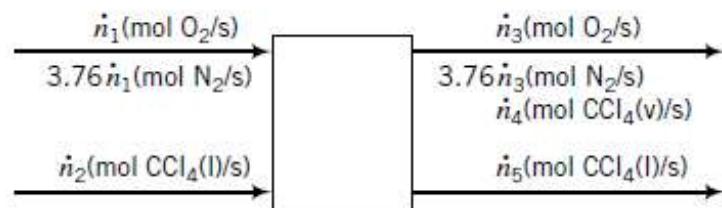
$$[2] \quad 2x - z = 2$$

$$[3] \quad 4y + z = 6$$

are not independent, because $[3] = 2 \times [1] - [2]$. (Prove it.)

If two molecular 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. Similarly, if two atomic species occur in the same ratio wherever they appear in a process, balances on those species will not be independent equations.

For example, consider a process in which a stream of liquid carbon tetrachloride is vaporized into a stream of air.

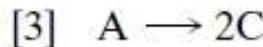
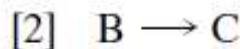
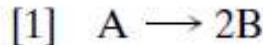


Since nitrogen and oxygen are shown as being in the same ratio wherever they appear on the flowchart ($3.76 \text{ mol N}_2/\text{mol O}_2$), you cannot count them as two independent species and so you may count only two independent molecular species balances in a degree-of-freedom analysis—one for either O₂ or N₂ and one for CCl₄. (Try writing separate O₂ and N₂ balances and see what you get.)

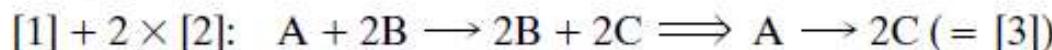
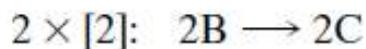
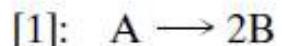
Similarly, atomic nitrogen (N) and atomic oxygen (O) are always in the same proportion to each other in the process (again 3.76:1) as are atomic chlorine and atomic carbon (4 mol Cl/1 mol C). Consequently, even though four atomic species are involved in this process, you may count only two independent atomic species balances in the degree-of-freedom analysis—one for either O or N and one for either C or Cl. (Again, convince yourself that the O and N balances yield the same equation, as do the C and Cl balances.)

Finally, when you are using either 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. *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.*

For example, consider the reactions



These three reactions are not all independent, since $[3] = [1] + 2 \times [2]$.



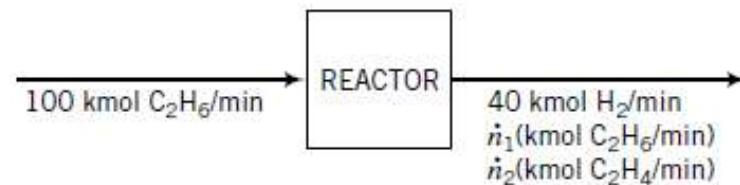
4.7c Molecular Species Balances

If molecular species balances are used to determine unknown stream variables for a reactive process, the balances on reactive species must contain generation and/or consumption terms. The degree-of-freedom analysis is as follows:

No. unknown labeled variables

- + No. independent chemical reactions (as defined in Section 4.7b)
 - No. independent molecular species balances (as defined in Section 4.7b)
 - No. other equations relating unknown variables
-
- = No. degrees of freedom

We will use the dehydrogenation of ethane (Figure 4.7-1) to illustrate the required procedures. The flowchart is shown again here for ease of reference.



Degree-of-Freedom Analysis

2 unknown labeled variables (\dot{n}_1, \dot{n}_2)

- + 1 independent chemical reaction
 - 3 independent molecular species balances (C_2H_6 , C_2H_4 , and H_2)
 - 0 other equations relating unknown variables
-
- = 0 degrees of freedom

H_2 Balance: generation = output

$$\text{Gen}_{H_2} \left(\frac{\text{kmol } H_2 \text{ generated}}{\text{min}} \right) = 40 \text{ kmol } H_2/\text{min}$$

C_2H_6 Balance: input = output + consumption

$$100 \frac{\text{kmol } C_2H_6}{\text{min}} = \dot{n}_1 \left(\frac{\text{kmol } C_2H_6}{\text{min}} \right)$$

$$+ \frac{40 \text{ kmol } H_2 \text{ generated}}{\text{min}} \left| \begin{array}{c} 1 \text{ kmol } C_2H_6 \text{ consumed} \\ 1 \text{ kmol } H_2 \text{ generated} \end{array} \right. \Rightarrow \boxed{\dot{n}_1 = 60 \text{ kmol } C_2H_6/\text{min}}$$

C_2H_4 Balance: generation = output

$$\frac{40 \text{ kmol } H_2 \text{ generated}}{\text{min}} \left| \begin{array}{c} 1 \text{ kmol } C_2H_4 \text{ generated} \\ 1 \text{ kmol } H_2 \text{ generated} \end{array} \right. = \dot{n}_2 \left(\frac{\text{kmol } C_2H_4}{\text{min}} \right)$$

$$\Rightarrow \boxed{\dot{n}_2 = 40 \text{ kmol } C_2H_4/\text{min}}$$

4.7d Atomic Species Balance

Degree-of-Freedom Analysis

- 2 unknown labeled variables
 - 2 independent atomic species balances (C and H)
 - 0 molecular balances on independent nonreactive species
 - 0 other equations relating unknown variables

- = 0 degrees of freedom

C Balance: input = output

$$\begin{array}{c|c} 100 \text{ kmol C}_2\text{H}_6 & 2 \text{ kmol C} \\ \hline \text{min} & 1 \text{ kmol C}_2\text{H}_6 \\ \hline \end{array} = \frac{\dot{n}_1(\text{kmol C}_2\text{H}_6)}{(\text{min})} \begin{array}{c|c} 2 \text{ kmol C} & 2 \text{ kmol C} \\ \hline 1 \text{ kmol C}_2\text{H}_6 & 1 \text{ kmol C}_2\text{H}_4 \\ \hline \end{array} + \frac{\dot{n}_2(\text{kmol C}_2\text{H}_4)}{(\text{min})} \begin{array}{c|c} 2 \text{ kmol C} & 2 \text{ kmol C} \\ \hline 1 \text{ kmol C}_2\text{H}_4 & 1 \text{ kmol C}_2\text{H}_4 \\ \hline \end{array}$$

\Downarrow

$$100 = \dot{n}_1 + \dot{n}_2$$

H Balance: input = output

$$\begin{array}{c|c} 100 \text{ kmol C}_2\text{H}_6 & 6 \text{ kmol H} \\ \hline \text{min} & 1 \text{ kmol C}_2\text{H}_6 \\ \hline \end{array} = \frac{40 \text{ kmol H}_2}{\text{min}} \begin{array}{c|c} 2 \text{ kmol H} & 2 \text{ kmol H} \\ \hline 1 \text{ kmol H}_2 & 1 \text{ kmol H}_2 \\ \hline \end{array}$$
$$+ \frac{\dot{n}_1(\text{kmol C}_2\text{H}_6)}{(\text{min})} \begin{array}{c|c} 6 \text{ kmol H} & 6 \text{ kmol H} \\ \hline 1 \text{ kmol C}_2\text{H}_6 & 1 \text{ kmol C}_2\text{H}_6 \\ \hline \end{array} + \frac{\dot{n}_2(\text{kmol C}_2\text{H}_4)}{(\text{min})} \begin{array}{c|c} 4 \text{ kmol H} & 4 \text{ kmol H} \\ \hline 1 \text{ kmol C}_2\text{H}_4 & 1 \text{ kmol C}_2\text{H}_4 \\ \hline \end{array}$$

\Downarrow

$$600 \text{ mol H/min} = 80 \text{ mol H/min} + 6\dot{n}_1 + 4\dot{n}_2 \quad (2)$$

