الجامعة التكنولوجية

قسم الهندسة الكيمياوية

المرحلة الاولى

مباديء الهندسة الكيمياوية

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(c) From four material balances, three of which are independent?

3. If you want to solve a set of independent equations that contain fewer unknown variables than equations (the over specified problem), how should you proceed with the solution?
4. What is the major category of implicit constraints (equations) you encounter in material balance problems?
5. If you want to solve a set of independent equations that contain more unknown variable than equations (the underspecified problem), what must you do to proceed with the solution?

Answers:

1. A solution means a (possibly unique) set of values for the unknowns in a problem that satisfies the equations formulated in the problem.
2. (a) one; (b) three; (c) three.
3. Delete nonpertinent equations, or find additional variables not included in the analysis.
4. The sum of the mass or mole fraction in a stream or inside a system is unity.
5. Obtain more equations or specifications, or delete variables of negligible importance.

Problems

1. A water solution containing 10% acetic acid is added to a water solution containing 30% acetic acid flowing at the rate of 20 kg/min. The product P of the combination leaves the rate of 100 kg/min. What is the composition of P? For this process,
   a. Determine how many independent balances can be written.
   b. List the names of the balances.
   c. Determine how many unknown variables can be solved for.
   d. List their names and symbols.
   e. Determine the composition of P.
2. Can you solve these three material balances for F, D, and P? Explain why not.

$$\begin{aligned} 0.1F + 0.3D &= 0.2P \\ 0.9F + 0.7D &= 0.8P \\ F + D &= P \end{aligned}$$

3. How many values of the concentrations and flow rates in the process shown in Figure SAT7.2P3 are unknown? List them. The streams contain two components, 1 and 2.

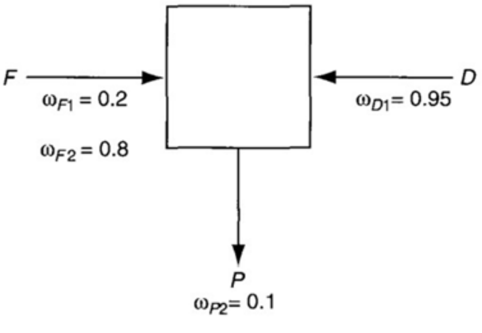


Figure SAT7.2P3

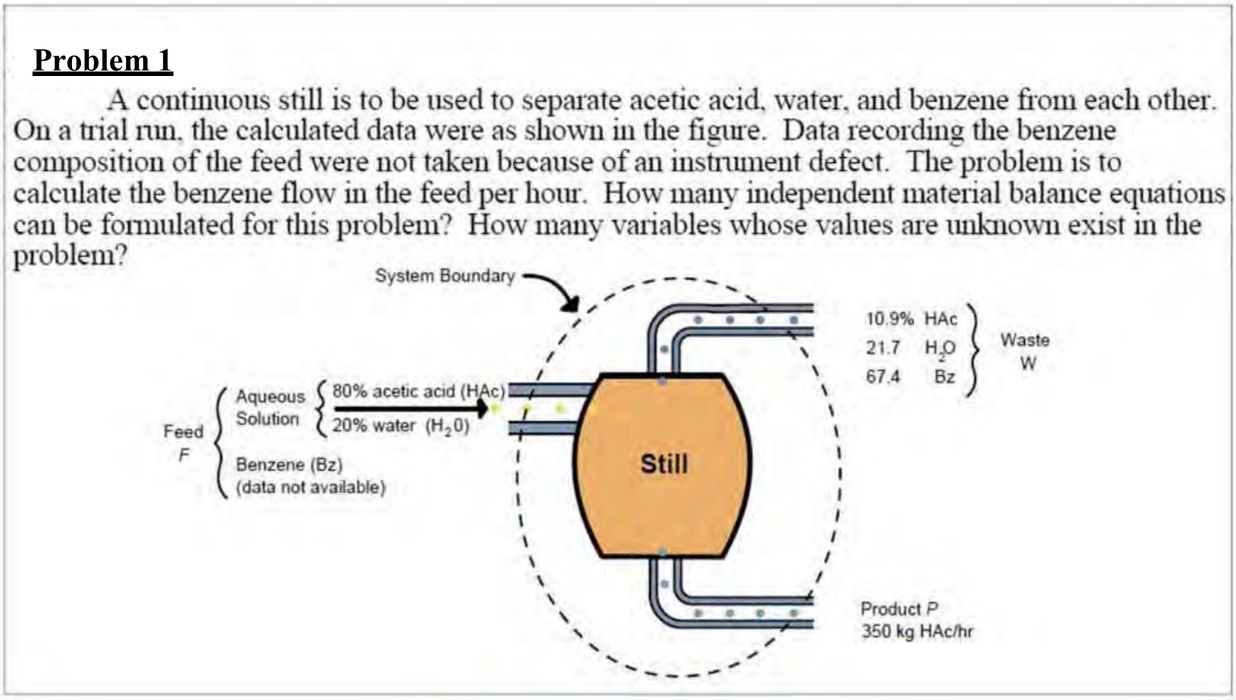
4. How many material balances are needed to solve problem 3? Is the number the same as the

number of unknown variables? Explain.

Answers:

1. (a) Two; (b) two of these three: acetic acid, water, total; (c) two; (d) feed of the 10% solution (say F) and mass fraction ω of the acetic acid in P; (e) 14% acetic acid and 86% water
2. Not for a unique solution because only two of the equations are independent.
3. F, D, P, ω_{D2}, ω_{P1}
4. Three unknowns exist. Because only two independent material balances can be written for the problem, one value of F, D, or P must be specified to obtain a solution. Note that specifying values of ω_{D2} or ω_{P1} will not help.

Supplementary Problems (Chapter Seven):



Problem 1

A continuous still is to be used to separate acetic acid, water, and benzene from each other. On a trial run, the calculated data were as shown in the figure. Data recording the benzene composition of the feed were not taken because of an instrument defect. The problem is to calculate the benzene flow in the feed per hour. How many independent material balance equations can be formulated for this problem? How many variables whose values are unknown exist in the problem?

Solution

Three components exist in the problem, hence three mass balances can be written down (the units are kg):

Balance	F in		W out		P out	
HAc:	$0.80(1-\omega_{Bz,F})F$	=	$0.109W$	+	350	(a)
H_2O:	$0.20(1-\omega_{Bz,F})F$	=	$0.217W$	+	0	(b)
Benzene:	$\omega_{Bz,F}F$	=	$0.67W$	+	0	(c)

The total balance would be: $F = W + 350$ (in kg).

Problem 8.1

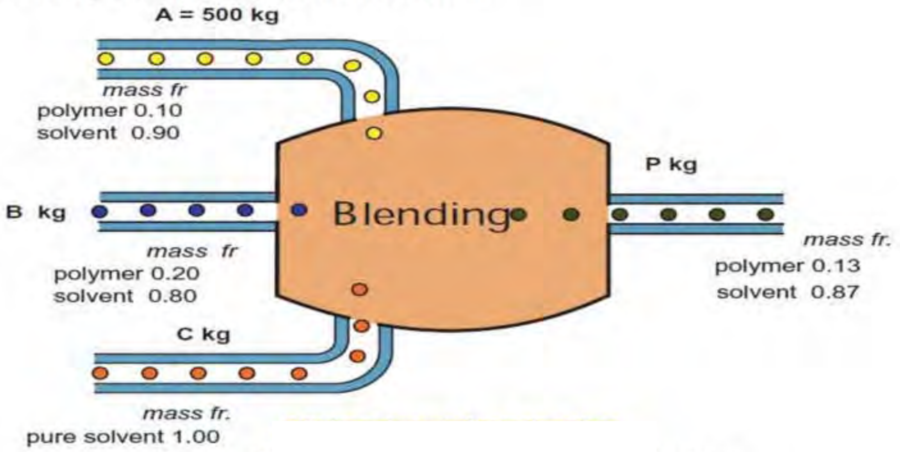
Problem 2

A liquid adhesive, which is used to make laminated boards, consists of a polymer lvent. The amount of polymer in the solution has to be carefully controlled for this n the supplier of the adhesive receives an order for 3000 kg of an adhesive solution containing 13 wt % polymer, all it has on hand is (1) 500 kg of a 10 wt % solution, (2) a very large quantity of a 20 wt % solution, and (3) pure solvent.

Calculate the weight of each of the three stocks that must be blended together to fill the order. Use all of the 10 wt % solution.

Solution

This is a steady state process without reaction.



Basis: 3000 kg 13 wt % polymer solution

Two unknowns: B and C . (A is not an unknown since all of it must be used).

Total balance: $500 + B + C = 3000$ (1)

Polymer balance: $0.10\,(500) + 0.20\,B + 0.00\,(C) = 0.13\,(3000)$ (2)

Solvent balance: $0.90\,(500) + 0.80\,B + 1.00\,(C) = 0.87\,(3000)$ (3)

We will use equations (1) and (2).

from (2) $0.1\,(500) + 0.20\,B = 0.13\,(3000)$

from (1) $500 + 1700 + C = 3000$

B = 1700 kg

C = Ê800 kg

Equation (3) can be used as a check.

$0.90\,A + 0.80\,B + C = 0.87\,P$

$0.90\,(500) + 0.80\,(1700) + 800 = 2610 = 0.87\,(3000) = 2610$

The use of material balances in a process allows you **(a)** to calculate the values of the total flows and flows of species in the streams that enter and leave the plant equipment, and **(b)** to calculate the change of conditions inside the equipment.

Example 8.1

Determine the mass fraction of Streptomycin in the exit organic solvent assuming that no water exits with the solvent and no solvent exits with the aqueous solution. Assume that the density of the aqueous solution is 1 g/cm^3 and the density of the organic solvent is 0.6 g/cm^3. Figure E8. 1 shows the overall process.

Solution

This is an **open** (flow), **steady-state** process without reaction. Assume because of the low concentration of Strep. in the aqueous and organic fluids that the **flow rates** of the **entering** fluids **equal** the flow rates of the **exit** fluids.

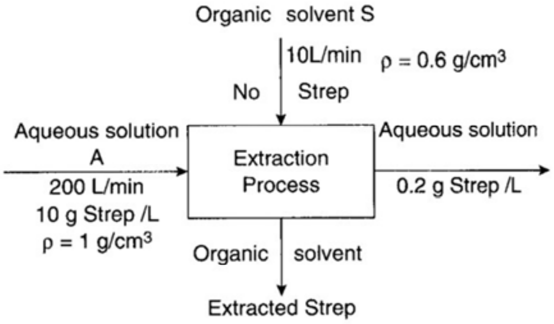


Figure E8.1

Basis: 1 min

Basis: Feed = 200 L (flow of aqueous entering aqueous solution)

- Flow of exiting aqueous solution (same as existing flow)
- Flow of exiting organic solution (same as existing flow)

The material balances are **in = out** in **grams**. Let **x** be the **g** of Strep per **L** of solvent **S**

Strep. balance:

$$\frac{200\ \text{L of A}}{}\Big|\frac{10\ \text{g Strep}}{1\ \text{L of A}} + \frac{10\ \text{L of S}}{}\Big|\frac{0\ \text{g Strep}}{1\ \text{L of S}} = \frac{200\ \text{L of A}}{}\Big|\frac{0.2\ \text{g Strep}}{1\ \text{L of A}} + \frac{10\ \text{L of S}}{}\Big|\frac{x\ \text{g Strep}}{1\ \text{L of S}}$$

x = 196 g Strep/L of solvent

To get the g Strep/g solvent, use the density of the solvent:

$$\frac{196 \text{ g Strep}}{1 \text{ L of S}}\left|\frac{1 \text{ L of S}}{1000 \text{ cm}^3 \text{ of S}}\right|\frac{1 \text{ cm}^3 \text{ of S}}{0.6 \text{ g of S}} = 0.3267 \text{ g Strep/g of S}$$

$$\text{The mass fraction Strep} = \frac{0.3267}{1 + 0.3267} = 0.246$$

Example 8.2

Membranes represent a relatively new technology for the separation of gases. One use that has attracted attention is the separation of nitrogen and oxygen from air. Figure E8.2a illustrates a nanoporous membrane that is made by coating a very thin layer of polymer on a porous graphite supporting layer. What is the composition of the waste stream if the waste stream amounts to 80% of the input stream?

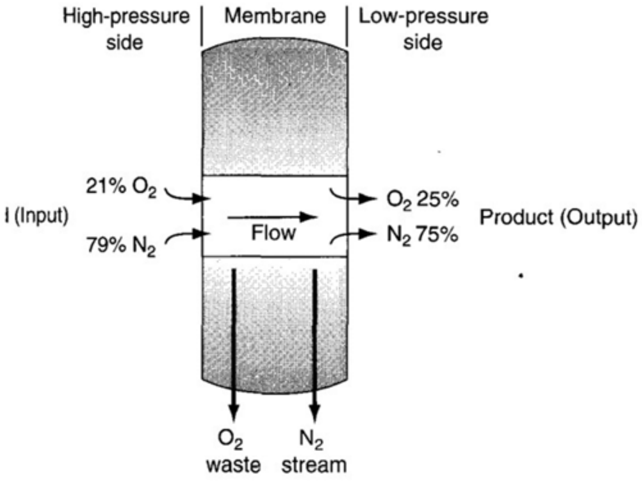
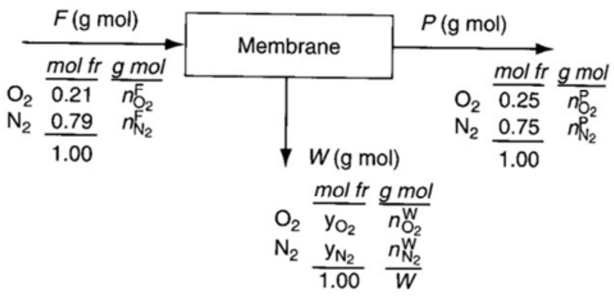


Figure E8.2a

Solution

This is an **open**, **steady-state process** without chemical reaction.



