Material Balances

2.1 Introduction to Material Balances

A material balance is nothing more than the application of the law of the conservation of mass: “Matter is neither created nor destroyed” التوازن المادي هو تطبيق لقانون الحفاظ على الكتلة: "المادة لا تخلق ولا تدمر"

Open and Closed Systems

نعني بالنظام أي جزء من أو عملية كاملة تريد وضعها في الاعتبار للتحليل. يمكنك تحديد نظام مثل المفاعل ، قسم من الأنبوب.

a. System أو يمكنك تحديد حدود النظام عن طريق رسم حدود النظام ، أي الخط الذي يحيط بجزء العملية الذي تريد تحليله

By system we mean any arbitrary portion of or a whole process that you want to consider for analysis. You can define a system such as a reactor, a section of a pipe. Or, you can define the limits of the system by drawing the system boundary, namely a line that encloses the portion of the process that you want to analyze. b. Closed System

Figure 1 shows a two-dimensional view of a three-dimensional vessel holding 1000 kg of H_2O. Note that material neither enters nor leaves the vessel, that is, no material crosses the system boundary. Changes can take place inside the system, but for a closed system, no mass exchange occurs with the surroundings.

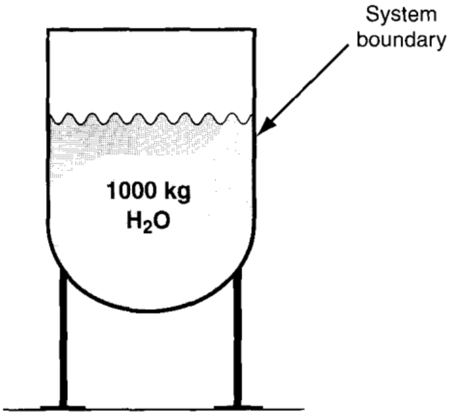


Figure 1 Closed system.

c. Open System

Figure 2 is an example of an open system (also called a flow system) because material crosses the system boundary.

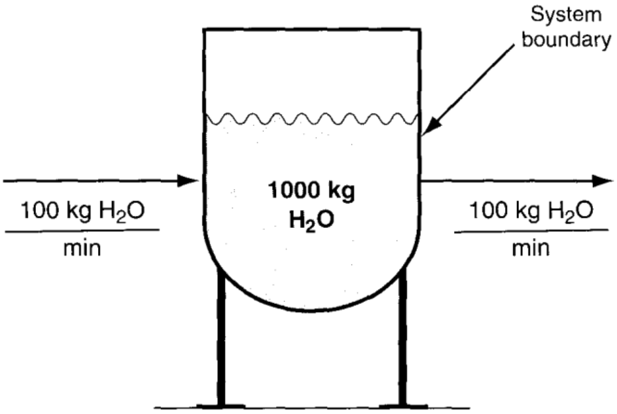


Figure 2 Open steady – state system.

Steady-State and Unsteady-State Systems

a. Steady – State System

Because the rate of addition of water is equal to the rate of removal, the amount of water in the vessel shown in Figure 2 remains constant at its original value (1000 kg). We call such a process or system a steady – state process or a steady – state system because

1. The unchanged with timeconditions inside the process (specifically the amount of water in the vessel in Figure 2) , and خل العملية دون تغيير مع مرور الوقتremain تظل الظروف دا

تظل ظروف التيارات المتدفقة ثابتة مع مرور الوقت.

2. The conditions of the flowing streams remain constant with time.

‘ Thus, in a steady-state process, by definition all of the conditions in the process (e.g., temperature, pressure, mass of material, flow rate, etc.) remain constant with time. A continuous process is one in which material enters and/or leaves the system without interruption. العملية المستمرة هي العملية التي تدخل فيها المادة و / أو تغادر النظام دون انقطاع. b. Unsteady – State System

Because the amount of water in the system changes with time (Figure 3), the process and system are deemed to be an unsteady – state (transient) process. نظرا لأن كمية المياه في النظام تتغير بمرور الوقت ، فإن العملية والنظام يعتبران عملية غير مستقرة

‘ For an unsteady-state process, not all of the conditions in the process (e.g., temperature, pressure, mass of material, etc.) remain constant with time, and/or the flows in and out of the system can vary with time.