Solving Equations (1) and (2) simultaneously yields the same solutions obtained with atomic species balances:

$$\dot{n}_1 = 60 \text{ kmol C}_2\text{H}_6/\text{min}$$

$$\dot{n}_2 = 40 \text{ kmol C}_2\text{H}_4/\text{min}$$

Lecture 12

4.7e Extent of Reaction

The third way to determine unknown molar flow rates for a reactive process is to write expressions for each product species flow rate (or molar amount) in terms of extents of reaction using Equation 4.6-3 (or Equation 4.6-6 for multiple reactions), substitute known feed and product flow rates, and solve for the extents of reaction and the remaining reactive species flow rates. The degree-of-freedom analysis follows:

$$\begin{aligned} & \text{No. unknown labeled variables} \\ + & \text{ No. independent reactions (one extent of reaction for each)} \\ - & \text{ No. independent reactive species} \\ & \quad (\text{one equation for each species in terms of extents of reaction}) \\ - & \text{ No. independent nonreactive species (one balance equation for each)} \\ - & \text{ No. other equations relating unknown variables} \\ = & \text{ No. degrees of freedom} \end{aligned}$$

In the dehydrogenation process (refer one final time to the flowchart), $DF = 2$ unknown variables (\dot{n}_1, \dot{n}_2) + 1 independent reaction – 3 independent reactive species (C_2H_6, C_2H_4, H_2) = 0. For the same process, Equation 4.6-2 ($\dot{n}_i = \dot{n}_{i0} + \nu_i \xi$) for the three species in the process becomes

$$H_2(\nu = 1): 40 \text{ kmol } H_2/\text{min} = \xi \implies \xi = 40 \text{ kmol/min}$$

$$C_2H_6(\nu = -1): \dot{n}_1 = 100 \text{ kmol } C_2H_6/\text{min} - \xi \xrightarrow{\xi = 40 \text{ kmol/min}} \boxed{\dot{n}_1 = 60 \text{ kmol } C_2H_6/\text{min}}$$

$$C_2H_4(\nu = 1): \dot{n}_2 = \xi \xrightarrow{\xi = 40 \text{ kmol/min}} \boxed{\dot{n}_2 = 40 \text{ kmol } C_2H_4/\text{min}}$$

Given that all three methods of carrying out material balances on reactive systems—molecular species balances, atomic species balances, and extents of reaction—necessarily yield the same results, the question is which one to use for a given process. There are no hard and fast rules but we suggest the following guidelines:

- *Atomic species balances generally lead to the most straightforward solution procedure, especially when more than one reaction is involved.*
- *Extents of reaction are convenient for chemical equilibrium problems and when equation-solving software is to be used.*
- *Molecular species balances require more complex calculations than either of the other two approaches and should be used only for simple systems involving one reaction.*

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



The feed to the reactor contains 7.80 mole% CH₄, 19.4% O₂, and 72.8% N₂. The percentage conversion of methane is 90.0%, and the gas leaving the reactor contains 8 mol CO₂/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.

SOLUTION

Degree-of-Freedom Analysis

The analysis can be based on any of the three solution methods:

- **Molecular species balances** (Section 4.7c). 5 unknown variables + 2 independent reactions – 6 independent molecular species balances (CH_4 , O_2 , N_2 , CO , CO_2 , H_2O) – 1 specified methane conversion = 0 degrees of freedom.
- **Atomic species balances** (Section 4.7d). 5 unknown variables – 3 independent atomic species balances (C, H, O) – 1 nonreactive molecular species balance (N_2) – 1 specified methane conversion = 0 degrees of freedom.
- **Extents of reaction** (Section 4.7e). 5 unknown labeled variables + 2 independent reactions – 5 expressions for $n_i(\xi)$ ($i = \text{CH}_4$, O_2 , CO , CO_2 , H_2O) – 1 nonreactive molecular species balance (N_2) – 1 specified methane conversion = 0 degrees of freedom.

Before balances are written, the specified methane conversion can be used to determine n_{CH_4} .

90% CH_4 Conversion: (10% remains unconverted)

$$n_{\text{CH}_4} = 0.100(7.80 \text{ mol CH}_4 \text{ fed}) = 0.780 \text{ mol CH}_4$$

All three solution methods involve writing a balance on nitrogen (the nonreactive species in the process), so we may as well do that now as well.

N_2 Balance: input = output

$$n_{\text{N}_2} = 72.8 \text{ mol N}_2$$

It remains to determine n_{CO} , $n_{\text{H}_2\text{O}}$, and n_{O_2} . We will proceed by each of the indicated methods.

Molecular Species Balances

Each balance on a reactive species will contain a generation or consumption term. We will use the notation $C_{\text{CH}_4,1}$ (mol CH₄) to denote the consumption of methane in Reaction 1, $G_{\text{H}_2\text{O},2}$ (mol H₂O) to denote the generation of water in Reaction 2, and so on. Note that any G and C term for a specified

Since the balances on CO and CO₂ each involve the same unknown molar amount (n_{CO}), we will begin with those balances. Make sure you understand the form of each balance (like the CO balance, which simplifies to “output = generation”).

CO Balance: output = generation

$$n_{\text{CO}} = G_{\text{CO},1} \quad (3)$$

CO₂ Balance: output = generation

$$8n_{\text{CO}} = G_{\text{CO}_2,2} \quad (4)$$

Since we know both the feed and output amounts of methane, a methane balance should involve only the two methane consumption terms (one for each reaction) as unknowns. Since $C_{\text{CH}_4,1}$ can be expressed in terms of $G_{\text{CO},1}$ and $C_{\text{CH}_4,2}$ can be expressed in terms of $G_{\text{CO}_2,2}$, the CO, CO₂, and CH₄ balances will yield three equations in three unknowns— n_{CO} , $G_{\text{CO},1}$, and $G_{\text{CO}_2,2}$.

CH₄ Balance: input = output + consumption

$$7.80 \text{ mol CH}_4 = 0.780 \text{ mol CH}_4 + C_{\text{CH}_4,1} + C_{\text{CH}_4,2}$$

$$\begin{array}{l} \Downarrow \\ C_{\text{CH}_4,1} = G_{\text{CO},1} \times (1 \text{ mol CH}_4 \text{ consumed}/1 \text{ mol CO generated}) \\ \Downarrow \\ C_{\text{CH}_4,2} = G_{\text{CO}_2,2} \times (1 \text{ mol CH}_4 \text{ consumed}/1 \text{ mol CO}_2 \text{ generated}) \end{array}$$

$$7.02 \text{ mol CH}_4 = G_{\text{CO},1} + G_{\text{CO}_2,2}$$

$$\Downarrow \text{ Equations 3 and 4}$$

$$7.02 \text{ mol CH}_4 = n_{\text{CO}} + 8n_{\text{CO}} = 9n_{\text{CO}}$$



$$n_{\text{CO}} = 0.780 \text{ mol CO}$$

$$n_{\text{CO}_2} = (8 \times 0.780) \text{ mol CO}_2 = 6.24 \text{ mol CO}_2$$

Equations 3 and 4 now yield

$$G_{\text{CO},1} = n_{\text{CO}} = 0.780 \text{ mol CO generated} \quad (5)$$

$$G_{\text{CO}_2,2} = 8n_{\text{CO}} = 6.24 \text{ mol CO}_2 \text{ generated} \quad (6)$$

Water and oxygen balances complete the calculation of the unknown flow rates.