Basis: 100 g mol = F

Basis: F = 100

Specifications: $n^F_{O_2} = 0.21(100) = 21$

$n^F_{N_2} = 0.79(100) = 79$

$$y_{O_2}^P = n_{O_2}^P/P = 0.25 \qquad n_{O_2}^P = 0.25P$$
$$y_{N_2}^P = n_{N_2}^P/P = 0.75 \qquad n_{N_2}^P = 0.75P$$
$$W = 0.80(100) = 80$$

Material balances: O_2 and N_2

Implicit equations: $\Sigma n_i^W = W$ or $\Sigma y_i^W = 1$

	In	*Out*		*In*	*Out*
O_2:	0.21 (100)	$= 0.25P + y_{O_2}^W (80)$	or	0.21 (100)	$= 0.25P + n_{O_2}^W$
N_2:	0.79 (100)	$= 0.75P + y_{N_2}^W (80)$	or	0.79 (100)	$= 0.75P + n_{N_2}^W$
	1.00	$= y_{O_2}^W + y_{N_2}^W$	or	80	$= n_{O_2}^W + n_{N_2}^W$

The solution of these equations is

$n_{O_2}^W = 16$ and $n_{N_2}^W = 64$, or $y_{O_2}^W = 0.20$ and $y_{N_2}^W = 0.80$, and $P = 20$ g mol.

Check: total balance 100 = 20 + 80 OK

❖ Another method for solution

The overall balance is easy to solve because

$F = P + W$ or $100 = P + 80$

Gives P = 20 straight off. Then, the oxygen balance would be

$$0.21(100) = 0.25(20) + n_{O_2}^W$$

$n_{O_2}^W = 16$ g mol, and $n_{O_2}^W = 80 - 16 = 64$ g mol.

Note (Example 8.2)

$n_{O_2}^F + n_{N_2}^F = F$ is a redundant equation because it repeats some of the specifications.

Also, $n_{O_2}^P + n_{N_2}^P = P$ is redundant. Divide the equation by P to get $y_{O_2}^P + y_{N_2}^P = 1$, a relation that is equivalent to the sum of two of the specifications.

Example 8.3

A novice manufacturer of ethyl alcohol (denoted as EtOH) for gasohol is having a bit of difficulty with a distillation column. The process is shown in Figure E8.3. It appears that too much alcohol is lost in the bottoms (waste). Calculate the composition of the bottoms and the mass of the alcohol lost in the bottoms based on the data shown in Figure E8.3 that was collected during 1 hour of operation.

Solution

The process is an **open system**, and we assume it is in the **steady state**. No **reaction** occurs.

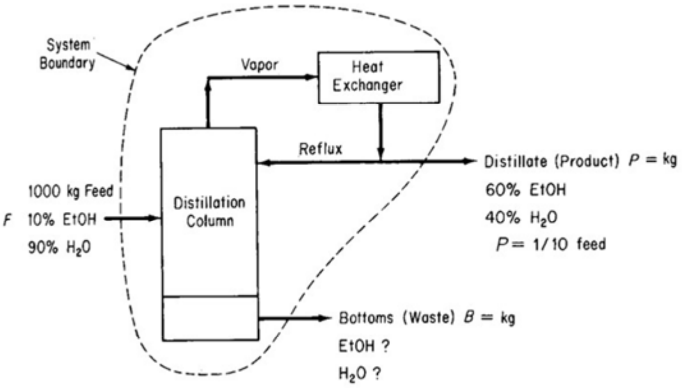


Figure E8.3

Basis: 1 hour so that **F = 1000 kg** of feed

We are given that P is (1/10) of F, so that P = 0.1(1000) = 100 kg

Basis: F= 1000 kg Specifications: $m^F_{EtOH} = 1000(0.10) = 100$

$$m^F_{H_2O} = 1000(0.90) = 900$$

$$m^P_{EtOH} = 0.60P$$

$$m^P_{H_2O} = 0.40P$$

P = (0.1) (F) = 100 kg

Material balances: EtOH and H_2O Implicit equations:

$\Sigma m_i^B = B$ or $\Sigma \omega_i^B = 1$

The total mass balance: F = P + B

B = 1000 – 100 = 900 kg

The solution for the composition of the **bottoms** can then be computed directly from the material balances:

	kg feed in		kg distillate out		kg bottoms out	Mass fraction
EtOH balance:	0.10(1000)	–	0.60(100)	=	40	0.044
H_2O balance:	0.90(1000)	–	0.40(100)	=	860	0.956
					900	1.000

As a **check** let's use the redundant equation

$$m^B_{EtOH} + m^B_{H_2O} = B \quad \text{or} \quad \omega^B_{EtOH} + \omega^B_{H_2O} = 1$$

40 + 860 = 900 = B

Example 8.4

You are asked to prepare a batch of 18.63% battery acid as follows. A tank of old weak battery acid (H_2SO_4) solution contains 12.43% H_2SO_4 (the remainder is pure water). If 200 kg of 77.7% H_2SO_4 is added to the tank, and the final solution is to be 18.63% H_2SO_4, how many kilograms of battery acid have been made? See Figure E8.4.

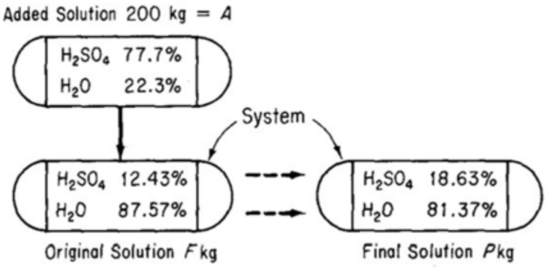


Figure E8.4

Solution

1. An unsteady-state process (the tank initially contains sulfuric acid solution).

Accumulation = In – Out

2. Steady-state process (the tank as initially being empty)

In = Out (Because no **accumulation** occurs in the tank)

1) Solve the problem with the mixing treated as an **unsteady-state process**.

Basis = 200 kg of A

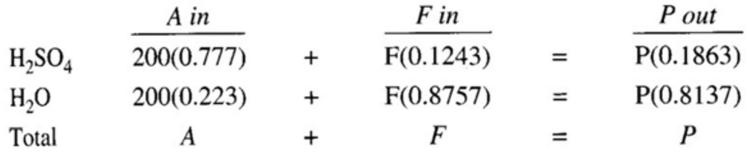
Material balances: H_2SO_4 and H_2O The balances will be in **kilograms**.

Type of Balance	*Accumulation in Tank*				*In*		*Out*
	Final		Initial				
H_2SO_4	$P(0.1863)$	−	$F(0.1243)$	=	200(0.777)	−	0
H_2O	$P(0.8137)$	−	$F(0.8757)$	=	200(0.223)	−	0
Total	P	−	F	=	200	−	0

Note that any **pair** of the three equations is **independent**.

P = 2110 kg acid & F = 1910 kg acid

2) The problem could also be solved by considering the mixing to be a **steady- state process**.



	A in		*F in*		*P out*
H_2SO_4	200(0.777)	+	F(0.1243)	=	P(0.1863)
H_2O	200(0.223)	+	F(0.8757)	=	P(0.8137)
Total	*A*	+	*F*	=	*P*

Note: You can see by inspection that these equations are no different than the first set of mass balances except for the arrangement and labels.

Example 8.5

In a given batch of fish cake that contains 80% water (the remainder is dry cake), 100 kg of water is removed, and it is found that the fish cake is then 40% water. Calculate the weight of the fish cake originally put into the dryer. Figure E8.5 is a diagram of the process.

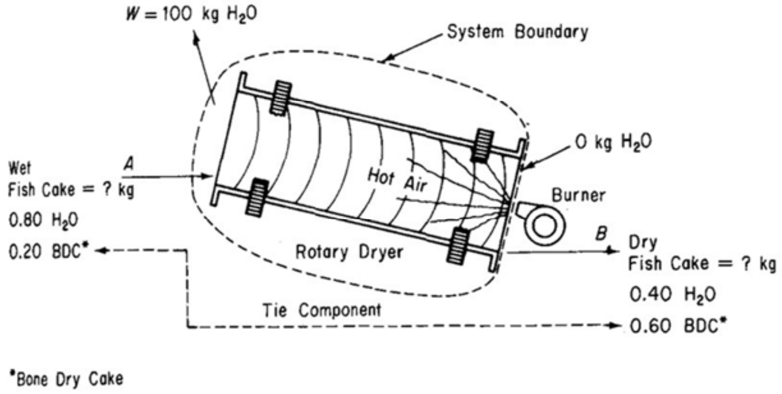


Figure E8.5

Solution

This is a steady-state process without reaction.

Basis: 100 kg of water evaporated = W

$$\left.\begin{array}{lll} & \underline{\mathit{In}} & \underline{\mathit{Out}} \\ \text{Total balance:} & A & = B + W = B + 100 \\ \text{BDC balance:} & 0.20A & = 0.60B \end{array}\right\}\text{mass balances}$$

A = 150 kg initial cake and B = (150)(0.20/0.60)

= 50kg Check via the water balance: 0.80 A =

0.40 B + 100

$$0.80(150) \approx 0.40(50) + 100$$

$$120 = 120$$

Note

In Example 8.5 the BDC in the wet and dry fish cake is known as a **tie component** because the BDC goes from a single stream in the process to another single stream **without loss, addition, or splitting**.

Example 8.6

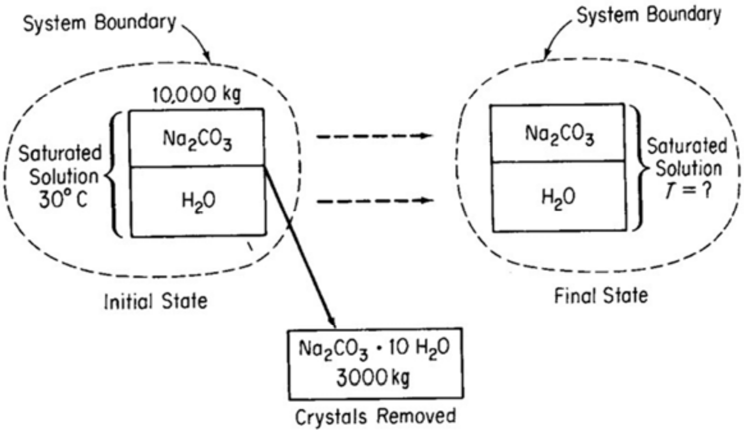
A tank holds 10,000 kg of a saturated solution of Na_2CO_3 at 30°C. You want to crystallize from this solution 3000 kg of $Na_2CO_3.10\ H_2O$ without any accompanying water. To what temperature must the solution be cooled?

You definitely need solubility data for Na_2CO_3 as a function of the temperature:

Temp.(°C)	Solubility (g Na_2CO_3/100 g H_2O)
0	7
10	12.5
20	21.5
30	38.8

Solution

No **reaction** occurs. Although the problem could be set up as a **steady-state problem** with flows in and out of the system (the tank), it is equally justified to treat the process as an -**unsteady-state process**.

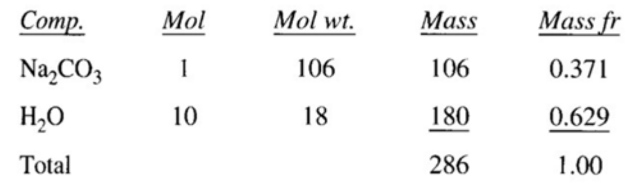


Because the initial solution is saturated at 30°C, you can calculate the composition of the initial solution:

$$\frac{38.8 \text{ g } Na_2CO_3}{38.8 \text{ g } Na_2CO_3 + 100 \text{ g } H_2O} = 0.280 \text{ mass fraction } Na_2CO_3$$

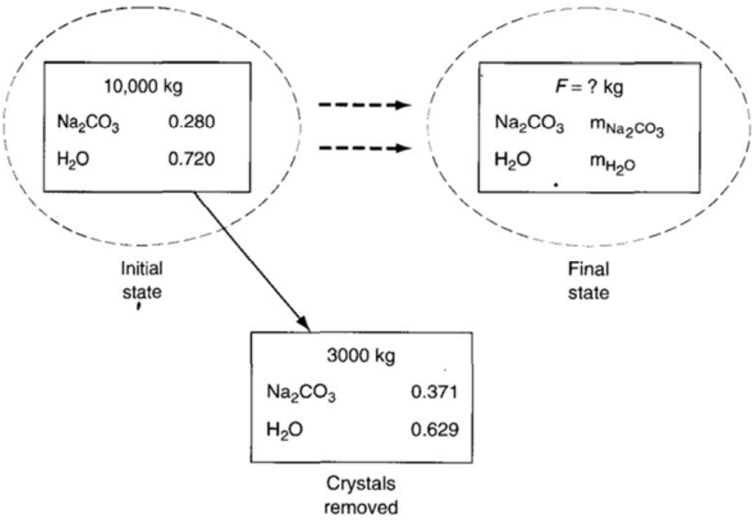
Next, you should calculate the composition of the crystals.