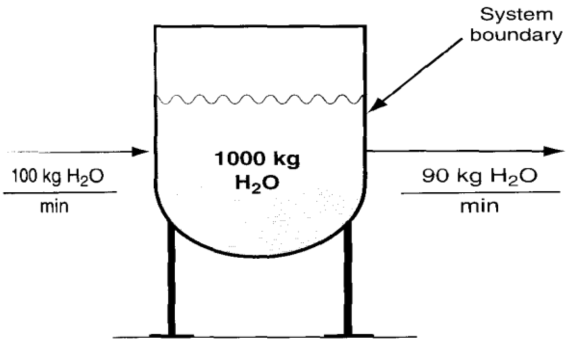


Figure 3 Initial conditions for an open unsteady – state system with accumulation.

‘ Figure 4 shows the system after 50 minutes of accumulation (Fifty minutes of accumulation at 10 kg/min amounts to 500 kg of total accumulation).

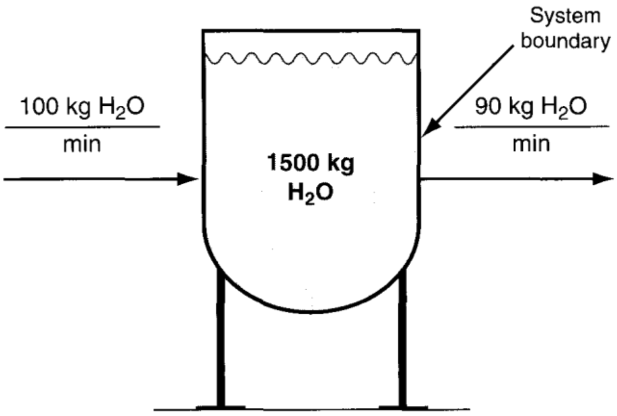


Figure 4 The condition of the open unsteady – state system with accumulation after 50 minutes.

Figures 5 and 6 demonstrate negative accumulation.

Note that the amount of water in the system decreases with time at the rate of 10 kg/min. Figure 6.6 shows the system after 50 minutes of operation.

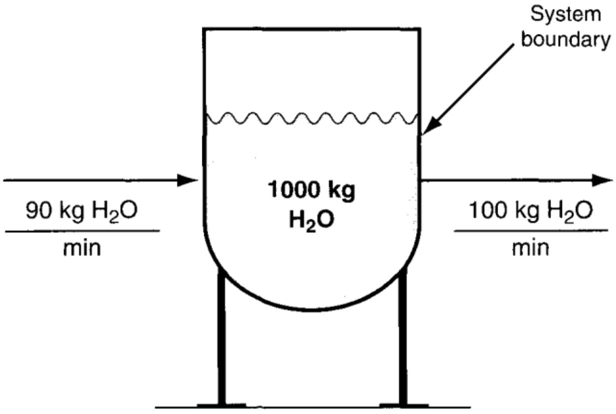


Figure 5 Initial conditions for an unsteady – state process with negative accumulation.

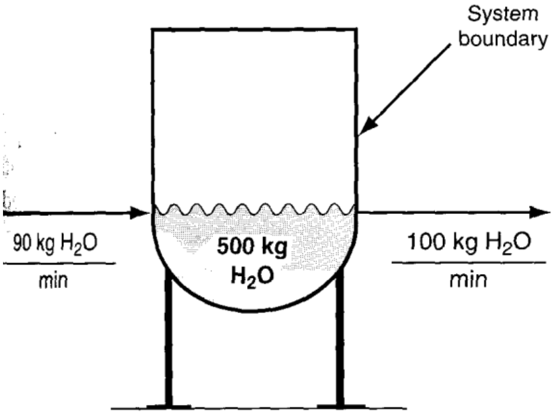


Figure 6 Condition of the open unsteady – state system with negative accumulation after 50 minutes.

☐ **The material balance for a single component process is**

$$\begin{Bmatrix}\textbf{Accumulation of material}\\ \textbf{within the system}\end{Bmatrix} = \begin{Bmatrix}\textbf{Total flow into}\\ \textbf{the system}\end{Bmatrix} - \begin{Bmatrix}\textbf{Total flow out}\\ \textbf{of the system}\end{Bmatrix} \quad \ldots 6.1$$

Equation 6.1 can apply to moles or any quantity that is conserved. As an example, look at Figure 6.7 in which we have converted all of the mass quantities in Figure 2 to their equivalent values in moles.