H₂O Balance: output = generation

$$n_{\text{H}_2\text{O}} = G_{\text{H}_2\text{O},1} + G_{\text{H}_2\text{O},2}$$

$$= G_{\text{CO},1} \left(\frac{2 \text{ mol H}_2\text{O generated}}{1 \text{ mol CO generated}} \right) + G_{\text{CO}_2,2} \left(\frac{2 \text{ mol H}_2\text{O generated}}{1 \text{ mol CO}_2 \text{ generated}} \right)$$

$$\downarrow G_{\text{CO},1} = 0.780 \text{ mol CO generated}, G_{\text{CO}_2,2} = 6.24 \text{ mol CO}_2 \text{ generated}$$

$$n_{\text{H}_2\text{O}} = 14.0 \text{ mol H}_2\text{O}$$

O₂ Balance: output = input – consumption

$$\begin{aligned}n_{\text{O}_2} &= 19.4 \text{ mol O}_2 - C_{\text{O}_2,1} - C_{\text{O}_2,2} \\&= 19.4 \text{ mol O}_2 - G_{\text{CO},1} \left(\frac{1.5 \text{ mol O}_2 \text{ consumed}}{1 \text{ mol CO generated}} \right) - G_{\text{CO}_2,2} \left(\frac{2 \text{ mol O}_2 \text{ consumed}}{1 \text{ mol CO}_2 \text{ generated}} \right)\\&\Downarrow G_{\text{CO},1} = 0.780 \text{ mol CO generated}, G_{\text{CO}_2,2} = 6.24 \text{ mol CO}_2 \text{ generated}\end{aligned}$$

$$n_{\text{O}_2} = 5.75 \text{ mol O}_2$$

In summary, the stack gas contains 0.780 mol CH₄, 0.780 mol CO, 6.24 mol CO₂, 14.0 mol H₂O, 5.75 mol O₂, and 72.8 mol N₂. The molar composition of the gas is therefore

$$0.78\% \text{ CH}_4, 0.78\% \text{ CO}, 6.2\% \text{ CO}_2, 14.0\% \text{ H}_2\text{O}, 5.7\% \text{ O}_2, \text{ and } 72.5\% \text{ N}_2$$

Atomic Species Balances

Referring to the flowchart, we see that a balance on atomic carbon involves only one unknown (n_{CO}) and a balance on atomic hydrogen also involves one unknown ($n_{\text{H}_2\text{O}}$), but a balance on atomic oxygen involves three unknowns. We will therefore write the C and H balances first, and then the O balance to determine the remaining unknown variable, n_{O_2} . All atomic balances have the form *input* = *output*. We will just determine the component amounts; calculation of the mole fractions then follows as in the previous part.

C Balance

$$\frac{7.8 \text{ mol CH}_4}{1 \text{ mol CH}_4} = \frac{0.78 \text{ mol CH}_4}{1 \text{ mol CH}_4}$$
$$+ \frac{n_{\text{CO}}(\text{mol CO})}{1 \text{ mol CO}} \frac{1 \text{ mol C}}{1 \text{ mol CO}} + \frac{8n_{\text{CO}}(\text{mol CO}_2)}{1 \text{ mol CO}_2} \frac{1 \text{ mol C}}{1 \text{ mol CO}_2}$$

\downarrow Solve for n_{CO}

$$n_{\text{CO}} = 0.780 \text{ mol CO}$$

$$n_{\text{CO}_2} = 8n_{\text{CO}} = (8 \times 0.780) \text{ mol CO}_2 = 6.24 \text{ mol CO}_2$$

H Balance

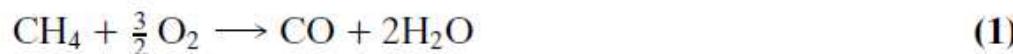
$$\frac{7.8 \text{ mol CH}_4}{1 \text{ mol CH}_4} = \frac{0.78 \text{ mol CH}_4}{1 \text{ mol CH}_4}$$
$$+ \frac{n_{\text{H}_2\text{O}}(\text{mol H}_2\text{O})}{1 \text{ mol H}_2\text{O}} \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \Rightarrow n_{\text{H}_2\text{O}} = 14.0 \text{ mol H}_2\text{O}$$

O Balance

$$\frac{19.4 \text{ mol O}_2}{1 \text{ mol O}_2} = \frac{n_{\text{O}_2}(\text{mol O}_2)}{1 \text{ mol O}_2} \frac{2 \text{ mol O}}{1 \text{ mol O}_2} + \frac{0.78 \text{ mol CO}}{1 \text{ mol CO}} \frac{1 \text{ mol O}}{1 \text{ mol CO}}$$
$$+ \frac{6.24 \text{ mol CO}_2}{1 \text{ mol CO}_2} \frac{2 \text{ mol O}}{1 \text{ mol CO}_2} + \frac{14.0 \text{ mol H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \frac{1 \text{ mol O}}{1 \text{ mol H}_2\text{O}}$$
$$\Rightarrow n_{\text{O}_2} = 5.75 \text{ mol O}_2$$

Extents of Reaction

For the reactions



Equation 4.6-6 ($n_i = n_{i0} + \sum \nu_{ij} \xi_j$) for the reactive species involved in the process yields the following five equations in five unknowns ($\xi_1, \xi_2, n_{\text{CO}}, n_{\text{H}_2\text{O}}, n_{\text{O}_2}$):

$$n_{\text{CH}_4} (= 0.78 \text{ mol}) = 7.80 \text{ mol} - \xi_1 - \xi_2 \implies 7.02 \text{ mol} = \xi_1 + \xi_2 \quad (3)$$

$$n_{\text{CO}} = \xi_1 \quad (4)$$

$$n_{\text{CO}_2} (= 8n_{\text{CO}}) = \xi_2 \quad (5)$$

$$n_{\text{H}_2\text{O}} = 2\xi_1 + 2\xi_2 \quad (6)$$

$$n_{\text{O}_2} = 19.4 \text{ mol} - \frac{3}{2}\xi_1 - 2\xi_2 \quad (7)$$

From Equation 4, $\xi_1 = n_{\text{CO}}$, and from Equation 5, $\xi_2 = 8n_{\text{CO}}$. If these two expressions are substituted into Equation 3, the resulting equation may be solved to yield

$$n_{\text{CO}} = 0.78 \text{ mol CO} \implies n_{\text{CO}_2} = 8n_{\text{CO}} = (8 \times 0.780) \text{ mol CO}_2 = 6.24 \text{ mol CO}_2$$

\downarrow
Equations 4 and 5

$$\xi_1 = n_{\text{CO}} = 0.78 \text{ mol}$$

$$\xi_2 = n_{\text{CO}_2} = 6.24 \text{ mol}$$

\downarrow
Substitute for ξ_1 and ξ_2 in Equations 6 and 7

$$n_{\text{H}_2\text{O}} = 14.0 \text{ mol H}_2\text{O}$$

$$n_{\text{O}_2} = 5.75 \text{ mol O}_2$$

4.7f Product Separation and Recycle

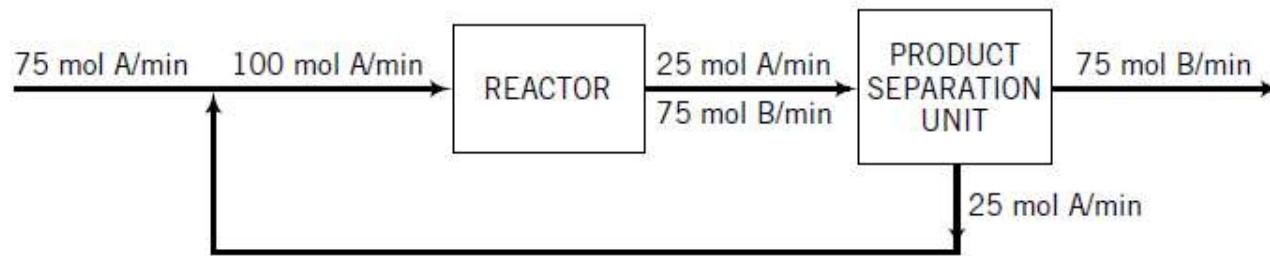
Two definitions of reactant conversion are used in the analysis of chemical reactors with product separation and recycle of unconsumed reactants:

Overall Conversion:
$$\frac{\text{reactant input to process} - \text{reactant output from process}}{\text{reactant input to process}} \quad (4.7-1)$$

Single-Pass Conversion:
$$\frac{\text{reactant input to reactor} - \text{reactant output from reactor}}{\text{reactant input to reactor}} \quad (4.7-2)$$

As usual, the corresponding percentage conversions are obtained by multiplying these quantities by 100%.