Basis: 1 g mol $Na_2CO_3.10\ H_2O$



Comp.	*Mol*	*Mol wt.*	*Mass*	*Mass fr*
Na_2CO_3	1	106	106	0.371
H_2O	10	18	180	0.629
Total			286	1.00

Basis: 10,000 kg of saturated solution at 30°C



An **unsteady-state** problem, the mass balance reduces to (the flow in = 0)

Accumulation = In – Out

Basis: I = 10,000 kg

Material balances: Na_2CO_3, H_2O

Note that $\omega_i{}^I I = m_i^I,\ \omega_i{}^F F = m_i^F$, and $\omega_i{}^C C = m_i^C$ are redundant equations. C = Crystals

Also redundant are equations such as

$$\Sigma\omega_i = 1 \text{ and } \Sigma m_i = m_{\text{total}}.$$

M.B.:

	Accumulation in Tank				
	Final		*Initial*		*Transport out*
Na_2CO_3	$m^F_{Na_2CO_3}$	–	10,000(0.280)	=	–3000(0.371)
H_2O	$m^F_{H_2O}$	–	10,000(0.720)	=	–3000(0.629)
Total	F	–	10,000	=	–3000

The solution for the composition and amount of the final solution is

Component	*kg*
$m^F_{Na_2CO_3}$	1687
$m^F_{H_2O}$	5313
F (total)	7000

Check using the total balance: 7,000 + 3,000 = 10,000

To find the temperature of the final solution

$$\frac{1{,}687\ \text{kg}\ Na_2CO_3}{5{,}313\ \text{kg}\ H_2O} = \frac{31.8\ \text{g}\ Na_2CO_3}{100\ \text{g}\ H_2O}$$

Thus, the temperature to which the solution must be cooled lies between **20°C** and **30°C**. By **linear interpolation**

$$30°\text{C} - \frac{38.8-31.8}{38.8-21.5}(10.0°\text{C}) = 26°\text{C}$$

Example 8.7

This example focuses on the plasma components of the streams: water, uric acid (UR), creatinine (CR), urea (U), P, K, and Na. You can ignore the initial filling of the dialyzer because the treatment lasts for an interval of two or three hours. Given the measurements obtained from one treatment shown in Figure E8.7b, calculate the grams per liter of each component of the plasma in the outlet solution.

Solution

This is an open steady-state system.

Basis: 1 minute

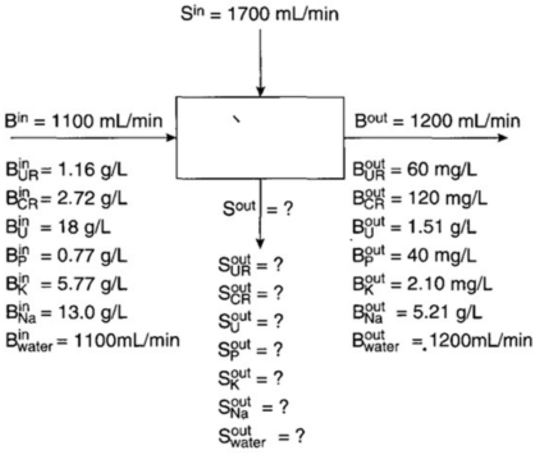


Figure E8.7b

- The **entering solution** is assumed to be essentially **water**.

The water balance in grams, assuming that 1 mL is equivalent to 1 gram, is:

$$1100 + 1700 = 1200 + S^{\text{out}}_{\text{water}} \quad \text{hence:} \qquad S^{\text{out}}_{\text{water}} = 1600 \text{ mL}$$

The component balances in grams are:

$$\begin{array}{llr} & & \underline{g/L} \\ \text{UR:} & 1.1(1.16) + 0 = 1.2(0.060) + 1.6\,S^{\text{out}}_{\text{UR}} & S^{\text{out}}_{\text{UR}} = 0.75 \\ \text{CR:} & 1.1(2.72) + 0 = 1.2(0.120) + 1.6\,S^{\text{out}}_{\text{CR}} & S^{\text{out}}_{\text{CR}} = 1.78 \end{array}$$

U: $1.1(18) + 0 = 1.2(1.51) + 1.6\,S_{U}^{out}$ $\quad S_{U}^{out} = 11.2$

P: $1.1(0.77) + 0 = 1.2(0.040) + 1.6\,S_{P}^{out}$ $\quad S_{P}^{out} = 0.50$

K: $1.1(5.77) + 0 = 1.2(0.120) + 16\,S_{K}^{out}$ $\quad S_{K}^{out} = 3.8$

Na: $1.1(13.0) + 0 = 1.2(3.21) + 1.6\,S_{Na}^{out}$ $\quad S_{Na}^{out} = 6.53$

Questions

1. Answer the following questions true or false:
    a. The most difficult part of solving material balance problems is the collection and formulation of the data specifying the compositions of the streams into and out of the system, and of the material inside the system.
    b. All open processes involving two components with three streams involve zero degrees of freedom.
    c. An unsteady-state process problem can be analyzed and solved as a steady-state process problem.
    d. If a flow rate is given in kg/min, you should convert it to kg mol/min.
2. Under what circumstances do equations or specifications become redundant?

Answers:

1. (a) T; (b) F; (c) T; (d) F
2. When they are not independent.

Problems

1. A cellulose solution contains 5.2% cellulose by weight in water. How many kilograms of 1.2% solution are required to dilute 100 kg of the 5.2% solution to 4.2%?
2. A cereal product containing 55% water is made at the rate of 500 kg/hr. You need to dry the product so that it contains only 30% water. How much water has to be evaporated per hour?
3. If 100 g of Na_2SO_4 is dissolved in 200 g of H_2O and the solution is cooled until 100 g of $Na_2SO_4.10H_2O$ crystallizes out; find (a) the composition of the remaining solution (the mother liquor) and (b) the grams of crystals recovered per 100 g of initial solution.
4. Salt in crude oil must be removed before the oil undergoes processing in a refinery. The crude oil is fed to a washing unit where freshwater fed to the unit mixes with the oil and dissolves a portion of the salt contained in the oil. The oil (containing some salt but no water), being less dense than the water, can be removed at the top of the washer. If the "spent" wash water contains 15% salt and the crude oil contains 5% salt, determine the concentration of salt in the "washed" oil product if the ratio of crud oil (with salt) to water

used is 4:1.

Answers:

1. 33.3 kg
2. 178 kg/hr
3. (a) 28% Na_2SO_4 ; (b) 33.3
4. Salt: 0.00617; Oil: 0.99393

Supplementary Problems (Chapter Eight):

Problem 1

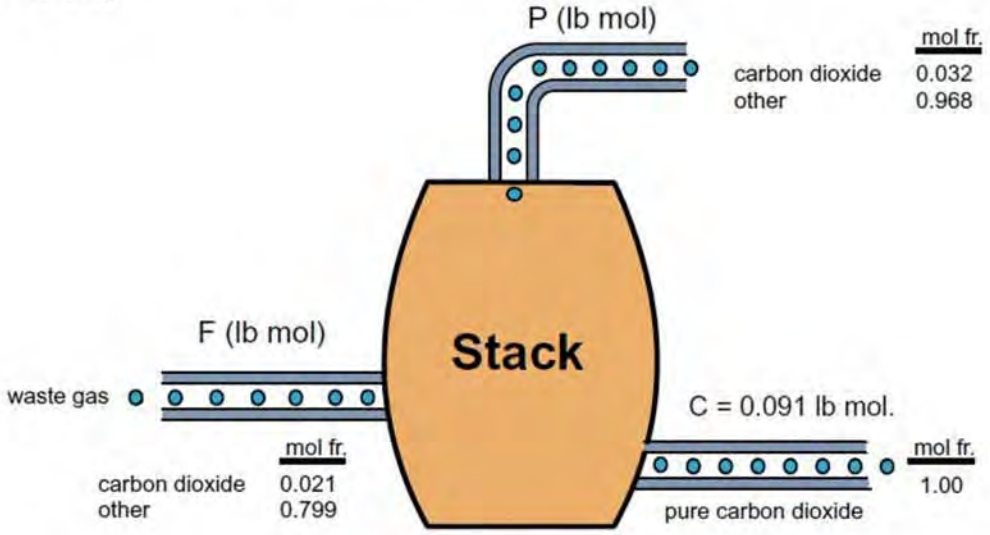
You are asked to measure the rate at which waste gases are being discharged from a stack. The gases entering contain 2.1 % carbon dioxide. Pure carbon dioxide is introduced into the bottom of the stack at a measured rate of 4.0 lb per minute. You measure the discharge of gases leaving the stack, and find the concentration of carbon dioxide is 3.2 %. Calculate the rate of flow, in lb mol/minute, of the entering waste gases.

Solution

A convenient basis to use is 1 minute of operation, equivalent to 0.091 lb mol of pure CO_2 feed.

This is a steady state problem without reaction.

$$\begin{array}{l|l} 4\text{ lb } CO_2 & 1\text{ lb mol } CO_2 \\ \hline & 44\text{ lb } CO_2 \end{array} = 0.091\text{ lb mol } CO_2$$



The unknowns are F and P (all compositions are known).

CO_2 balance : $0.021\ F + 0.091 = 0.032\ P$ (1)

waste gas balance: $0.979\ F = 0.968\ P$ (2)

Solving (1) and (2) **P = 8.10 lb mol/min** **F = 8.01 lb mol/min**

To check above values, substitute them in the total balance

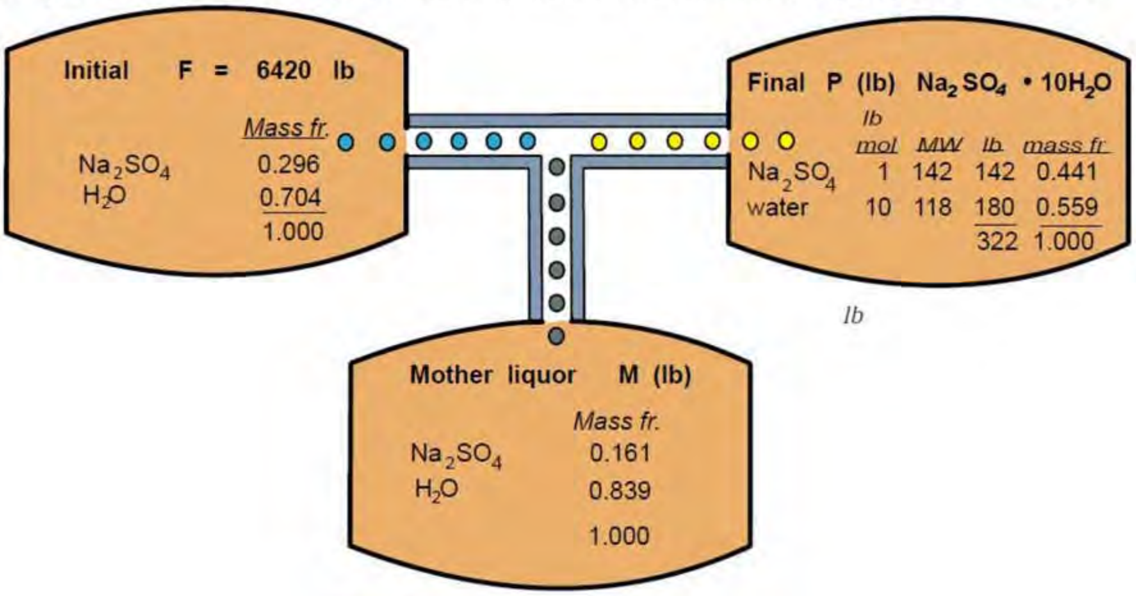
$$F + 0.091 = 8.00 = P = 8.00$$

Problem 2

A crystallizer contains 6420 lb of aqueous solution of anhydrous sodium sulfate (concentration 29.6 wt %) at 104 °C. The solution is cooled to 20 °C to crystallize out the desired $Na_2SO_4 . 10 H_2O$. The remaining solution (the mother liquor) is found to contain 16.1 % anhydrous sodium sulfate. What is the weight of this mother liquor.

Solution

This problem will be analyzed as unsteady state problem although it could be treated as a steady state problem with flows. The concentrations have to be calculated for some consistent components. Na_2SO_4 and H_2O are the easiest to use here rather than $Na_2SO_4 \cdot 10H_2O$ and H_2O.



Basis : 6420 lb of 29.6 wt% Na_2SO_4 solution

We need 2 independent balances, and will pick the total balance plus the Na_2SO_4 balance.

Accumulation = In - out

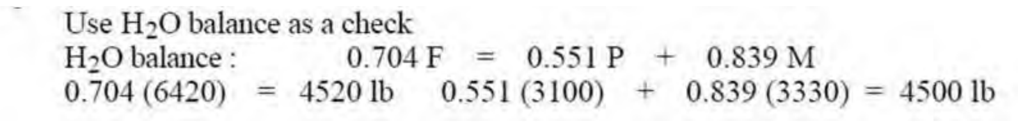
Total: $P - F = 0 - M$ (1)

Na_2SO_4: $0.441P - 0.296F = 0 - 0.161M$ (2)

from (1) $P = 6240 - M$

Substituting in (2) $0.441 (6240 - M) - 6240 (0.296) = - 0.161 M$

M = 3330 lb **P = 3100 lb**



Use H_2O balance as a check

H_2O balance : $0.704\ F = 0.551\ P + 0.839\ M$

$0.704\ (6420) = 4520$ lb $\quad 0.551\ (3100) + 0.839\ (3330) = 4500$ lb

Chapter 9

The Chemical Reaction Equation and Stoichiometry

9.1 Stoichiometry

- The stoichiometric coefficients in the chemical reaction equation

$C_7H_{16}(\ell) + 11\ O_2(g) \rightarrow 7\ CO_2(g) + 8\ H_2O(g)$ Is (1 for C_7H_{16}, 11 for O_2 and so on).

- Another way to use the chemical reaction equation is to indicate that **1 mole of CO_2** is formed from each **(1/7) mole of C_7H_{16}**, and **1 mole of H_2O** is formed with each **(7/8) mole of CO_2**. The latter ratios indicate the use of **stoichiometric ratios** in determining the relative proportions of products and reactants.