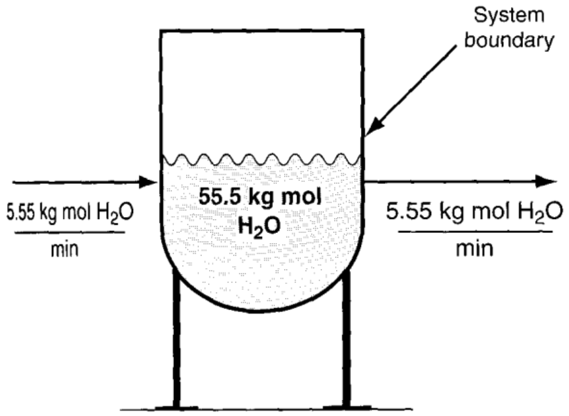


Figure 7 The system in Figure 2 with the flow rates shown in kg mol.

If the process is in the **steady state**, the **accumulation** term by definition is **zero** Equation 6.1 simplifies to a famous truism

What goes in must come out (In = Out) …6.2

If you are analyzing an unsteady-state process, the accumulation term over a time interval can be calculated as

$$\{\textbf{Accumulation}\} = \begin{Bmatrix}\textbf{Final material}\\ \textbf{in the system}\end{Bmatrix} - \begin{Bmatrix}\textbf{Initial material}\\ \textbf{in the system}\end{Bmatrix} \quad (6.3)$$

The times you select for the final and initial conditions can be anything, but you usually select an interval such as 1 minute or 1 hour rather than specific times.

‘ When you combine Equations 6.1 and 6.3 you get the general material balance for a component in the system in the **absence of reaction**

absence of reaction

$$\begin{Bmatrix}\textbf{Final material}\\ \textbf{in the system}\\ \textbf{at } t_2\end{Bmatrix} - \begin{Bmatrix}\textbf{Initial material}\\ \textbf{in the system}\\ \textbf{at } t_1\end{Bmatrix} = \begin{Bmatrix}\textbf{Flow into}\\ \textbf{the system}\\ \textbf{from } t_1 \textbf{ to } t_2\end{Bmatrix} - \begin{Bmatrix}\textbf{Flow out of}\\ \textbf{the system}\\ \textbf{from } t_1 \textbf{ to } t_2\end{Bmatrix} \quad \ldots 6.4$$

Example 1

Will you save money if instead of buying premium 89 octane gasoline at $1.269 per gallon that has the octane you want, you blend sufficient 93 octane supreme gasoline at $l.349 per gallon with 87 octane regular gasoline at $1.149 per gallon?

Solution

Choose a basis of 1 gallon of 89 octane gasoline, the desired product. The system is the gasoline tank.

- For simplicity, assume that no gasoline exists in the tank at the start of the blending, and one gallon exists in the tank at the end of the blending.
- This arrangement corresponds to an unsteady-state process. Clearly it is an open system.

The initial number of gallons in the system is zero and the final number of gallons is one.

Let x = the number of gallons of 87 octane gasoline added, and y = the number of gallons of 93 octane added to the blend. Since x + y = 1 is the total flow into the tank,

∴ y = 1 – x

According to Equation (6.4) the balance on the octane number is

$$\overset{\textit{Accumulation}}{\left|\frac{89\text{ octane}}{1\text{ gal}}\right|\frac{1\text{ gal}}{} - 0} = \overset{\textit{Inputs}}{\left|\frac{87\text{ octane}}{1\text{ gal}}\right|\frac{x\text{ gal}}{} + \left|\frac{93\text{ octane}}{1\text{ gal}}\right|\frac{(1-x)\text{ gal}}{}}$$

The solution is x = 2/3 gal and thus y = 1 – x = 1/3 gal.

The cost of the blended gasoline is (2/3) ($l.l49) + (1/3) ($l.349) = $ 1.216 A value less than the cost of the 89 octane gasoline ($l.269).

Multiple Component Systems

Suppose the input to a vessel contains **more than one component** such as 100 kg/min of a 50% water and 50% sugar (sucrose, $C_{12}H_{22}O_{11}$, MW = 342.3) mixture (see Figure 8). The mass balances with respect to the sugar and water, balances that we call component balances.