For example, consider the following labeled flowchart for a simple chemical process based on the reaction A \rightarrow B:



The overall conversion of A is from Equation 4.7-1:

$$\frac{(75 \text{ mol A/min})_{\text{in}} - (0 \text{ mol/min})_{\text{out}}}{(75 \text{ mol A/min})_{\text{in}}} \times 100\% = 100\%$$

The single-pass conversion is from Equation 4.7-2:

$$\frac{(100 \text{ mol A/min})_{\text{in}} - (25 \text{ mol A/min})_{\text{out}}}{(100 \text{ mol A/min})_{\text{in}}} \times 100\% = 75\%$$

EXAMPLE 4.7-2

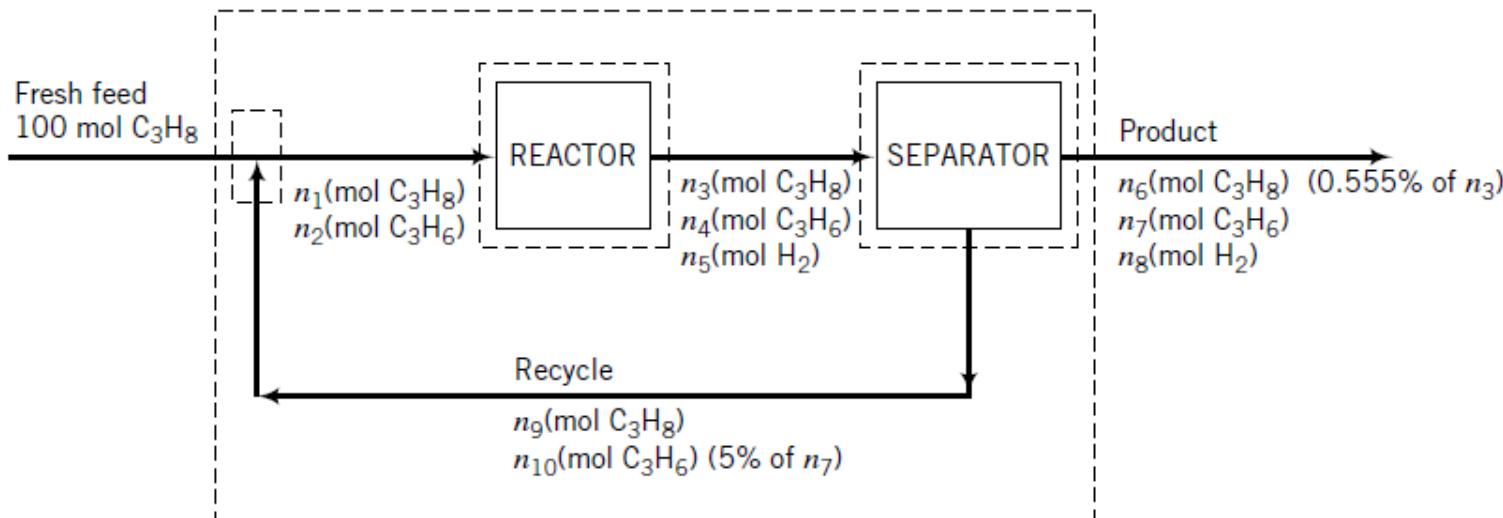
Dehydrogenation of Propane

Propane is dehydrogenated to form propylene in a catalytic reactor:



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.

SOLUTION



Degree-of-Freedom Analysis

When analyzing subsystems in which reactions occur (the overall system and the reactor), we will count atomic balances; for nonreactive subsystems (the recycle mixing point and the separation unit) we will count molecular species balances.

- **Overall system** (the outer dashed box on the flowchart). 3 unknown variables (n_6, n_7, n_8) – 2 independent atomic balances (C and H) – 1 additional relation (95% overall propane conversion)
⇒ 0 degrees of freedom. We will therefore be able to determine n_6, n_7 , and n_8 by analyzing the overall system. Let us count these three variables as known at this point.
- **Recycle-fresh feed mixing point.** 4 unknown variables (n_9, n_{10}, n_1, n_2) – 2 balances (C_3H_8, C_3H_6)
⇒ 2 degrees of freedom. Since we do not have enough equations to solve for the unknowns associated with this subsystem, we proceed to the next one.
- **Reactor.** 5 unknown variables (n_1 through n_5) – 2 atomic balances (C and H) ⇒ 3 degrees of freedom. No help here. Let us consider the remaining unit.
- **Separator.** 5 unknown variables ($n_3, n_4, n_5, n_9, n_{10}$) (n_6 through n_8 are known from the overall system analysis) – 3 balances (C_3H_8, C_3H_6, H_2) – 2 additional relations ($n_6 = 0.00555n_3, n_{10} = 0.05n_7$) ⇒ 0 degrees of freedom.

We can therefore determine the five given variables associated with the separator and then return to analyze either the mixing point or the reactor; in either case we can write two atomic balances to solve for the two remaining unknowns (n_1 and n_2), thereby completing the solution. (In fact, not all of the system variables are required by the problem statement so we will be able to stop well short of the full analysis.) The calculations follow, beginning with the analysis of the overall system.

95% Overall Propane Conversion (\Rightarrow 5% unconverted)

$$n_6 = 0.05(100 \text{ mol}) = 5 \text{ mol C}_3\text{H}_8$$

We are left with two overall system atomic balances to write. An H balance involves both remaining unknowns (n_7 and n_8) but a C balance involves only n_7 ; we therefore begin with the latter balance.

Overall C Balance

$$(100 \text{ mol C}_3\text{H}_8)(3 \text{ mol C/mol C}_3\text{H}_8) = [n_6(\text{mol C}_3\text{H}_8)](3 \text{ mol C/mol C}_3\text{H}_8) + [n_7(\text{mol C}_3\text{H}_6)](3 \text{ mol C/mol C}_3\text{H}_6)$$

$$\xrightarrow{n_6 = 5 \text{ mol}} n_7 = 95 \text{ mol C}_3\text{H}_6$$

Overall H Balance (Fill in units.)

$$(100)(8) = n_6(8) + n_7(6) + n_8(2) \xrightarrow{n_6 = 5 \text{ mol}, n_7 = 95 \text{ mol}} n_8 = 95 \text{ mol H}_2$$

The product therefore contains

$$\begin{array}{ll} 5 \text{ mol C}_3\text{H}_8 & 2.6 \text{ mole \% C}_3\text{H}_8 \\ 95 \text{ mol C}_3\text{H}_6 & 48.7 \text{ mole \% C}_3\text{H}_6 \\ 95 \text{ mol H}_2 & 48.7 \text{ mole \% H}_2 \end{array}$$

Given Relations Among Separator Variables

$$n_6 = 0.00555n_3 \xrightarrow{n_6 = 5 \text{ mol}} n_3 = 900 \text{ mol C}_3\text{H}_8$$

$$n_{10} = 0.0500n_7 \xrightarrow{n_7 = 95 \text{ mol}} n_{10} = 4.75 \text{ mol C}_3\text{H}_6$$

Propane Balance About Separation Unit

$$n_3 = n_6 + n_9 \xrightarrow{n_3 = 900 \text{ mol}, n_6 = 5 \text{ mol}} n_9 = 895 \text{ mol C}_3\text{H}_8$$

Propane Balance About Mixing Point

$$100 \text{ mol} + n_9 = n_1 \xrightarrow{n_9 = 895 \text{ mol}} n_1 = 995 \text{ mol C}_3\text{H}_8$$

We now have all the variable values we need. The desired quantities are

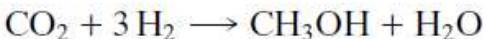
$$\text{Recycle ratio} = \frac{(n_9 + n_{10}) \text{ mol recycle}}{100 \text{ mol fresh feed}} \xrightarrow{n_9 = 895 \text{ mol}, n_{10} = 4.75 \text{ mol}} 9.00 \frac{\text{mol recycle}}{\text{mol fresh feed}}$$

$$\text{Single-pass conversion} = \frac{n_1 - n_3}{n_1} \times 100\% \xrightarrow{n_1 = 995 \text{ mol}, n_3 = 900 \text{ mol}} 9.6\%$$