For example how many kg of CO_2 will be produced as the product if 10 kg of C_7H_{16} react completely with the **stoichiometric quantity** of O_2? On the basis of 10 kg of C_7H_6

$$\frac{10\ \text{kg}\ C_7H_{16}}{} \left| \frac{1\ \text{kg mol}\ C_7H_{16}}{100.1\ \text{kg}\ C_7H_{16}} \right| \frac{7\ \text{kg mol}\ CO_2}{1\ \text{kg mol}\ C_7H_{16}} \left| \frac{44.0\ \text{kg}\ CO_2}{1\ \text{kg mol}\ CO_2} \right. = 30.8\ \text{kg}\ CO_2$$

Example 9.1

The primary energy source for cells is the aerobic catabolism (oxidation) of glucose ($C_6H_{12}O_6$, a sugar). The overall oxidation of glucose produces CO_2 and H_2O by the following reaction

$$C_6H_{12}O_6 + aO_2 \rightarrow b\ CO_2 + c\ H_2O$$

Determine the values of a, b, and c that balance this chemical reaction equation.

Solution

Basis: The given reaction

By inspection, the carbon balance gives b = 6, the hydrogen balance gives c = 6, and an oxygen balance

$$6 + 2a = 6 * 2 + 6$$

Gives a = 6. Therefore, the balanced equation is $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Example 9.2

In the combustion of heptane, CO_2 is produced. Assume that you want to produce 500 kg of dry ice per hour, and that 50% of the CO_2 can be converted into dry ice, as shown in Figure E9.2. How many kilograms of heptane must be burned per hour? (MW: CO_2 = 44 and C_7H_{16} =100.1)

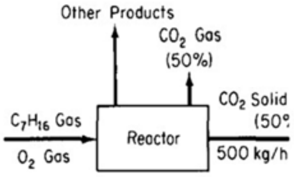


Figure E9.2

Solution

The chemical equation is

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$$

Basis: 500 kg of dry ice (equivalent to 1 hr)

The calculation of the amount of C_7H_{16} can be made in one sequence:

$$\frac{500\ \text{kg dry ice}}{} \left| \frac{1\ \text{kg } CO_2}{0.5\ \text{kg dry ice}} \right| \frac{1\ \text{kg mol } CO_2}{44.0\ \text{kg } CO_2} \left| \frac{1\ \text{kg mol } C_7H_{16}}{7\ \text{kg mol } CO_2} \right| \frac{100.1\ \text{kg } C_7H_{16}}{1\ \text{kg mol } C_7H_{16}} = 325\ \text{kg } C_7H_{16}$$

Example 9.3

A limestone analyses (weight %): $CaCO_3$ 92.89%, $MgCO_3$ 5.41% and Inert 1.70%

By heating the limestone you recover oxides known as lime.

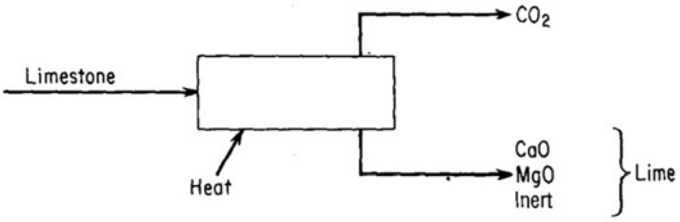
(a) How many pounds of calcium oxide can be made from 1 ton of this limestone?

(b) How many pounds of CO_2 can be recovered per pound of limestone?

(c) How many pounds of limestone are needed to make 1 ton of lime?

Mol. Wt.: $CaCO_3$ (100.1) $MgCO_3$ (84.32) CaO (56.08) MgO (40.32) CO_2 (44.0)

Solution



Chemical Equation:

$$CaCO_3 \rightarrow CaO + CO_2$$
$$MgCO_3 \rightarrow MgO + CO_2$$

Basis: 100 lb of limestone

Limestone			Solid Products		
Component	lb = percent	lb mol	Compound	lb mol	lb
$CaCO_3$	92.89	0.9280	CaO	0.9280	52.04
$MgCO_3$	5.41	0.0642	MgO	0.0642	2.59
Inert	1.70		Inert		1.70
Total	100.00	0.9920	Total	0.9920	56.33

The quantities listed under Products are calculated from the chemical equations. For example, for the last column:

$$\frac{92.89\ \text{lb CaCO}_3}{}\left|\frac{1\ \text{lb mol CaCO}_3}{100.1\ \text{lb CaCO}_3}\right|\frac{1\ \text{lb mol CaO}}{1\ \text{lb mol CaCO}_3}\left|\frac{56.08\ \text{lb CaO}}{1\ \text{lb mol CaO}}\right. = 52.04\ \text{lb CaO}$$

$$\frac{5.41\ \text{lb MgCO}_3}{}\left|\frac{1\ \text{lb mol MgCO}_3}{84.32\ \text{lb MgCO}_3}\right|\frac{1\ \text{lb mol MgO}}{1\ \text{lb mol MgCO}_3}\left|\frac{40.32\ \text{lb MgO}}{1\ \text{lb mol MgO}}\right. = 2.59\ \text{lb MgO}$$

The production of $\mathbf{CO_2}$ is:

0.9280 lb mol CaO is equivalent to **0.9280 lb mol** $\mathbf{CO_2}$

0.0642 lb mol MgO is equivalent to **0.0642 lb mol** $\mathbf{CO_2}$

Total lb mol CO_2 = 0.9280 + 0.0642 = **0.992 lb mol** $\mathbf{CO_2}$

$$\frac{0.992\ \text{lb mol CO}_2}{}\left|\frac{44.0\ \text{lb CO}_2}{1\ \text{lb mol CO}_2}\right. = 44.65\ \text{lb CO}_2$$

Alternately, you could have calculated the **lb** $\mathbf{CO_2}$ from a total balance: **100 - 56.33 = 44.67**.

Now, to calculate the quantities originally asked for:

(a) CaO produced = $\dfrac{52.04\ \text{lb CaO}}{100\ \text{lb limestone}}\left|\dfrac{2000\ \text{lb}}{1\ \text{ton}}\right. = 1041\ \text{lb CaO/ton}$

(b) CO_2 recovered = $\dfrac{43.65\ \text{lb CO}_2}{100\ \text{lb limestone}} = 0.437\ \text{lb CO}_2\text{/lb limestone}$

(c) Limestone required = $\dfrac{100\ \text{lb limestone}}{56.33\ \text{lb lime}}\left|\dfrac{2000\ \text{lb}}{1\ \text{ton}}\right. = \dfrac{3550\ \text{lb limestone/}}{\text{ton lime}}$

9.2 Terminology for Applications of Stoichiometry

9.2.1 Extent of Reaction

The **extent of reaction**, ξ, is based on a particular stoichiometric equation, and denotes how much reaction occurs.

The extent of reaction is defined as follows: $\xi = \dfrac{n_i - n_{io}}{v_i}$ … 9.1

Where:

n_i = moles of species *i* present in the system after the reaction occurs

n_{io} = moles of species *i* present in the system when the reaction starts

v_i = coefficient for species *i* in the particular chemical reaction equation (moles of species *i* produced or consumed per moles reacting)

ξ = extent of reaction (moles reacting)

- The **coefficients** of the **products** in a chemical reaction are assigned **positive** values and the

reactants assigned **negative** values. Note that (n_i - n_{io}) is equal to the **generation** or **consumption** of component *i* by reaction.

Equation (9.1) can be rearranged to calculate the number of moles of component *i* from the value of the extent of reaction

$$n_i = n_{i0} + \xi v_i \qquad \dots 9.2$$

Example 9.4

Determine the extent of reaction for the following chemical reaction $N_2 + 3H_2 \rightarrow 2NH_3$ given the following analysis of feed and product:

	N_2	H_2	NH_3
Feed	100 g	50 g	5 g
Product			90 g

Also, determine the g and g mol of N_2 and H_2 in the product.

Solution

The extent of reaction can be calculated by applying Equation 9.1 based on NH_3:

$$n_i = \frac{90 \text{ g } NH_3}{} \bigg| \frac{1 \text{ g mol } NH_3}{17 \text{ g } NH_3} = 5.294 \text{ g mol } NH_3$$

$$n_{i0} = \frac{5 \text{ g } NH_3}{} \bigg| \frac{1 \text{ g mole } NH_3}{17 \text{ g } NH_3} = 0.294 \text{ g mol } NH_3$$

$$\xi = \frac{n_i - n_{i0}}{v_i} = \frac{(5.294 - 0.204) \text{g mol } NH_3}{2 \text{ g mol } NH_3\text{/moles reacting}} = 2.50 \text{ moles reacting}$$

Equation 9.2 can be used to determine the g mol of N_2 and H_2 in the products of the reaction

$$N_2\text{:} \quad n_{i0} = \frac{100 \text{ g } N_2}{} \bigg| \frac{1 \text{ g mol } N_2}{28 \text{ g } N_2} = 3.57 \text{ g mol } N_2$$

$$n_{N_2} = 3.57 + (-1)(2.5) = 1.07 \text{ g mol } N_2$$

$$m_{N_2} = \frac{1.07 \text{ g mol } N_2}{} \bigg| \frac{28 \text{ g } N_2}{1 \text{ g mol } N_2} = 30 \text{ g } N_2$$

$$H_2\text{:} \quad n_{i0} = \frac{50 \text{ g } H_2}{} \bigg| \frac{1 \text{ g mol } H_2}{2 \text{ g } H_2} = 25 \text{ g mol } H_2$$

$$n_{H2} = 25 + (-3)(2.5) = 17.5 \text{ g mol } H_2$$

$$= \frac{17.5 \text{ g mol } H_2}{} \bigg| \frac{2\text{g } H_2}{1 \text{ g mol } H_2} = 35 \text{ g } H_2$$

Note: If several independent reactions occur in the reactor, say k of them, ξ can be defined for each reaction, with v_{ki} being the stoichiometric coefficient of species i in the kth reaction, the total number of moles of species i is

$$n_i = n_{i0} + \sum_{k=1}^{R} \nu_{ki}\, \xi_k \qquad \text{… 9.3}$$

Where *R* is the total number of independent reactions.

9.2.2 Limiting and Excess Reactants

- The **excess material** comes out together with, or perhaps separately from, the product, and sometimes can be used again.
- The **limiting reactant** is the species in a chemical reaction that would theoretically run out first (**would be completely consumed**) if the reaction were to proceed to completion according to the chemical equation—**even if the reaction does not proceed to completion!** All the other reactants are called **excess reactants**.

$$\%\ \text{excess reactant} = \frac{\left\{\begin{array}{c}\text{amount of the excess reactant fed - amount of the excess reactant required to}\\ \text{react with the limiting reactant}\end{array}\right\}}{\left\{\text{amount of the excess reactant required to react with the limiting reactant}\right\}} \times 100$$

- **For example**, using the chemical reaction equation in **Example 9.2**,

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$$

If **1 g mol of C_7H_{16}** and **12 g mol of O_2** are mixed.

As a straightforward way of determining the **limiting reactant**, you can determine the **maximum extent of reaction**, $\xi^{\max}$, for each reactant based on the **complete reaction** of the reactant. **The reactant with the smallest maximum extent of reaction is the limiting reactant**. For the example, for **1 g mol** of **C_7H_{16}** plus **12 g mole** of **O_2**, you calculate

$$\xi^{max}\ (\text{based on } O_2) = \frac{0 \text{ g mol } O_2 - 12 \text{ g mol } O_2}{-11 \text{ g mol } O_2/\text{moles reacting}} = 1.09 \text{ moles reacting}$$

$$\xi^{max}\ (\text{based on } C_7H_{16}) = \frac{0 \text{ g mol } C_7H_{16} - 1 \text{ g mol } C_7H_{16}}{-1 \text{ g mol } C_7H_{16}/\text{moles reacting}} = 1.00 \text{ moles reacting}$$

Therefore, **heptane** is the **limiting reactant** and **oxygen** is the **excess reactant**.

As an **alternate** to determining the **limiting reactant**,

$$\begin{array}{lccc} & \underline{\textit{Ratio in feed}} & & \underline{\textit{Ratio in chemical equation}} \\ \dfrac{O_2}{C_7H_{16}}: & \dfrac{12}{1} = 12 & > & \dfrac{11}{1} = 11 \end{array}$$

- Consider the following reaction $\mathrm{A} + 3\mathrm{B} + 2\mathrm{C} \rightarrow \text{Products}$

If the feed to the reactor contains **1.1 moles of A**, **3.2 moles of B**, and **2.4 moles of C**. The extents of reaction based on complete reaction of **A, B,** and **C** are

$$\xi^{\max}\,(\text{based on A}) = \frac{-1.1\ \text{mol A}}{-1} = 1.1$$

$$\xi^{\max}\,(\text{based on B}) = \frac{-3.2\ \text{mol B}}{-3} = 1.07$$

$$\xi^{\max}\,(\text{based on C}) = \frac{-2.4\ \text{mol C}}{-2} = 1.2$$

As a result, **B** is identified as the **limiting reactant** in this example while **A** and **C** are the **excess reactants**.

As an **alternate** to determining the **limiting reactant** for same example:
We **choose A** as the **reference substance** and calculate

	Ratio in feed		*Ratio in chemical equation*
$\frac{B}{A}$:	$\frac{3.2}{1.1} = 2.91$	$<$	$\frac{3}{1} = 3$
$\frac{C}{A}$:	$\frac{2.4}{1.1} = 2.18$	$>$	$\frac{2}{1} = 2$

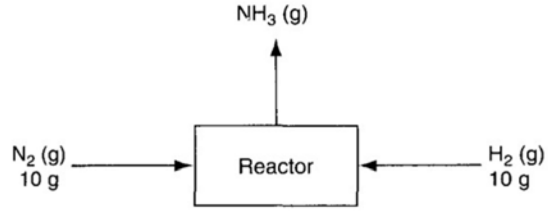
We conclude that **B** is the **limiting reactant relative to A**, and that **A** is the **limiting reactant relative** to **C**, hence **B** is the **limiting reactant** among the set of **three reactant**. In symbols we have **B < A, C > A (i.e., A < C)**, so that **B < A < C**.