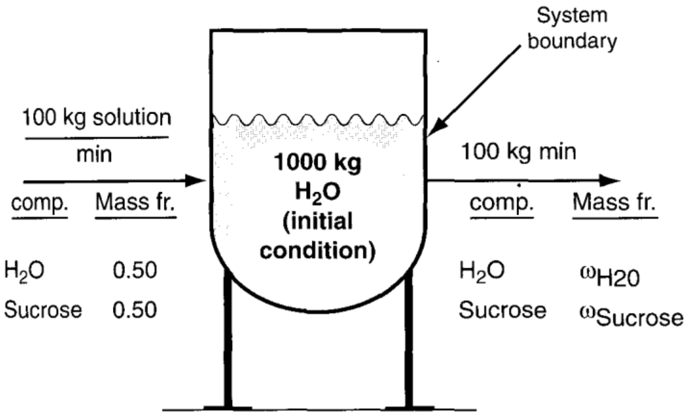


Figure 8 An open system involving two components.

For Example, look at the mixer shown in Figure 9, an apparatus that mixes two streams to increase the concentration of NaOH in a dilute solution. **The mixer is a steady – state open system**. Initially the mixer is empty, and after 1 hour it is empty again.

Basis = 1 hour for convenience. As an alternate to the basis we selected you could select F_1 = 9000 kg/hr as the basis, or F_2 = 1000 kg/hr as the basis; the numbers for this example would not change – just the units would change. Here are the components and total balances in kg:

	Flow in			
Balances	F_1	F_2	**Flow out**	**Accum.**
NaOH	450	500	950	= 0
H_2O	8,550	500	9,050	= 0
Total	9,000	1,000	10,000	= 0

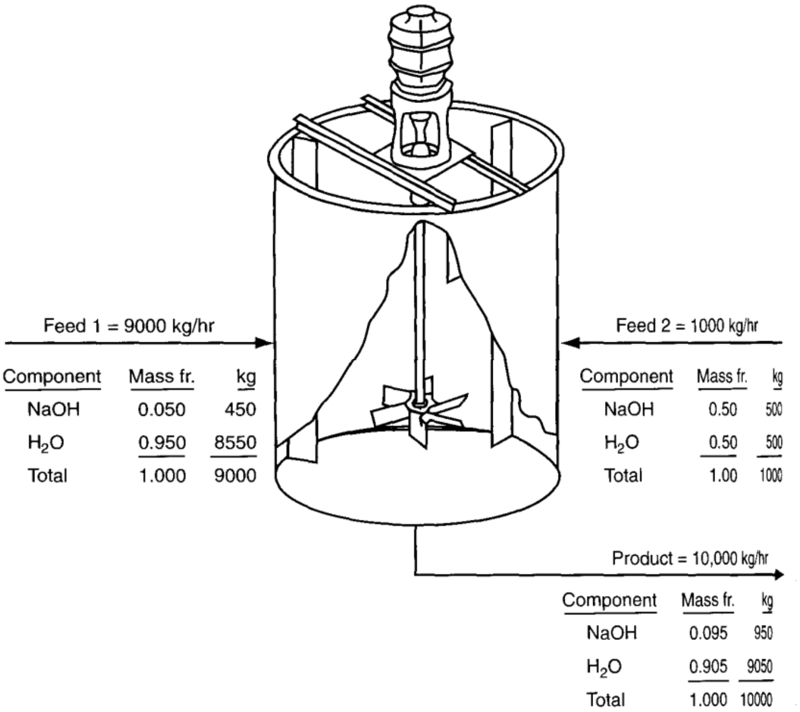
We can convert the kg shown in Figure 6.9 to kg moles by dividing each compound by its respective molecular weight (NaOH = 40 and H_2O = 18).

$$\text{NaOH:}\quad \frac{450}{40} = 11.25 \qquad \frac{500}{40} = 12.50 \qquad \frac{950}{40} = 23.75$$

$$\text{H}_2\text{O:}\quad \frac{8550}{18} = 475 \qquad \frac{500}{18} = 27.78 \qquad \frac{9050}{18} = 502.78$$

Then the component and total balances in kg mol are:

	Flow in			
Balances	F_1	F_2	**Flow out**	**Accum.**
NaOH	11.25	12.50	23.75	= 0
H_2O	475	27.78	502.78	= 0
Total	486.25	40.28	536.53	= 0



Component	Mass fr.	kg
NaOH	0.050	450
H_2O	0.950	8550
Total	1.000	9000

Component	Mass fr.	kg
NaOH	0.50	500
H_2O	0.50	500
Total	1.00	1000

Component	Mass fr.	kg
NaOH	0.095	950
H_2O	0.905	9050
Total	1.000	10000

Figure 9 Mixing of a dilute stream of NaOH with a concentrated stream of NaOH. Values below the stream arrows are based on 1 hour of operation.