4.7g Purging

Recycle and Purge in the Synthesis of Methanol

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

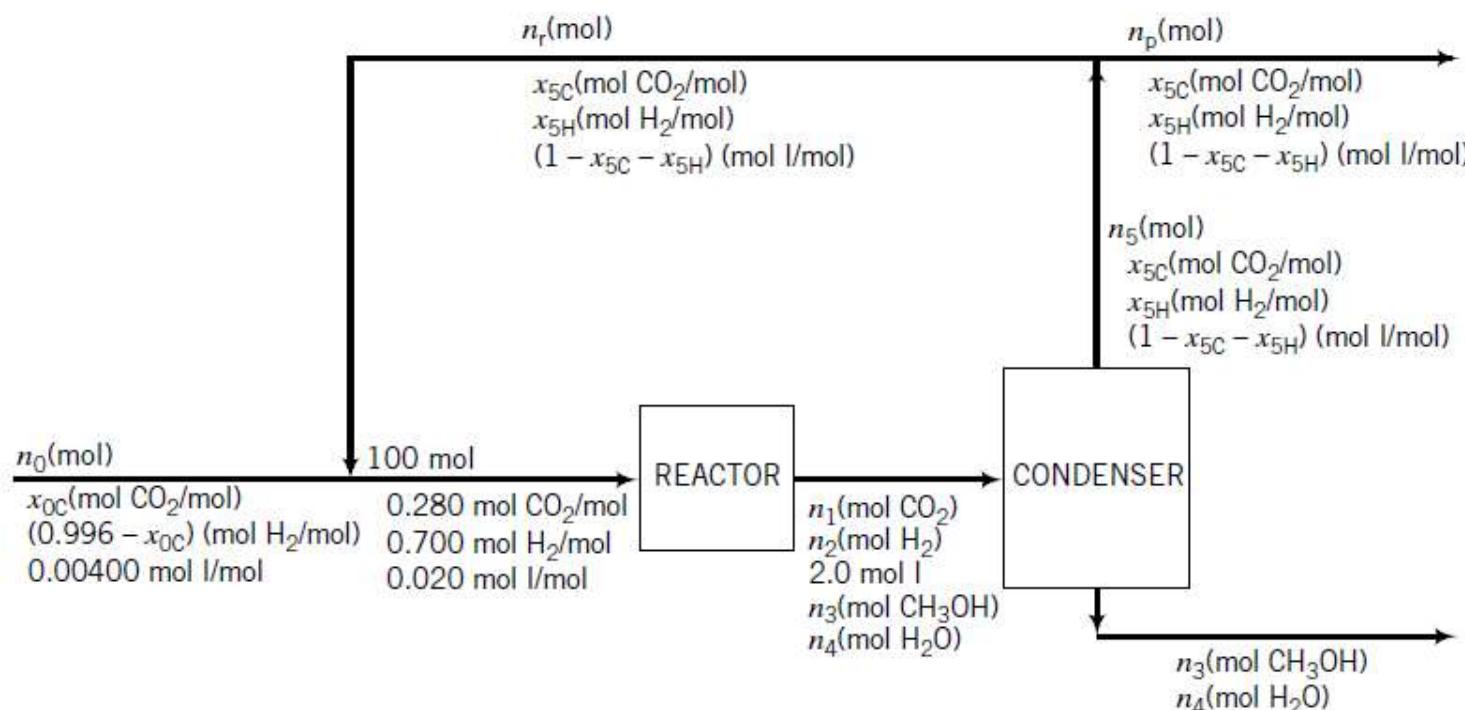


EXAMPLE 4.7-3

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 % CO₂, 70.0 mole % H₂, 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 CH₃OH/h.

Basis: 100 mol Combined Feed to the Reactor



Degree-of-Freedom Analysis

- **Overall system.** 7 unknowns ($n_0, x_{0C}, n_3, n_4, n_p, x_{5C}, x_{5H}$) + 1 reaction – 5 independent balances (CO₂, H₂, I, CH₃OH, H₂O) \Rightarrow 3 degrees of freedom. Since we do not have enough equations to solve for the number of unknowns in the overall system, we check subsystems to see if one can be found with zero degrees of freedom.
- **Recycle-fresh feed mixing point.** 5 unknowns ($n_0, x_{0C}, n_r, x_{5C}, x_{5H}$) – 3 independent balances (CO₂, H₂, I) \Rightarrow 2 degrees of freedom.
- **Reactor.** 4 unknowns (n_1, n_2, n_3, n_4) + 1 reaction – 4 independent balances (CO₂, H₂, CH₃OH, H₂O) – 1 single-pass conversion \Rightarrow 0 degrees of freedom. We will therefore be able to determine n_1, n_2, n_3 , and n_4 and proceed from there.

Notice that we only subtracted four balances and not one for each of the five species. The reason is that when we labeled the outlet flow of I as 2.0 mol, we implicitly used the balance on I (*input = output*) and so can no longer count it in the degree-of-freedom analysis. We will use the same reasoning in the analysis of the condenser.

- **Condenser.** 3 unknowns (n_5, x_{5C}, x_{5H}) – 3 independent balances (CO₂, H₂, I) \Rightarrow 0 degrees of freedom. We may now presume that n_5, x_{5C} , and x_{5H} are known.

In this analysis we presumed that we knew n_1, n_2, n_3 , and n_4 from the reactor analysis, and since we used the methanol and water balances when we labeled the bottom product stream we only counted three available balances in the degree-of-freedom analysis.

- **Purge-recycle splitting point.** 2 unknowns (n_r, n_p) – 1 independent balance \Rightarrow 1 degree of freedom. Since the labeled component mole fractions are the same in all three streams in this subsystem, balances on all three species reduce to the same equation (try it and see).
- **Recycle-fresh feed mixing point** (revisited). 3 unknowns (n_0, x_{0C}, n_r) – 3 independent balances \Rightarrow 0 degrees of freedom. We can now determine (n_0, x_{0C} , and n_r).
- **Purge-recycle splitting point** (revisited). 1 unknown (n_p) – 1 independent balance \Rightarrow 0 degrees of freedom. The final unknown variable can now be calculated.

Reactor Analysis

We will use molecular balances. Recall that the stoichiometric reaction is



60% Single-Pass H₂ Conversion: (\Rightarrow 40% is unconverted and emerges at the reactor outlet)

$$n_2 = 0.40(70.0 \text{ mol H}_2 \text{ fed}) = 28.0 \text{ mol H}_2$$

H₂ Balance: consumption = input – output

$$\text{Cons}_{\text{H}_2} = (70.0 - 28.0) \text{ mol H}_2 = 42.0 \text{ mol H}_2 \text{ consumed}$$

CO₂ Balance: output = input – consumption

$$n_1 = 28.0 \text{ mol CO}_2 - \frac{42.0 \text{ mol H}_2 \text{ consumed}}{3 \text{ mol H}_2 \text{ consumed}} \left| \begin{array}{l} 1 \text{ mol CO}_2 \text{ consumed} \\ \hline 3 \text{ mol H}_2 \text{ consumed} \end{array} \right. = 14.0 \text{ mol CO}_2$$

CH₃OH Balance: output = generation

$$n_3 = \frac{42.0 \text{ mol H}_2 \text{ consumed}}{3 \text{ mol H}_2 \text{ consumed}} \left| \begin{array}{l} 1 \text{ mol CH}_3\text{OH generated} \\ \hline 3 \text{ mol H}_2 \text{ consumed} \end{array} \right. = 14.0 \text{ mol CH}_3\text{OH}$$

H₂O Balance: output = generation

$$n_4 = \frac{42.0 \text{ mol H}_2 \text{ consumed}}{3 \text{ mol H}_2 \text{ consumed}} \left| \begin{array}{l} 1 \text{ mol H}_2\text{O generated} \\ \hline 3 \text{ mol H}_2 \text{ consumed} \end{array} \right. = 14.0 \text{ mol H}_2\text{O}$$