Example 9.5

If you feed 10 grams of N_2 gas and 10 grams of H_2 gas into a reactor:

a. What is the maximum number of grams of NH_3 that can be produced?
b. What is the limiting reactant?
c. What is the excess reactant?

Solution


NH3 (g)
N2 (g)
10 g
Reactor
H2 (g)
10 g

$$N_2(g) \quad + \quad 3H_2(g) \quad \rightarrow \quad 2NH_3(g)$$

	$N_2(g)$	$3H_2(g)$	$2NH_3(g)$
Given g:	10	10	0
MW:	28	2.016	17.02
Calculated g mol:	0.357	4.960	0

$$\xi^{\max}\,(\text{based on } N_2) = \frac{-0.357 \text{ g mol } N_2}{-1 \text{ g mol } N_2/\text{moles reacting}} = 0.357 \text{ moles reacting}$$

$$\xi^{\max}\,(\text{based on } H_2) = \frac{-4.960 \text{ g mol } H_2}{-3 \text{ g mol } H_2/\text{moles reacting}} = 1.65 \text{ moles reacting}$$

(b) N_2 is the limiting reactant, and that (c) H_2 is the excess reactant.

The excess H_2 = 4.960 – 3(0.357) = 3.89 g mol. To answer question (a), the maximum amount of NH_3 that can be produced is based on assuming **complete conversion** of the limiting reactant

$$\frac{0.357 \text{ g mol } N_2}{} \left| \frac{2 \text{ g mol } NH_3}{1 \text{ g mol } N_2} \right| \frac{17.02 \text{ g } NH_3}{1 \text{ g mol } NH_3} = 12.2 \text{ g } NH_3$$

9.2.3 Conversion and degree of completion

- ☒ **Conversion** is the fraction of the feed or some key material in the feed that is converted into products.
- ☒ **Conversion** is related to the **degree of completion** of a reaction namely the percentage or fraction of the limiting reactant converted into products.

Thus, **percent conversion** is

$$\%\text{conversion} = \frac{\text{moles (or mass) of feed (or a compound in the feed) that react}}{\text{moles (or mass) of feed (or a component in the feed) introduced}} \times 100$$

<u>For example</u>, for the reaction equation described in **Example 9.2**, if 14.4 kg of CO_2 are formed in the reaction of 10 kg of C_7H_{16}, you can calculate what percent of the C_7H_{16} is converted to CO_2 (reacts) as follows: $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

C_7H_{16} equivalent to CO_2 in the product $\dfrac{14.4 \text{ kg } CO_2}{} \left| \dfrac{1 \text{ kg mol } CO_2}{44.0 \text{ kg } CO_2} \right| \dfrac{1 \text{ kg mol } C_7H_{16}}{7 \text{ kg mol } CO_2} = 0.0468 \text{ kg mol } C_7H_{16}$

$$\frac{10 \text{ kg } C_7H_{16}}{} \left| \frac{1 \text{ kg mol } C_7H_{16}}{100.1 \text{ kg } C_7H_{16}} \right. = 0.0999 \text{ kg mol } C_7H_{16}$$

C_7H_{16} in the reactants

$$\% \text{ conversion} = \frac{0.0468 \text{ mol reacted}}{0.0999 \text{ kg mol fed}} 100 = 46.8\% \text{ of the } C_7H_{16}$$

☒ The conversion can also be calculated using the **extent of reaction** as follows:

Conversion is equal to the extent of reaction based on CO_2 formation (i.e., the **actual extent of reaction**) divided by the extent of reaction assuming **complete reaction** of C_7H_{16} (i.e., the **maximum possible extent of reaction**).

$$\text{Conversion} = \frac{\text{extent of reaction that actually occurs}}{\text{extent of reaction that would occur if complete reaction took place}} = \frac{\xi}{\xi^{\max}}$$

9.2.4 Selectivity

Selectivity is the ratio of the moles of a particular (usually the desired) product produced to the moles of another (usually undesired or by-product) product produced in a set of reactions.

For example, methanol (CH_3OH) can be converted into ethylene (C_2H_4) or propylene (C_3H_6) by the reactions

$$2\,CH_3OH \rightarrow C_2H_4 + 2H_2O$$
$$3\,CH_3OH \rightarrow C_3H_6 + 3H_2O$$

What is the selectivity of C_2H_4 relative to the C_3H_6 at 80% conversion of the CH_3OH? At 80% conversion: C_2H_4 19 mole % and for C_3H_6 8 mole %. Because the basis for both values is the same, **the selectivity** = **19/8 = 2.4 mol C_2H_4 per mol C_3H_6**.

9.2.5 Yield

No universally agreed-upon definitions exist for **yield**—in fact, quite the contrary. Here are **three** common ones:

- **Yield (based on feed)**—the amount (mass or moles) of desired product obtained divided by the amount of the key (frequently the limiting) reactant fed.

- **Yield (based on reactant consumed)**—the amount (mass or moles) of desired product obtained divided by amount of the key (frequently the limiting) reactant consumed.
- **Yield (based on theoretical consumption of the limiting reactant)**—the amount (mass or moles) of a product obtained divided by the theoretical (expected) amount of the product that would be obtained based on the limiting reactant in the chemical reaction equation if it were completely consumed.

Example 9.6

The following overall reaction to produce biomass, glycerol, and ethanol

$$\begin{aligned} C_6H_{12}O_6(\text{glucose}) + 0.118\ NH_3 \rightarrow\ & 0.59\ CH_{1.74}N_{0.2}O_{0.45}\ (\text{biomass}) \\ & + 0.43\ C_3H_8O_3(\text{glycerol}) + 1.54\ CO_2 + 1.3\ C_2H_5OH\ (\text{ethanol}) + 0.03\ H_2O \end{aligned}$$

Calculate the theoretical yield of biomass in g of biomass per g of glucose. Also, calculate the yield of ethanol in g of ethanol per g of glucose.

Solution

Basis: 0.59 g mol of biomass

$$\frac{0.59\text{ g mol biomass}}{1\text{ g mol glucose}}\left|\frac{23.74\text{ g biomass}}{1\text{ g mol biomass}}\right|\frac{1\text{ g mol glucose}}{180\text{ g glucose}} = 0.0778\text{ g biomass/g glucose}$$

$$\frac{1.3\text{ g mol }C_2H_5OH}{1\text{ g mol glucose}}\left|\frac{46\text{ g }C_2H_5OH}{1\text{ g mol }C_2H_5OH}\right|\frac{1\text{ g mol glucose}}{180\text{ g glucose}} = 0.332\text{ g }C_2H_5OH\text{/g glucose}$$

Example 9.7

For this example, large amounts of single wall carbon nanotubes can be produced by the catalytic decomposition of ethane over Co and Fe catalysts supported on silica

$$\begin{array}{lr} C_2H_6 \rightarrow 2\,C + 3\,H_2 & (a) \\ \quad\ \searrow C_2H_4 + H_2 & (b) \end{array}$$

If you collect 3 g mol of H_2 and 0.50 g mol of C_2H_4, what is the selectivity of C relative to C_2H_4?

Solution

Basis: 3 g mol H_2 ~~by Reaction (a)~~

0.50 g mol C_2H_4 by Reaction (b)

The 0.5 g mol of C_2H_4 corresponds to 0.50 g mol of H_2 produced in Reaction (b).

The H_2 produced by Reaction (a) = 3 - 0.50 = 2.5 g mol.

The nanotubes (the C) produced by Reaction (a) = (2/3)(2.5) = 1.67 g mol C

The selectivity = 1.67/0.50 = 3.33 g mol C/g mol C_2H_4

Example 9.8

The two reactions of interest for this example are

$$Cl_2(g) + C_3H_6(g) \rightarrow C_3H_5Cl(g) + HCl(g) \qquad \text{(a)}$$

$$Cl_2(g) + C_3H_6(g) \rightarrow C_3H_6Cl_2(g) \qquad \text{(b)}$$

C_3H_6 is propylene (propene) (MW = 42.08)

C_3H_5C1 is allyl chloride (3-chloropropene) (MW = 76.53)

$C_3H_6Cl_2$ is propylene chloride (1,2-dichloropropane) (MW = 112.99)

The species recovered after the reaction takes place for some time are listed in Table E9.8.

species	Cl_2	C_3H_6	C_3H_5Cl	$C_3H_6Cl_2$	HCl
g mol	141	651	4.6	24.5	4.6

Based on the product distribution assuming that no allyl chlorides were present in the feed, calculate the following:

a. How much Cl_2 and C_3H_6 were fed to the reactor in g mol?
b. What was the limiting reactant?
c. What was the excess reactant?
d. What was the fraction conversion of C_3H_6 to C_3H_5Cl?
e. What was the selectivity of C_3H_5Cl relative to $C_3H_6Cl_2$?
f. What was the yield of C_3H_5Cl expressed in g of C_3H_5Cl to the g of C_3H_6 fed to the reactor?
g. What was the extent of reaction of the first and second reactions?

Solution

Figure E9.8 illustrates the process as an open-flow system. A batch process could alternatively be used.

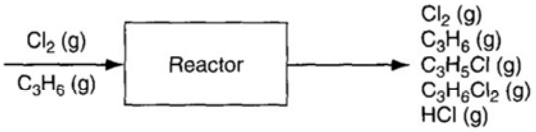


Figure E9.8

A convenient **basis** is what is given in the product list in Table E9.8.

Reaction (a)

$$\frac{4.6\text{ g mol }C_3H_5Cl}{}\left|\frac{1\text{ g mol }Cl_2}{1\text{ g mol }C_3H_5Cl}\right. = 4.6\text{ g mol }Cl_2\text{ reacts}$$

Reaction (b)

$$\frac{24.5\text{ g mol }C_3H_6Cl_2}{}\left|\frac{1\text{ g mol }Cl_2}{1\text{ g mol }C_3H_6Cl_2}\right. = 24.5\text{ g mol }Cl_2\text{ reacts}$$

Total = 4.6 + 24.5 = 29.1 g mol Cl_2 reacts

Cl_2 in product = 141.0 from Table E9.8

(a) Total Cl_2 fed = 141.0 + 29.1 = 170.1 g mol Cl_2

Total C_3H_6 fed = 651.0 + 29.1 = 680.1 g mol of C_3H_6

(b) and (c) Since both reactions involve the **same** value of the respective reaction **stoichiometric coefficients**, both reactions will have the **same limiting** and **excess** reactants

$$\xi^{\max}\text{ (based on } C_3H_6) = \frac{-680.1\text{ g mol } C_3H_6}{-1\text{ g mol } C_3H_6/\text{moles reacting}} = 680.1\text{ moles reacting}$$

$$\xi^{\max}\text{ (based on } Cl_2) = \frac{-170.1\text{ g mole } Cl_2}{-1\text{ g mol } Cl_2/\text{moles reacting}} = 170.1\text{ moles reacting}$$

Thus, **C_3H_6** was the **excess reactant** and **Cl_2** the **limiting reactant**.

(d) The fraction conversion of C_3H_6 to C_3H_5C1 was

$$\frac{4.6\text{ g mol } C_3H_6\text{ that reacted}}{680.1\text{ g mol } C_3H_6\text{ fed}} = 6.76 \times 10^{-3}$$

(e) The selectivity was

$$\frac{4.6\text{ g mol } C_3H_5Cl}{24.5\text{ g mol } C_3H_6Cl_2} = 0.19\,\frac{\text{g mol } C_3H_5Cl}{\text{g mol } C_3H_6Cl_2}$$

(f) The yield was

$$\frac{(76.53)(4.6)\text{g } C_3H_5Cl}{(42.08)(680.1)\text{g } C_3H_6} = 0.012\,\frac{\text{g } C_3H_5Cl}{\text{g } C_3H_6}$$

(g) Because **C_3H_5C1** is produced only by the **first reaction**, the **extent of reaction** of the first reaction is

$$\xi_1 = \frac{n_i - n_{io}}{v_i} = \frac{4.6 - 0}{1} = 4.6$$

Because **$C_3H_6C_{12}$** is produced only by the **second reaction**, the **extent of reaction** of the second reaction is

$$\xi_2 = \frac{n_i - n_{io}}{v_i} = \frac{24.5 - 0}{1} = 24.5$$

Example 9.9

Five pounds of bismuth (MW=209) is heated along with one pound of sulfur (MW=32) to form Bi_2S_3 (MW=514). At the end of the reaction, the mass is extracted and the free sulfur recovered is 5% of the reaction mass. Determine $2\,Bi + 3\,S \longrightarrow Bi_2S_3$

1. The limiting reactant.
2. The percent excess reactant.
3. The percent conversion of sulfur to Bi_2S_3

Solution

a. Find the Limiting reactant

Ratio in the feed

$$\frac{\text{Bi}}{\text{S}} = \frac{\begin{array}{c|c} 5.00\ \text{lb Bi} & 1\ \text{lb mol Bi} \\ \hline & 209\ \text{lb Bi} \end{array}}{\begin{array}{c|c} 1.00\ \text{lb S} & 1\ \text{lb mol S} \\ \hline & 32\ \text{lb S} \end{array}} = \frac{0.0239\ \text{mol Bi}}{0.0313\ \text{mol S}} = 0.774$$

$$\text{Ratio in the chemical equation} = \frac{2\ \text{lb mol Bi}}{3\ \text{lb mol S}} = 0.667$$

Compare the two ratios; **S is the limiting reactant.**

b. % Excess reactant

$$\text{Bi required} = \begin{array}{c|c|c} 1\ \text{lb S} & 1\ \text{lb mol S} & 2\ \text{mol Bi} \\ \hline & 32\ \text{lb S} & 3\ \text{mol S} \end{array} = 0.0208\ \text{lb mol Bi}$$

$$\%\ \text{excess Bi} = \frac{(0.0239 - 0.028)}{0.028} \times 100 = \mathbf{14.9\ \%}$$

c. We will assume that no gaseous products are formed, so that the total mass of the reaction mixture is conserved at 6 lb (5 lb Bi + 1 lb S). The free sulfur at the end of the reaction = 5%.

$$\begin{array}{c|c|c} 6.00\ \text{lb rxn mass} & 5.00\ \text{lb S} & 1\ \text{lb mol S} \\ \hline & 100\ \text{lb rxn mass} & 32.0\ \text{lb S} \end{array} = 0.00938\ \text{lb mol S}$$

$$\%\ \text{Conversion} = \frac{\text{moles of feed that react}}{\text{moles of feed introduced}} \times 100$$

$$= \frac{0.0313 - 0.00938}{0.0313} \times 100 = \mathbf{70.0\ \%}$$

<u>Questions</u>

1. What is a limiting reactant?
2. What is an excess reactant?
3. How do you calculate the extent of reaction from experimental data?