Condenser Analysis

Total Mole Balance: input = output

$$n_1 + n_2 + n_3 + n_4 + 2.0 \text{ mol} = n_3 + n_4 + n_5$$
$$\downarrow n_2 = 28.0 \text{ mol}, n_1 = n_3 = n_4 = 14.0 \text{ mol}$$
$$n_5 = 44.0 \text{ mol}$$

CO₂ Balance: input = output

$$n_1 = n_5 x_{5C}$$
$$\downarrow n_1 = 14.0 \text{ mol}, n_5 = 44.0 \text{ mol}$$
$$x_{5C} = 0.3182 \text{ mol CO}_2/\text{mol}$$

H₂ Balance: input = output

$$n_2 = n_5 x_{5H}$$
$$\downarrow n_2 = 28.0 \text{ mol}, n_5 = 44.0 \text{ mol}$$
$$x_{5H} = 0.6364 \text{ mol CO}_2/\text{mol}$$
$$\downarrow$$
$$x_I = 1 - x_{5C} - x_{5H} = 0.04545 \text{ mol I/mol}$$

Fresh Feed–Recycle Mixing Point Analysis

Total Mole Balance: input = output

$$n_0 + n_r = 100 \text{ mol}$$

I Balance: input = output

$$n_0(0.00400) + n_r(0.04545) = 2.0 \text{ mol I}$$

Solving these two equations simultaneously yields

$$n_0 = 61.4 \text{ mol fresh feed}, n_r = 38.6 \text{ mol recycle}$$

CO₂ Balance: input = output

$$n_0x_{0C} + n_r x_{5C} = 28.0 \text{ mol CO}_2$$

$$\downarrow n_0 = 61.4 \text{ mol}, n_r = 38.6 \text{ mol}, x_{5C} = 0.3182 \text{ mol CO}_2/\text{mol}$$

$$x_{0C} = 0.256 \text{ mol CO}_2/\text{mol}$$

$$\downarrow$$

$$x_{0H} = (1 - x_{0C} - x_{0I}) = 0.740 \text{ mol H}_2/\text{mol}$$

Recycle–Purge Splitting Point Analysis

Total Mole Balance: input = output

$$n_5 = n_r + n_p$$

$$\downarrow n_5 = 44.0 \text{ mol}, n_r = 38.6 \text{ mol}$$

$$n_p = 5.4 \text{ mol purge}$$

Flowchart Scaling

For the assumed basis of 100 mol feed to the reactor, the production rate of methanol is $n_3 = 14.0 \text{ mol CH}_3\text{OH}$. To scale the process to a methanol production rate of 155 kmol CH₃OH/h, we multiply each total and component molar flow rate by the factor

$$\left(\frac{155 \text{ kmol CH}_3\text{OH/h}}{14.0 \text{ mol CH}_3\text{OH}} \right) = \frac{11.1 \text{ kmol/h}}{\text{mol}}$$

The mole fractions remain unchanged by the scaling. The results follow.

Variable	Basis Value	Scaled Value
<i>Fresh feed</i>	<u>61.4 mol</u>	<u>681 kmol/h</u>
	25.6 mole % CO ₂	25.6 mole % CO ₂
	74.0 mole % H ₂	74.0 mole % H ₂
	0.400 mole % I	0.400 mole % I
<i>Feed to reactor</i>	<u>100 mol</u>	<u>1110 kmol/h</u>
	28.0 mole % CO ₂	28.0 mole % CO ₂
	70.0 mole % H ₂	70.0 mole % H ₂
	2.0 mole % I	2.0 mole % I
<i>Recycle</i>	<u>38.6 mol</u>	<u>428 kmol/h</u>
	31.8 mole % CO ₂	31.8 mole % CO ₂
	63.6 mole % H ₂	63.6 mole % H ₂
	4.6 mole % I	4.6 mole % I
<i>Purge</i>	<u>5.4 mol</u>	<u>59.9 kmol/h</u>
	31.8 mole % CO ₂	31.8 mole % CO ₂
	63.6 mole % H ₂	63.6 mole % H ₂
	4.6 mole % I	4.6 mole % I

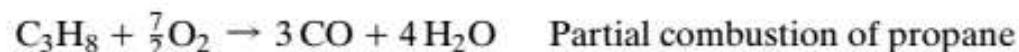
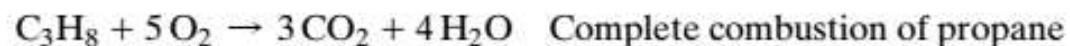
Lecture 13

4.8 Combustion Reactions

4.8a Combustion Chemistry

When a fuel is burned, carbon in the fuel reacts to form either CO_2 or CO , hydrogen forms H_2O , and sulfur forms SO_2 . At temperatures greater than approximately 1800°C , some of the nitrogen in the air reacts to form nitric acid (NO). A combustion reaction in which CO is formed from a hydrocarbon is referred to as **partial combustion** or **incomplete combustion** of the hydrocarbon.

Examples:



For obvious economic reasons, air is the source of oxygen in most combustion reactors. Dry air has the following average molar composition:

N_2	78.03%	Average molecular weight = 29.0
O_2	20.99%	
Ar	0.94%	
CO_2	0.03%	
$\text{H}_2, \text{He}, \text{Ne}, \text{Kr}, \text{Xe}$	0.01%	
	100.00%	

In most combustion calculations, it is acceptable to simplify this composition to 79% N_2 , 21% $\text{O}_2 \implies 79 \text{ moles N}_2 / 21 \text{ moles O}_2 = 3.76 \text{ moles N}_2/\text{mole O}_2$.

The term **composition on a wet basis** is commonly used to denote the component mole fractions of a gas that contains water, and **composition on a dry basis** signifies the component mole fractions of the same gas without the water. For example, a gas that contains 33.3 mole% CO₂, 33.3% N₂, and 33.3% H₂O (wet basis) contains 50% CO₂ and 50% N₂ on a dry basis.

EXAMPLE 4.8-1

Composition on Wet and Dry Bases

1. Wet Basis \Rightarrow Dry Basis.

A stack gas contains 60.0 mole% N₂, 15.0% CO₂, 10.0% O₂, and the balance H₂O. Calculate the molar composition of the gas on a dry basis.

SOLUTION

Basis: 100 mol Wet Gas

$$60.0 \text{ mol N}_2$$

$$15.0 \text{ mol CO}_2$$

$$\underline{10.0 \text{ mol O}_2}$$

$$85.0 \text{ mol dry gas}$$



$$\frac{60.0}{85.0} = 0.706 \frac{\text{mol N}_2}{\text{mol dry gas}}$$

$$\frac{15.0}{85.0} = 0.176 \frac{\text{mol CO}_2}{\text{mol dry gas}}$$

$$\frac{10.0}{85.0} = 0.118 \frac{\text{mol O}_2}{\text{mol dry gas}}$$

2. Dry Basis \Rightarrow Wet Basis.

An **Orsat analysis** (a technique for stack analysis) yields the following dry basis composition:

N ₂	65%
CO ₂	14%
CO	11%
O ₂	10%

A humidity measurement shows that the mole fraction of H₂O in the stack gas is 0.0700. Calculate the stack gas composition on a wet basis.