<u>Answers:</u>

<u>Q.3</u> Reactant present in the least stoichiometric quantity.

<u>Q.4</u> All other reactants than the limiting reactant.

<u>Q.5</u> For a species in

$$\xi = \frac{n_{\text{out},\,i} - n_{\text{in},\,i}}{v_i} \qquad \xi = \frac{n_{\text{final},\,i} - n_{\text{initial},\,i}}{v_i}$$

Open system: Closed system:

Problems

1. Write balanced reaction equations for the following reactions:
   a. C_9H_{18} and oxygen to form carbon dioxide and water.
   b. FeS_2 and oxygen to form Fe_2O_3 and sulfur dioxide.
2. If 1 kg of benzene (C_6H_6) is oxidized with oxygen, how many kilograms of O_2 are needed to convert all the benzene to CO_2 and H_2O?
3. The electrolytic manufacture of chlorine gas from a sodium chloride solution is carried out by the following reaction:

$$2\,NaCl + 2\,H_2O \rightarrow 2\,NaOH + H_2 + Cl_2$$

   How many kilograms of Cl_2 can be produced from 10 m^3 of brine solution containing 5% by weight of NaCl? The specific gravity of the solution relative to that of water at 4°C is 1.07.

4. Can you balance the following chemical reaction equation?

$$a_1NO_3 + a_2HClO \rightarrow a_3HNO_3 + a_4HCl$$

5. For the reaction in which stoichiometric quantities of the reactants are fed

$$2\,C_5H_{10} + 15\,O_2 \rightarrow 10\,CO_2 + 10\,H_2O$$

   and the reaction goes to completion, what is the maximum extent of reaction based on C_5H_{10}? On O_2? Are the respective values different or the same? Explain the result.

6. Calcium oxide (CaO) is formed by decomposing limestone (pure $CaCO_3$). In one kiln the reaction goes to 70% completion.
   a. What is the composition of the solid product withdrawn from the kiln?
   b. What is the yield in terms of pounds of CO_2 produced per pound of limestone fed into the process?
7. Aluminum sulfate can be made by reacting crushed bauxite ore with sulfuric acid, according to the following chemical equation:

$$Al_2O_3 + 3\,H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\,H_2O$$

   The bauxite ore contains 55.4% by weight of aluminum oxide, the remainder being impurities. The sulfuric acid solution contains 77.7% pure sulfuric acid, the remainder being water. To produce crude aluminum sulfate containing 1798 lb of pure aluminum sulfate, 1080 lb of bauxite ore and 2510 lb of sulfuric acid solution are reacted.

a. Identify the excess reactant.
b. What percentage of the excess reactant was consumed?

   c. What was the degree of completion of the reaction?

8. Two well-known gas phase reactions take place in the dehydration of ethane:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad \text{(a)}$$

$$C_2H_6 + H_2 \rightarrow 2\,CH_4 \qquad \text{(b)}$$

Given the product distribution measured in the gas phase reaction of C_2H_6 as follows

C_2H_6 27%, C_2H_4 33%, H_2 13%, and CH_4 27%

   a. What species was the limiting reactant?
   b. What species was the excess reactant?
   c. What was the conversion of C_2H_6 to CH_4?
   d. What was the degree of completion of the reaction?
   e. What was the selectivity of C_2H_4 relative to CH_4?
   f. What was the yield of C_2H_4 expressed in kg mol of C_2H_4 produced per kg mol of C_2H_6?
   g. What was the extent of reaction of C_2H_6?

Answers:

1. (a) $C_9H_{18} + \frac{27}{2}O_2 \rightarrow 9\,CO_2 + 9\,H_2O$; (b) $4\,FeS_2 + 11\,O_2 \rightarrow 2Fe_2O_3 + 8\,SO_2$
2. 3.08
3. 323
4. No
5. (a) 1,
   (b) 1,
   (c) The same,
   (d) The extent of reaction depends on the reaction equation as a whole and not on one species in the equation.
6. $CaCO_3$: 43.4%, CaO: 56.4%; (b) 0.308
7. (a) H_2SO_4

(b) 79.2%;

(c) 0.89

8. (a) C_2H_6 (the hydrogen is from reaction No.2, not the feed);

   (b) None;

(c) Fraction conversion = 0.184;

(d) 0.45;

(e) 1.22

(f) Based on reactant in the feed: 0.45, based on reactant consumed: 0.84, based on theory: 0.50;

(g) Reaction (a) is 33 mol reacting and reaction (b) is 13.5 mol reacting, both based on 100 mol product.

Supplementary Problems (Chapter Nine):

Problem 1

Gypsum (plaster of Paris : $CaSO_4 \cdot 2H_2O$) is produced by the reaction of calcium carbonate and sulfuric acid. A certain lime stone analyzes: $CaCO_3$ 96.89 %; $MgCO_3$ 1.41 %; inerts 1.70 %. For 5 metric tons of limestone reacted completely, determine:

a. kg of anhydrous gypsum ($CaSO_4$) produced.
b. kg of sulfuric acid solution (98 wt%) required.
c. kg of carbon dioxide produced.

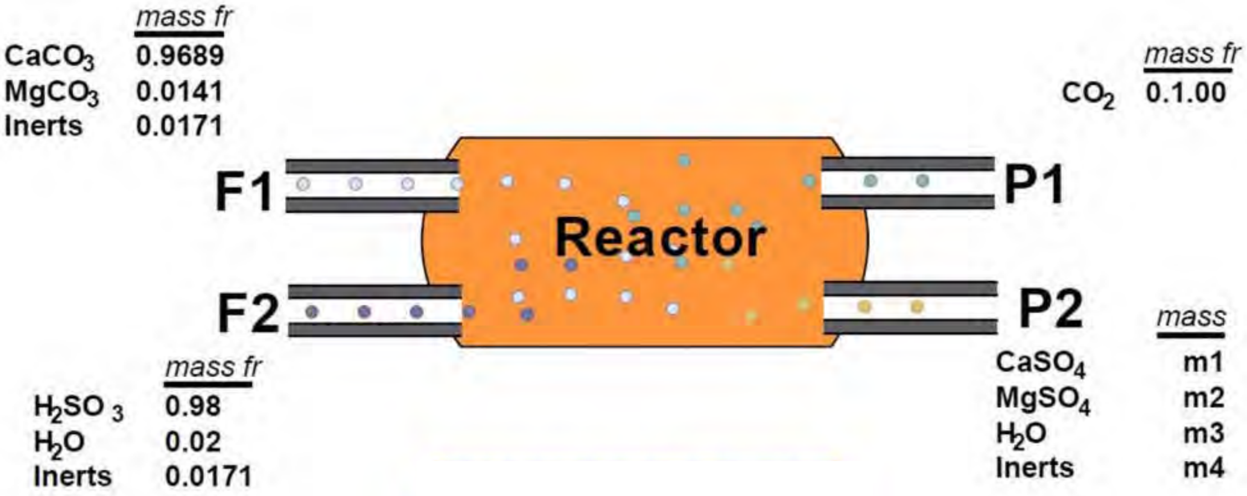
(MW : $CaCO_3$ 100.1; $MgCO_3$ 84.32; H_2SO_4 98; $CaSO_4$ 136; $MgSO_4$ 120; H_2O 18; CO_2 44)

Solution

The problem involves 2 reactions. Both calcium carbonate and magnesium carbonate react with sulfuric acid. The stoichiometric equations are

$$CaCO_3 + H_2SO_4 \text{ ------> } CaSO_4 + H_2O + CO_2 \qquad (1)$$

$$MgCO_3 + H_2SO_4 \text{ ------> } MgSO_4 + H_2O + CO_2 \qquad (2)$$



Basis : 5000 kg limestone

a. $CaSO_4$ produced

$$\frac{5000\text{kglimestone}}{}\;\Big|\;\frac{96.89\text{kgCaCO}_3}{100\text{kglimestone}}\;\Big|\;\frac{1\text{kgmolCaCO}_3}{100.1\text{kgCaCO}_3}\;\Big|\;\frac{1\text{kgmolCaSO}_4}{1\text{kgmolCaCO}_3}\;\Big|\;\frac{136\text{kgCaSO}_4}{1\text{kgmolCaSO}_4}$$

$$= \mathbf{6600\ kg\ CaSO_4}$$

b. Sulfuric acid required

Both $CaCO_3$ and $MgCO_3$ react with sulfuric acid in a 1 to 1 molar ratio.

$$\frac{5000\text{kg limestone}}{}\;\Big|\;\frac{96.89\text{kg CaCO}_3}{100\text{kg limestone}}\;\Big|\;\frac{1\text{kg mol CaCO}_3}{100.1\text{kg CaCO}_3}\;\Big|\;\frac{1\text{kg mol H}_2\text{SO}_4}{\text{kgmolCaCO}_3}\;\Big|\;\frac{98\text{kg H}_2\text{SO}_4}{\text{kgmol H}_2\text{SO}_4}$$

$$= 4740\text{ kg H}_2\text{SO}_4$$

$$\frac{5000\text{ kg limestone}}{}\;\Big|\;\frac{1.41\text{ kg MgCO}_3}{100\text{ kg limestone}}\;\Big|\;\frac{1\text{ kg mol MgCO}_3}{84.32\text{ kg MgCO}_3}\;\Big|\;\frac{1\text{ kg mol H}_2\text{SO}_4}{\text{kg mol MgCO}_3}\;\Big|\;\frac{98.0\text{ kg H}_2\text{SO}_4}{\text{kg mol H}_2\text{SO}_4}$$

$$= 81.94\text{ kg H}_2\text{SO}_4$$

total acid required = 4739.9 + 81.94 kg = 4822 kg 100 % acid.

We need to correct for the fact that acid is available as a 98 % solution.

$$\frac{4821.84\text{ kg H}_2\text{SO}_4}{}\;\Big|\;\frac{100\text{ kg acid solution}}{98.0\text{ kg H}_2\text{SO}_4} = \mathbf{4920\ kg\ H_2SO_4\ solution}$$

c. Carbon dioxide generated

Both $CaCO_3$ and $MgCO_3$ react with sulfuric acid to produce carbon dioxide.

$$\frac{5000\text{ kg limestone}}{}\;\Big|\;\frac{96.83\text{ kg CaCO}_3}{100\text{ kg CaCO}_3}\;\Big|\;\frac{1\text{ kg mol CaCO}_3}{100.1\text{ kg CaCO}_3}\;\Big|\;\frac{1\text{ kg mol CO}_2}{1\text{ kg mol CaCO}_3}\;\Big|\;\frac{44\text{ kg CO}_2}{1\text{ kg mol CO}_2} +$$

$$\frac{5000\text{ kg limestone}}{}\;\Big|\;\frac{1.41\text{ kg MgCO}_3}{100\text{ kg MgCO}_3}\;\Big|\;\frac{1\text{ kg MgCO}_3}{84.32\text{ kg MgCO}_3}\;\Big|\;\frac{1\text{ kg mol CO}_2}{1\text{ kg mol MgCO}_3}\;\Big|\;\frac{44\text{ kg CO}_2}{1\text{kg mol CO}_2}$$

$$= 2128.1 + 36.8 = \mathbf{2165\ kg\ CO_2}$$

The synthesis of ammonia proceeds according to the following reaction

$$N_2 + 3\,H_2 \dashrightarrow 2\,NH_3$$

In a given plant, 4202 lb of nitrogen and 1046 lb of hydrogen are fed to the synthesis reactor per hour. Production of pure ammonia from this reactor is 3060 lb per hour.

a. What is the limiting reactant.
b. What is the percent excess reactant.
c. What is the percent conversion obtained (based on the limiting reactant).