Basis: 100 lb-moles Dry Gas

$$0.0700 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole wet gas}} \Leftrightarrow 0.930 \frac{\text{lb-mole dry gas}}{\text{lb-mole wet gas}}$$



$$\frac{0.0700 \text{ lb-mole H}_2\text{O/lb-mole wet gas}}{0.930 \text{ lb-mole dry gas/lb-mole wet gas}} = 0.0753 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole dry gas}}$$

Hence the gas in the assumed basis contains

$$\frac{100 \text{ lb-moles dry gas}}{} \left| \begin{array}{l} \frac{0.0753 \text{ lb-mole H}_2\text{O}}{\text{lb-mole dry gas}} \\ \hline \end{array} \right. = 7.53 \text{ lb-moles H}_2\text{O}$$

$$\frac{100 \text{ lb-moles dry gas}}{} \left| \begin{array}{l} \frac{0.650 \text{ lb-mole N}_2}{\text{lb-mole dry gas}} \\ \hline \end{array} \right. = 65.0 \text{ lb-moles N}_2$$

$$(100)(0.140) \text{ lb-moles CO}_2 = 14.0 \text{ lb-moles CO}_2$$

$$(100)(0.110) \text{ lb-moles CO} = 11.0 \text{ lb-moles CO}$$

$$(100)(0.100) \text{ lb-moles O}_2 = \frac{10.0 \text{ lb-moles O}_2}{107.5 \text{ lb-moles wet gas}}$$

The mole fractions of each stack gas component may now easily be calculated:

$$y_{\text{H}_2\text{O}} = \frac{7.53}{107.5} \frac{\text{lb-moles H}_2\text{O}}{\text{lb-moles wet gas}} = 0.070 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole wet gas}}, \dots$$

4.8b Theoretical and Excess Air

Theoretical Oxygen: The moles (batch) or molar flow rate (continuous) of O₂ needed for complete combustion of all the fuel fed to the reactor, assuming that all carbon in the fuel is oxidized to CO₂ and all the hydrogen is oxidized to H₂O.

Theoretical Air: The quantity of air that contains the theoretical oxygen.

Excess Air: The amount by which the air fed to the reactor exceeds the theoretical air.

Percent Excess Air:
$$\frac{(\text{moles air})_{\text{fed}} - (\text{moles air})_{\text{theoretical}}}{(\text{moles air})_{\text{theoretical}}} \times 100\% \quad (4.8-1)$$

EXAMPLE 4.8-2

Theoretical and Excess Air

One hundred mol/h of butane (C₄H₁₀) and 5000 mol/h of air are fed into a combustion reactor. Calculate the percent excess air.

SOLUTION

First, calculate the theoretical air from the feed rate of fuel and the stoichiometric equation for complete combustion of butane:



$$(\dot{n}_{\text{O}_2})_{\text{theoretical}} = \frac{100 \text{ mol C}_4\text{H}_{10}}{\text{h}} \left| \begin{array}{l} 6.5 \text{ mol O}_2 \text{ required} \\ \text{mol C}_4\text{H}_{10} \end{array} \right. \\ = 650 \frac{\text{mol O}_2}{\text{h}}$$

$$(\dot{n}_{\text{air}})_{\text{theoretical}} = \frac{650 \text{ mol O}_2}{\text{h}} \left| \begin{array}{l} 4.76 \text{ mol air} \\ \text{mol O}_2 \end{array} \right. = 3094 \frac{\text{mol air}}{\text{h}}$$

Hence

$$\% \text{ excess air} = \frac{(\dot{n}_{\text{air}})_{\text{fed}} - (\dot{n}_{\text{air}})_{\text{theoretical}}}{(\dot{n}_{\text{air}})_{\text{theoretical}}} \times 100\% = \frac{5000 - 3094}{3094} \times 100\% = \boxed{61.6\%}$$

If instead you had been given 61.6% excess air, you could have calculated the feed rate of air as $(\dot{n}_{\text{air}})_{\text{fed}} = 1.616(\dot{n}_{\text{air}})_{\text{theoretical}} = 1.616(3094 \text{ mol/h}) = 5000 \text{ mol/h}$.

4.8c Materials Balances on Combustion Reactors

The procedure for writing and solving material balances for a combustion reactor is the same as that for any other reactive system. Bear in mind these points, however:

1. When you draw and label the flowchart, be sure the outlet stream (the stack gas) includes (a) unreacted fuel unless you are told that all the fuel is consumed, (b) unreacted oxygen, (c) water and carbon dioxide, as well as carbon monoxide if the problem statement says any is present, and (d) nitrogen if the fuel is burned with air and not pure oxygen.
2. To calculate the oxygen feed rate from a specified percent excess oxygen or percent excess air (both percentages have the same value, so it doesn't matter which one is stated), first calculate the theoretical O₂ from the fuel feed rate and the reaction stoichiometry for complete combustion, then calculate the oxygen feed rate by multiplying the theoretical oxygen by (1 + fractional excess oxygen).
3. If only one reaction is involved, all three balance methods (molecular species balances, atomic species balances, extent of reaction) are equally convenient. If several reactions occur simultaneously, however—such as combustion of a fuel to form both CO and CO₂—atomic species balances are usually most convenient.

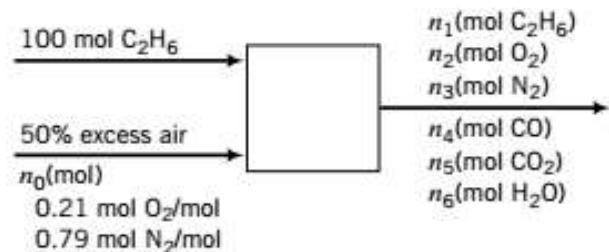
EXAMPLE 4.8-3

Combustion of Ethane

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.

SOLUTION

Basis: 100 mol C_2H_6 Fed



Notes

1. Since no product stream mole fractions are known, subsequent calculations are easier if individual component amounts rather than a total amount and mole fractions are labeled.
2. The composition of air is taken to be approximately 21 mole% O_2 , 79 mole% N_2 .
3. If the ethane reacted completely, n_1 would be omitted. Since excess air is supplied, O_2 must appear in the product stream.
4. In material balance calculations on combustion processes it is reasonable to assume that nitrogen is inert—that is, to neglect the trace amounts of NO , NO_2 , and N_2O_4 (collectively referred to as NO_x) that might form in the burner. On the other hand, in environmental impact studies NO_x may not automatically be neglected; trace amounts of nitrogen oxides may have little impact on the nitrogen balance but may have a significant polluting effect if they are released into the atmosphere.

Degree-of-Freedom Analysis

- 7 unknowns (n_0, n_1, \dots, n_6)
 - 3 atomic balances (C, H, O)
 - 1 N_2 balance
 - 1 excess air specification (relates n_0 to the quantity of fuel fed)
 - 1 ethane conversion specification
 - 1 CO/CO₂ ratio specification
-
- = 0 degrees of freedom

50% Excess Air

$$(n_{O_2})_{\text{theoretical}} = \frac{100 \text{ mol C}_2\text{H}_6}{1 \text{ mol C}_2\text{H}_6} \left| \frac{3.50 \text{ mol O}_2}{\text{1 mol C}_2\text{H}_6} \right. = 350 \text{ mol O}_2$$

\Downarrow 50% excess air

$$0.21n_0 = 1.50(350 \text{ mol O}_2) \implies n_0 = 2500 \text{ mol air fed}$$

90% Ethane Conversion: (implies 10% unreacted)

$$n_1 = 0.100(100 \text{ mol C}_2\text{H}_6 \text{ fed}) = \boxed{10.0 \text{ mol C}_2\text{H}_6}$$

$$0.900(100 \text{ mol C}_2\text{H}_6 \text{ fed}) = 90.0 \text{ mol C}_2\text{H}_6 \text{ react}$$

25% Conversion to CO

$$n_4 = \frac{(0.25 \times 90.0) \text{ mol C}_2\text{H}_6 \text{ react to form CO}}{1 \text{ mol C}_2\text{H}_6 \text{ react}} \left| \frac{2 \text{ mol CO generated}}{\text{1 mol C}_2\text{H}_6 \text{ react}} \right. = \boxed{45.0 \text{ mol CO}}$$

Nitrogen Balance: output = input

$$n_3 = 0.79(2500 \text{ mol}) = \boxed{1975 \text{ mol N}_2}$$

Atomic Carbon Balance: input = output

$$\frac{100 \text{ mol C}_2\text{H}_6}{1 \text{ mol C}_2\text{H}_6} = \frac{n_1(\text{mol C}_2\text{H}_6)}{1 \text{ mol C}_2\text{H}_6} + \frac{n_4(\text{mol CO})}{1 \text{ mol C}_2\text{H}_6} + \frac{n_5(\text{mol CO}_2)}{1 \text{ mol CO}_2}$$