Solution

Problem 2

a.

$$\begin{array}{c|c|c} 4202\text{ lb }N_2 & 1\text{ lb mol }N_2 & 2\text{ lb mol }NH_3 \\ \hline & 28\text{ lb }N_2 & 1\text{ lb mol }N_2 \end{array} = 300\text{ lb mol }NH_3$$

$$\begin{array}{c|c|c} 1046\text{ lb }H_2 & 1\text{ lb mol }H_2 & 2\text{ lb mol }NH_3 \\ \hline & 2\text{ lb }H_2 & 3\text{ lb mol }H_2 \end{array} = 348.6\text{ lb mol }NH_3$$

If all of the N_2 were to react, 300 lb mol of ammonia would be produced while if all of the hydrogen were to react, 348.6 lb mol ammonia would be produced. **N_2 is the limiting reactant.**

b. H_2 required : based on the limiting reactant

$$\begin{array}{c|c|c} 4202\text{ lb }N_2 & 1\text{ lb mol }N_2 & 3\text{ lb mol }H_2 \\ \hline & 28\text{ lb }N_2 & 1\text{ lb mol }N_2 \end{array} = 450\text{ lb mol }H_2\text{ required}$$

H_2 available :

$$\begin{array}{c|c} 1046\text{ lb }H_2 & 1\text{ lb mol }H_2 \\ \hline & 2\text{ lb }H_2 \end{array} = 523\text{ lb mol }H_2$$

$$\%\text{ excess reactant} = \frac{\text{mol in excess}}{\text{mol required to react with limiting reactant}} \times 100$$

$$\%\text{ excess }H_2 = \frac{(523 - 450)}{450} \times 100 = \mathbf{16.2\ \%}$$

c. $$\text{Percentage conversion} = \frac{\text{moles (or mass) of feed that react}}{\text{moles (or mass) of feed introduced}} \times 100$$

$$N_2\text{ reacted} = \begin{array}{c|c|c|c} 3060\text{ lb }NH_3 & 1\text{ lb mol }NH_3 & 1\text{ lb mol }N_2 & 28\text{ lb }N_2 \\ \hline & 17\text{ lb }NH_3 & 2\text{ lb mol }NH_3 & 1\text{ lb mol }N_2 \end{array} = 2520\text{ lb }N_2$$

$$\%\text{ conversion} = \frac{2520\text{ lb}}{4202\text{ lb}} \times 100 = \mathbf{60.0\ \%}$$

Chapter 10

Material Balances for Processes Involving Reaction

10.1 Species Material Balances

10.1.1 Processes Involving a Single Reaction

The material balance for a **species** must be augmented to include **generation** and **consumption** terms when **chemical reactions** occur in a process.

$$\left\{\begin{array}{l}\text{moles of}\\ i \text{ at } t_2\\ \text{in the}\\ \text{system}\end{array}\right\} - \left\{\begin{array}{l}\text{moles of}\\ i \text{ at } t_1\\ \text{in the}\\ \text{system}\end{array}\right\} = \left\{\begin{array}{l}\text{moles of } i\\ \text{entering}\\ \text{the system}\\ \text{between } t_2 \text{ and } t_1\end{array}\right\} - \left\{\begin{array}{l}\text{moles of } i\\ \text{leaving}\\ \text{the system}\\ \text{between } t_2 \text{ and } t_1\end{array}\right\} + \left\{\begin{array}{l}\text{moles of } i\\ \text{generated}\\ \text{by reaction}\\ \text{between } t_2 \text{ and } t_1\end{array}\right\} - \left\{\begin{array}{l}\text{moles of } i\\ \text{consumed}\\ \text{by reaction}\\ \text{between } t_2 \text{ and } t_1\end{array}\right\} \quad \ldots 10.1$$

Note that we have written Equation (10.1) in **moles** rather than **mass** because the **generation** and **consumption** terms are more conveniently represented in **moles**.

For example : Figure 10.1 presents the process as an open, steady-state system operating for 1 min so that the accumulation terms are zero. The data in Figure 10.1 are in g mol. Using Equation 10.1 you can calculate via a value in g mol for the **generation** or **consumption**, as the case may be, for each of the three species involved in the reaction:

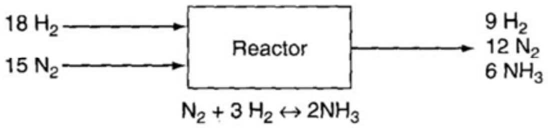


Figure 10.1. A reactor to produce NH_3.

NH_3 (generation): 6 – 0 = 6 gmol

H_2 (consumption): 9 – 18 = - 9 gmol

N_2 (consumption): 12 – 15 = - 3 gmol

Here is where the extent of reaction ξ becomes useful. Recall that for an open system

$$\xi = \frac{n_i^{\text{out}} - n_i^{\text{in}}}{v_i} \qquad i = 1, \cdots N \tag{10.2}$$

Where v_i is the stoichiometric coefficient of species *i* in the reaction equation

$$v_{NH_3} = 2$$
$$v_{H_2} = -3$$
$$v_{N_2} = -1$$

And the extent of reaction can be calculated via any species:

$$\xi = \frac{n_{NH_3}^{out} - n_{NH_3}^{in}}{v_{NH_3}} = \frac{6 - 0}{2} = 3$$

$$\xi = \frac{n_{H_2}^{out} - n_{H_2}^{in}}{v_{H_2}} = \frac{9 - 18}{-3} = 3$$

$$\xi = \frac{n_{N_2}^{out} - n_{N_2}^{in}}{v_{N_2}} = \frac{12 - 15}{-1} = 3$$

The three species balances corresponding to the process in Figure 10.1 are

Component	*Out*	*In*	=	*Generation or Consumption*
i	n_i^{out}	$-n_i^{in}$	=	$v_i\,\xi$
NH_3:	6	−0	=	2 (3) = 6
H_2:	9	−18	=	−3 (3) = −9
N_2:	12	−15	=	−1 (3) = −3

The term $v_i\,\xi$ corresponds to the moles of *i* **generated or consumed**.

- The value of the **fraction conversion *f*** of the **limiting** reactant; ξ is related to *f* by

$$\xi = \frac{(-f)\,n_{\text{limiting reactant}}^{in}}{v_{\text{limiting reactant}}} \qquad \ldots 10.3$$

Consequently, you can calculate the value of ξ from the fraction conversion (or vice versa) plus information identifying the limiting reactant.

Example 10.1

The chlorination of methane occurs by the following reaction $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

You are asked to determine the product composition if the conversion of the limiting reactant is 67%, and the feed composition in mole % is given as: 40% CH_4, 50% Cl_2, and 10% N_2. **Solution**

Assume the reactor is an **open**, **steady-state** process.

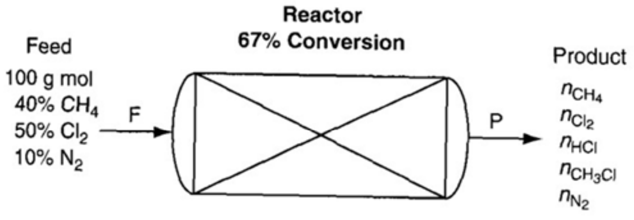


Figure E10.1

Basis 100 g mol feed

Limiting reactant:

$$\xi^{\max}(CH_4) = \frac{-n^{in}_{CH_4}}{\nu_{CH_4}} = \frac{-40}{(-1)} = 40$$

$$\xi^{\max}(Cl_2) = \frac{-n^{in}_{Cl_2}}{\nu_{Cl_2}} = \frac{-50}{(-1)} = 50$$

Therefore, **CH_4 is the limiting reactant**.

Calculate the extent of reaction using the specified **conversion** rate and Equation 10.3.

$$\xi = \frac{-f\, n^{in}_{lr}}{\nu_{lr}} = \frac{(-0.67)(40)}{-1} = 26.8 \text{ g moles reacting}$$

The **species material balances** (in moles) using Equation 10.2 gives a direct solution for each species in the product:

$$\begin{aligned}
n^{out}_{CH_4} &= 40 - 1(26.8) = 13.2\\
n^{out}_{Cl_2} &= 50 - 1(26.8) = 23.2\\
n^{out}_{CH_3Cl} &= 0 + 1(26.8) = 26.8\\
n^{out}_{HCl} &= 0 + 1(26.8) = 26.8\\
n^{out}_{N_2} &= 10 - 0(26.8) = \underline{10.0}\\
& \qquad\qquad\qquad\quad 100.0 = P
\end{aligned}$$

Therefore, the **composition** of the product stream is: **13.2% CH_4, 23.2% Cl_2, 26.8% CH_3C1, 26.8% HCl, and 10% N_2** because the total number of product moles is conveniently 100 gmol.

Example 10.2

A proposed process to remove H_2S is by reaction with SO_2:

$$2\,H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(g)$$

In a test of the process, a gas stream containing 20% H_2S and 80% CH_4 were combined with a stream of pure SO_2. The process produced 5000 lb of S(s), and in the product gas the ratio of SO_2 to H_2S was equal to 3, and the ratio of H_2O to H_2S was 10. You are asked to determine the fractional conversion of the limiting reactant, and the feed rates of the H_2S and SO_2 streams.

Solution

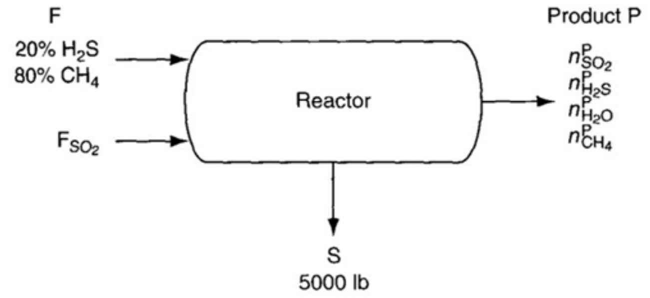

F
20% H_2S
80% CH_4
F_{SO_2}
Reactor
Product P
$n^P_{SO_2}$
$n^P_{H_2S}$
$n^P_{H_2O}$
$n^P_{CH_4}$
S
5000 lb

Figure E10.2

Basis is 5000 lb S (156.3 lb mol S)

Basis: S = 5000 lb (156.3 lb mol)

Specifications: 4 (3 independent)

$$x^F_{H_2S} = 0.20 \text{ or } x^F_{CH_4} = 0.80, (n^P_{SO_2}/n^P_{H_2S}) = 3, (n^P_{H_2O}/n^P_{H_2S}) = 10$$

The **species balances** in pound moles after introduction of most of the specifications are:

$$\text{S:}\quad 156.3 = 0 + 3\,\xi \qquad \text{(a)}$$

$$\text{H}_2\text{S:}\quad n^P_{H_2S} = 0.20F - 2\,\xi \qquad \text{(b)}$$

$$\text{SO}_2\text{:}\quad n^P_{SO_2} = F_{SO_2} - 1\,\xi \qquad \text{(c)}$$

$$\text{H}_2\text{O:}\quad n^P_{H_2O} = 0 + 2\,\xi \qquad \text{(d)}$$

$$\text{CH}_4\text{:}\quad n^P_{CH_4} = 0.80F + 0\,(\xi) \qquad \text{(e)}$$

The remaining specifications are

$$n^P_{SO_2} = 3n^P_{H_2S} \qquad \text{(f)}$$

$$n^P_{H_2O} = 10n^P_{H_2S} \qquad \text{(g)}$$

If you solve the equations without using a computer, you should start by calculating ξ from Equation (a)

$$\xi = \frac{156.3 \text{ mol}}{3} = 52.1 \text{ mol rxn}$$

Then Equation (d) gives

$n^P_{H_2O} = 2(52.1) = 104.2 \text{ lb mol H}_2\text{O}$ Next, Equation

(g) gives $n^P_{H_2S} = \frac{1}{10} n^P_{H_2O} = 10.4 \text{ lb mol } H_2S$ And

Equation (f) gives $n^P_{SO_2} = 3(10.4) = 31.2 \text{ lb mol } SO_2$

If you solve the rest of the equations in the order (b), (c), and (e),
you find F = 573 lb mol $F_{SO_2} = 83.3 \text{ lb mol}$

$n^F_{CH_4} = 458 \text{ lb mol}$

Finally, you can identify H_2S as the **limiting reactant** because the **molar ratio** of SO_2 to H_2S in the product gas **(3/1)** is greater than the molar ratio in the chemical reaction equation **(2/1)**.

The fractional conversion from Equation 10.3 is the consumption of H_2S divided by the total feed of H_2S

$$\xi = \frac{(-f)n^{\text{in}}_{\text{limiting reactant}}}{\nu_{\text{limiting reactant}}} \qquad f = \frac{-(-2)\xi}{0.2F} = \frac{(2)(52.1)}{(0.2)(573)} =$$

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10.1.2 Processes Involving Multiple Reactions

For **open** system, **steady-state** processes with multiple reactions, Equation 10.1 in moles becomes for component *i*

$$n_i^{\text{out}} = n_i^{\text{in}} + \sum_{j=1}^{R} v_{ij}\,\xi_j \qquad \ldots 10.4$$

Where:

v_{ij} is the stoichiometric coefficient of species *i* in reaction *j* in the minimal set. ξ_j is the extent of reaction for the *j*th reaction in the minimal set.

R is the number of independent chemical reaction equations (the size of the minimal set). What this latter term means is the smallest set of chemical reaction equations that can be assembled so as to include all of the species involved in the process.

An equation analogous to Equation 10.4 can be written for a **closed**, **unsteady-state** system. The total moles, **N**, exiting a reactor are

$$N = \sum_{i=1}^{S} n_i^{\text{out}} = \sum_{i=1}^{S} n_i^{\text{in}} + \sum_{i=1}^{S}\sum_{j=1}^{R} v_{ij}\xi_j \qquad \ldots 10.5$$

Where S is the number of species in the system.

Example 10.3

Formaldehyde (CH_2O) is produced industrially by the catalytic oxidation of methanol (CH_3OH) according to the following reaction:

$$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O \qquad (1)$$

Unfortunately, under the conditions used to produce formaldehyde at a profitable rate, a significant portion of the formaldehyde reacts with oxygen to produce CO and H_2O, that is,

$$CH_2O + 1/2O_2 \rightarrow CO + H_2O \qquad (2)$$

Assume that methanol and twice the stoichiometric amount of air needed for complete conversion of the CH_3OH to the desired products (CH_2O and H_2O) are fed to the reactor. Also assume that 90% conversion of the methanol results, and that a 75% yield of formaldehyde occurs based on the theoretical production of CH_2O by Reaction 1. Determine the composition of the product gas leaving the reactor.