\downarrow
 $n_1 = 10 \text{ mol}$
 $n_4 = 45 \text{ mol}$

$n_5 = 135 \text{ mol CO}_2$

Atomic Hydrogen Balance: input = output

$$\frac{100 \text{ mol C}_2\text{H}_6}{1 \text{ mol C}_2\text{H}_6} = \frac{10 \text{ mol C}_2\text{H}_6}{1 \text{ mol C}_2\text{H}_6} + \frac{n_6(\text{mol H}_2\text{O})}{1 \text{ mol C}_2\text{H}_6} + \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}}$$

\downarrow

$n_6 = 270 \text{ mol H}_2\text{O}$

Atomic Oxygen Balance: input = output

$$\frac{525 \text{ mol O}_2}{1 \text{ mol O}_2} = \frac{n_2(\text{mol O}_2)}{1 \text{ mol O}_2} + \frac{45 \text{ mol CO}}{1 \text{ mol CO}} + \frac{135 \text{ mol CO}_2}{1 \text{ mol CO}_2} + \frac{270 \text{ mol H}_2\text{O}}{1 \text{ mol H}_2\text{O}}$$

\downarrow

$n_2 = 232 \text{ mol O}_2$

The analysis of the stack gas is now complete. Summarizing:

$$n_1 = 10 \text{ mol C}_2\text{H}_6$$

$$n_2 = 232 \text{ mol O}_2$$

$$n_3 = 1974 \text{ mol N}_2$$

$$n_4 = 45 \text{ mol CO}$$

$$n_5 = \frac{135 \text{ mol CO}_2}{2396 \text{ mol dry gas}}$$

$$+ n_6 = \frac{270 \text{ mol H}_2\text{O}}{2666 \text{ mol total}}$$

Hence the stack gas composition on a dry basis is

$$y_1 = \frac{10 \text{ mol C}_2\text{H}_6}{2396 \text{ mol dry gas}} = 0.00417 \frac{\text{mol C}_2\text{H}_6}{\text{mol}}$$

$$y_2 = \frac{232 \text{ mol O}_2}{2396 \text{ mol dry gas}} = 0.0970 \frac{\text{mol O}_2}{\text{mol}}$$

$$y_3 = \frac{1974 \text{ mol N}_2}{2396 \text{ mol dry gas}} = 0.824 \frac{\text{mol N}_2}{\text{mol}}$$

$$y_4 = \frac{45 \text{ mol CO}}{2396 \text{ mol dry gas}} = 0.019 \frac{\text{mol CO}}{\text{mol}}$$

$$y_5 = \frac{135 \text{ mol CO}_2}{2396 \text{ mol dry gas}} = 0.0563 \frac{\text{mol CO}_2}{\text{mol}}$$

and the mole ratio of water to dry stack gas is

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

EXAMPLE 4.8-4

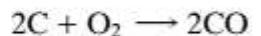
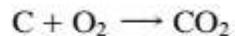
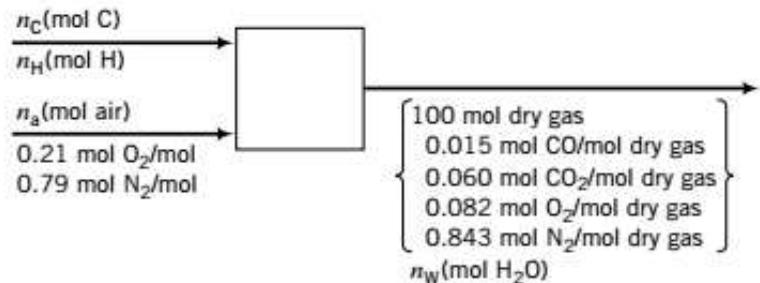
Combustion of a Hydrocarbon Fuel of Unknown Composition

A hydrocarbon gas is burned with air. The dry-basis product gas composition is 1.5 mole% CO, 6.0% CO₂, 8.2% O₂, and 84.3% N₂. There is no atomic oxygen in the fuel. Calculate the ratio of hydrogen to carbon in the fuel gas and speculate on what the fuel might be. Then calculate the percent excess air fed to the reactor.

SOLUTION

Basis: 100 mol Product Gas

Since the molecular composition of the fuel is unknown, we label its atomic species composition. We also recognize that since the fuel is a hydrocarbon, water must be one of the combustion products.



Degree-of-Freedom Analysis

4 unknowns (n_H , n_C , n_a , n_w)

-3 independent atomic balances (C, H, O)

-1 N₂ balance

= 0 degrees of freedom

A solution procedure that does not require solving simultaneous equations is as follows:

N₂ Balance $0.79n_a = (100)(0.843) \text{ mol N}_2 \implies n_a = 106.7 \text{ mol air}$

Atomic C Balance $n_C = \frac{100 \text{ mol}}{\text{mol}} \left| \frac{0.015 \text{ mol CO}}{1 \text{ mol CO}} \right| + (100)(0.060)(1) \text{ mol C}$
 $\implies n_C = 7.5 \text{ mol C}$

Atomic O Balance $0.21n_a(2) = n_w(1) + 100[\overbrace{(0.015)(1)}^{\text{CO}} + \overbrace{(.060)(2)}^{\text{CO}_2} + \overbrace{(0.082)(2)}^{\text{O}_2}] \text{ mol O}$
 $\xrightarrow{n_a = 106.7 \text{ mol}} n_w = 14.9 \text{ mol H}_2\text{O}$

Atomic H Balance $n_H = \overbrace{n_w(2)}^{\text{H}_2\text{O}} \xrightarrow{n_w = 14.9 \text{ mol}} n_H = 29.8 \text{ mol H}$

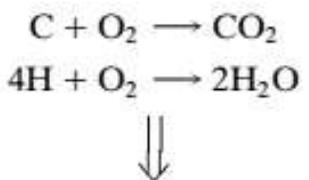
$$C/H \text{ Ratio in the Fuel} \quad \frac{n_H}{n_C} = \frac{29.8 \text{ mol H}}{7.5 \text{ mol C}} = \boxed{3.97 \text{ mol H/mol C}}$$

The fuel composition may therefore be described by the formula $(\text{CH}_{3.97})_N$.

Since there is only one hydrocarbon for which the ratio of H to C is close to 3.97—that is, CH_4 —we may conclude in this case that the fuel is essentially pure methane, perhaps with trace amounts of other hydrocarbons. [If we had obtained, say, $n_H/n_C \approx 2$, we could have gone no further than to label the fuel as $(\text{CH}_2)_n$; from the information given, there would have been no way to distinguish between C_2H_4 , C_3H_6 , a mixture of CH_4 and C_2H_2 , and so on.]

Percent Excess Air

We must first determine the theoretical oxygen required to consume the carbon and hydrogen in the fuel. The reactions may be written as



$$(n_{\text{O}_2})_{\text{theoretical}} = \frac{7.5 \text{ mol C}}{1 \text{ mol C}} \left| \frac{1 \text{ mol O}_2}{1 \text{ mol C}} \right. + \frac{29.8 \text{ mol H}}{4 \text{ mol H}} \left| \frac{1 \text{ mol O}_2}{4 \text{ mol H}} \right. = 14.95 \text{ mol O}_2$$

$$(n_{\text{O}_2})_{\text{fed}} = 0.21(106.7 \text{ mol air}) = 22.4 \text{ mol O}_2$$

$$\begin{aligned} \% \text{ excess air} &= \frac{(n_{\text{O}_2})_{\text{fed}} - (n_{\text{O}_2})_{\text{theoretical}}}{(n_{\text{O}_2})_{\text{theoretical}}} \times 100\% = \frac{(22.4 - 14.95) \text{ mol O}_2}{14.95 \text{ mol O}_2} \times 100\% \\ &= \boxed{49.8\% \text{ excess air}} \end{aligned}$$