Solution

Figure El0.3 is a sketch of the process with y_i indicating the **mole fraction** of the respective components in P (a gas).

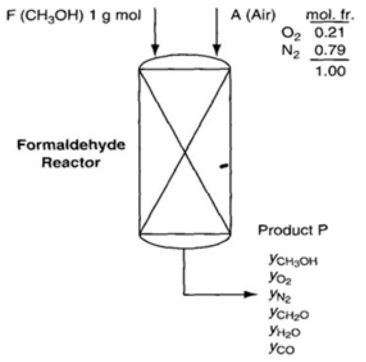


Figure E10.3

Basis: 1 gmol F

The **limiting** reactant is CH_3OH.

Use the fraction conversion, Equation 10.3: $\xi = \frac{-0.90}{-1}(1) = 0.9$ g moles reacting

The yield is related to ξ_i as follows

By reaction 1: $n_{CH_2O}^{out,1} = n_{CH_2O}^{in,1} + 1(\xi_1) = 0 + \xi_1 = \xi_1$

By reaction 2: $n_{CH_2O}^{out,2} = n_{CH_2O}^{in,2} - 1(\xi_2) = n_{CH_2O}^{out,1} - \xi_2 = \xi_1 - \xi_2$

The yield is $\frac{n_{CH_2O}^{out,2}}{F} = \frac{\xi_1 - \xi_2}{1} = 0.75$

$\xi_2 = 0.15$ g moles reacting

The entering oxygen is **twice** the required **oxygen** based on Reaction **1**, namely

$$n_{O_2}^{A} = 2\left(\frac{1}{2}F\right) = 2\left(\frac{1}{2}\right)(1.00) = 1.00 \text{ g mol}$$

$$A = \frac{n_{O_2}^{A}}{0.21} = \frac{1.00}{0.21} = 4.76 \text{ g mol}$$

$$n_{N_2}^{A} = 4.76 - 1.00 = 3.76 \text{ g mol}$$

Implicit equation:

$\Sigma y_i^P = 1$ Calculate P

using Equation 10.5:

$$\begin{aligned} P &= \sum_{i=1}^{S} n_i^{in} + \sum_{i=1}^{S}\sum_{j=1}^{R} v_{i_j}\xi_j \\ &= 1 + 4.76 + \sum_{i=1}^{6}\sum_{j=1}^{2} v_{i_j}\xi_j \\ &= 5.76 + [(-1) + (-1/2) + (1) + 0 + (1) + 0]\,0.9 \\ &\quad + [0 + (-1/2) + (-1) + 0 + (1) + (1)]\,0.15 = 6.28 \text{ g mol} \end{aligned}$$

The material balances:

$$n_{CH_3OH}^{out} = y_{CH_3OH}\,(6.28) = 1 - (0.9) + 0 = 0.10$$

$$n_{O_2}^{out} = y_{O_2}\,(6.28) = 1.0 - (^1\!/_2)(0.9) - (^1\!/_2)(0.15) = 0.475$$

$$n_{CH_2O}^{out} = y_{CH_2O}\,(6.28) = 0 + 1\,(0.9) - 1\,(0.15) = 0.75$$

$$n_{H_2O}^{out} = y_{H_2O}\,(6.28) = 0 + 1\,(0.9) + 1\,(0.15) = 1.05$$

$$n_{CO}^{out} = y_{CO}\,(6.28) = 0 + 0 + 1\,(0.15) = 0.15$$

$$n_{N_2}^{out} = y_{N_2}\,(6.28) = 3.76 - 0 - 0 = 3.76$$

The six equations can be solved for the y_i :

$$y_{CH_3OH} = 1.6\%, \quad y_{O_2} = 7.6\%, \quad y_{N_2} = 59.8\%,$$

$$y_{CH_2O} = 11.9\%, \quad y_{H_2O} = 16.7\%, \quad y_{CO} = 2.4\%.$$

Example 10.4

A bioreactor is a vessel in which biological conversion is carried out involving enzymes, microorganisms, and/or animal and plant cells. In the anaerobic fermentation of grain, the yeast Saccharomyces cerevisiae digests glucose ($C_6H_{12}O_6$) from plants to form the products ethanol (C_2H_5OH) and propionic acid ($C_2H_3CO_2H$) by the following overall reactions:

$$\text{Reaction 1:} \quad C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

$$\text{Reaction 2:} \quad C_6H_{12}O_6 \rightarrow 2C_2H_3CO_2H + 2H_2O$$

In a batch process, a tank is charged with 4000 kg of a 12% solution of glucose in water. After fermentation, 120 kg of CO_2 are produced and 90 kg of unreacted glucose remains in the broth. What are the weight (mass) percent of ethanol and propionic acid in the broth at the end of the fermentation process? Assume that none of the glucose is assimilated into the bacteria.

Solution

An unsteady-state process in a closed system

$$n_i^{final} = n_i^{initial} + \sum_{j=1}^{R} v_{ij}\,\xi_j$$

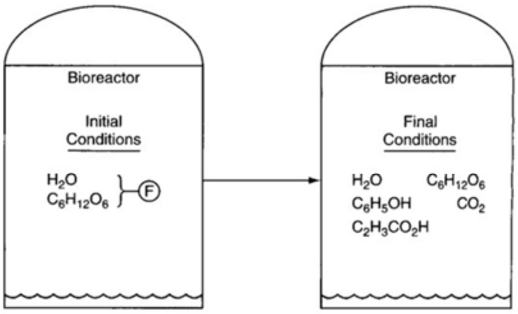

Bioreactor
Initial
Conditions
H₂O
C₆H₁₂O₆
F
Bioreactor
Final
Conditions
H₂O
C₆H₁₂O₆
C₆H₅OH
CO₂
C₂H₃CO₂H

Figure E10.4

Basis: 4000 kg F

$$n_{H_2O}^{Initial} = \frac{4000(0.88)}{18.02} = 195.3$$

$$n_{C_6H_{12}O_6}^{Initial} = \frac{4000(0.12)}{180.1} = 2.665$$

Specifications: 4 (3 independent)

$n_{H_2O}^{Initial} = 195.3$ or $n_{C_6H_{12}O_6}^{Initial} = 2.665$ (one is independent, the sum is F in mol)

$n_{C_6H_{12}O_6}^{Final} = \frac{90}{180.1} = 0.500 \qquad n_{CO_2}^{Final} = \frac{120}{44} = 2.727.$

The material balance equations, after introducing the known values for the variables, are:

H_2O: $\quad n_{H_2O}^{Final} = 195.3 + (0)\xi_1 + (2)\xi_2 \qquad$ (a)

$C_6H_{12}O_6$: $\quad 0.500 = 2.665 + (-1)\xi_1 + (-1)\xi_2 \qquad$ (b)

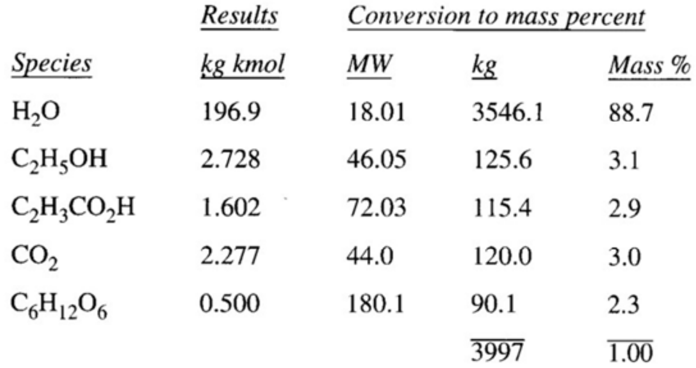
C_2H_5OH: $\quad n_{C_2H_5OH}^{Final} = 0 + 2\xi_1 + (0)\xi_2 \qquad$ (c)

$C_2H_3CO_2H$: $\quad n_{C_2H_3CO_2H}^{Final} = 0 + (0)\xi_1 + (2)\xi_2 \qquad$ (d)

CO_2 $2.727 = 0 + (2)\,\xi_1 + (0)\xi_2 \qquad$ (e)

Solution of equations: (e) (b) simultaneously, and then solve, (a), (c), and (d)

in order. $\xi_1 = 1.364$ kg moles reacting $\qquad \xi_2 = 0.801$ kg moles reacting



	Results	*Conversion to mass percent*		
Species	*kg kmol*	*MW*	*kg*	*Mass %*
H_2O	196.9	18.01	3546.1	88.7
C_2H_5OH	2.728	46.05	125.6	3.1
$C_2H_3CO_2H$	1.602	72.03	115.4	2.9
CO_2	2.277	44.0	120.0	3.0
$C_6H_{12}O_6$	0.500	180.1	90.1	2.3
			3997	1.00

Note: The total mass of **3997 kg** is close enough to **4000 kg** of feed to validate the results of the calculations.

10.2 Element Material Balances

- Elements in a process are **conserved**, and consequently you can apply Equation 10.1to the elements in a process.
- Because elements are **not generated or consumed**, the generation and consumption terms in Equation 10.1 can be **ignored**.

For Example: Carbon dioxide is absorbed in water in the process shown in Figure 10.2. The reaction is

$$CO_2(g) + H_2O(\ell) \rightarrow H_2CO_3(\ell)$$

Three unknowns exist: W, F, and P, and the process involves **three element C, H,** and **O**. It would appear that you can use the **three element balances** (in **moles**) [Basis P =100 mol]

$$\text{C:}\quad W(0) + F(1) = 0.05P\ (1)$$

$$\text{H:}\quad W(2) + F(0) = [0.05(2) + 0.95(2)]P = 2P$$

$$\text{O:}\quad W(1) + F(2) = [0.05(3) + 0.95(1)]P = 1.10P$$

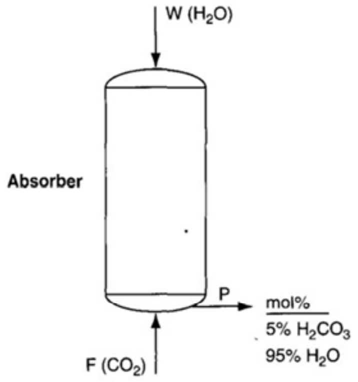


Figure 10.2 Schematic of the CO_2 absorber.

Example 10.5

Solution of **Examples 10.1** and **10.3** Using Element Balances: All of the given data for this example is the same as in Examples 10.1 and 10.3

Solution

1. Example 10.1

The element material balances are:

$$\text{C:}\quad 100\,(0.40) = n^{\text{out}}_{\text{CH}_4}(1) + n^{\text{out}}_{\text{CH}_3\text{Cl}}(1)$$

$$\text{H:}\quad 100\,(0.40)(4) = n^{\text{out}}_{\text{CH}_4}(4) + n^{\text{out}}_{\text{HCl}}(1) + n^{\text{out}}_{\text{CH}_3\text{Cl}}(3)$$

$$\text{Cl:}\quad 100\,(0.50)(2) = n^{\text{out}}_{\text{Cl}_2}(2) + n^{\text{out}}_{\text{HCl}}(1) + n^{\text{out}}_{\text{CH}_3\text{Cl}}(1)$$

$$\text{2N:}\quad 100\,(0.10)(1) = n^{\text{out}}_{\text{N}_2}(1)$$

The solution of the problem will be the same as found in Example 10.1.

2. Example 10.3

The element balances are:

$$
\begin{aligned}
\text{C:}\quad & 1(1) + 4.76(0) = P[y^P_{CH_3OH}(1) + y^P_{CH_2O}(1) + y^P_{CO}(1)] \\
\text{H:}\quad & 1(4) + 4.76(0) = P[y^P_{CH_3OH}(4) + y^P_{CH_2O}(2) + y^P_{H_2O}(2)] \\
\text{O:}\quad & 1(1) + 1.00 \quad = P[y^P_{CH_3OH}(1) + y^P_{O_2}(2) + y^P_{CH_2O}(1) \\
& \qquad + y^P_{H_2O}(1) + y^P_{CO}(1)] \\
\text{2N:}\quad & 1(0) + 3.76 \quad = P[y^P_{N_2}(1)]
\end{aligned}
$$

The solution of the problem will not change.

Note: It would be easier to use the term $y_i^P P = n_i^P$ in the equations above in place of the product of two variables, y_i^P and P.

---

❶ **Element balances** are especially **useful** when you do **not know** what **reactions** occur in a process. You only know information about the **input** and **output stream** components.

Example 10.6

In one such experiment for the hydrocracking (cracking reactions) of octane (C_8H_{18}), the cracked products had the following composition in mole percent: 19.5% C_3H_8, 59.4% C_4H_{10}, and 21.1% C_5H_{12}. You are asked to determine the molar ratio of hydrogen consumed to octane reacted for this process.

Solution

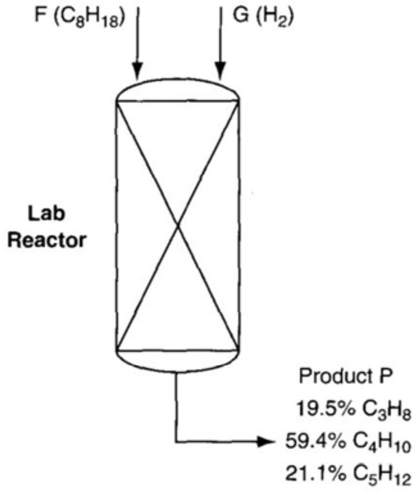


Figure E10.6

Basis: P= 100 g mol

Element balances: 2 H, C