Example 2

Centrifuges are used to separate particles in the range of 0.1 to 100 µm in diameter from a liquid using centrifugal force. Yeast cells are recovered from a broth (a liquid mixture containing cells) using a tubular centrifuge (a cylindrical system rotating about a cylindrical axis). Determine the amount of the cell-free discharge per hour if 1000 L/hr is fed to the centrifuge, the feed contains 500 mg cells/L, and the product stream contains 50 wt.% cells. Assume that the feed has a density of 1 g/cm^3.

Solution

This problem involves a steady state, open (flow) system without reaction.

Basis = 1 hour

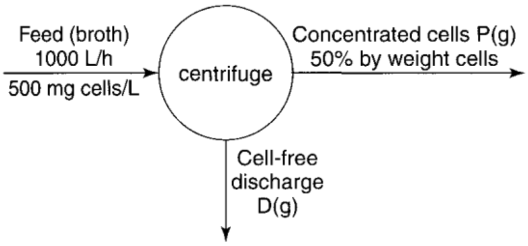


Figure E6.2

M.B. on cells

In (mass) = Out (mass)

$$\frac{1000\text{ L feed}}{} \left| \frac{500\text{ mg cells}}{1\text{ L feed}} \right| \frac{1\text{ g}}{1000\text{ mg}} = \frac{0.5\text{ g cells}}{1\text{ g } P} \left| \frac{P\text{ g}}{} \right.$$

P = 1000 g

M.B. on fluid

In (mass) = Out (mass)

$$\frac{1000\text{ L}}{} \left| \frac{1000\text{ cm}^3}{1\text{ L}} \right| \frac{1\text{ g fluid}}{1\text{ cm}^3} = \frac{1000\text{ g } P}{} \left| \frac{0.50\text{ g fluid}}{1\text{ g } P} \right. + D\text{ g fluid}$$

$D = (10^6 - 500)$ g

Accounting for Chemical Reactions in Material Balances

Chemical reaction in a system requires the augmentation of Equation 6.4 to take into account the effects of the reaction. To illustrate this point, look at Figure 10, which shows a steady – state system in which HC1 reacts with NaOH by the following reaction:

$$\text{NaOH} + \text{HCl} \longrightarrow \text{NaC1} + \text{H}_2\text{O}$$

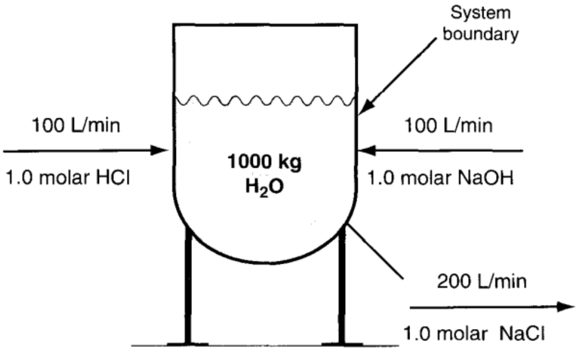


Figure 10 Reactor for neutralizing HC1 with NaOH.

Equation 4 must be augmented to include terms for the generation and consumption of components by the chemical reaction in the system as follows

$$\left\{\begin{matrix}\textbf{Accumulation}\\ \textbf{within the}\\ \textbf{system}\end{matrix}\right\} = \left\{\begin{matrix}\textbf{Input}\\ \textbf{through}\\ \textbf{the system}\\ \textbf{boundaries}\end{matrix}\right\} - \left\{\begin{matrix}\textbf{Output}\\ \textbf{through}\\ \textbf{the system}\\ \textbf{boundaries}\end{matrix}\right\} + \left\{\begin{matrix}\textbf{Generation}\\ \textbf{within the}\\ \textbf{system}\end{matrix}\right\} - \left\{\begin{matrix}\textbf{Consumption}\\ \textbf{within the}\\ \textbf{system}\end{matrix}\right\} \qquad \ldots 6.5$$

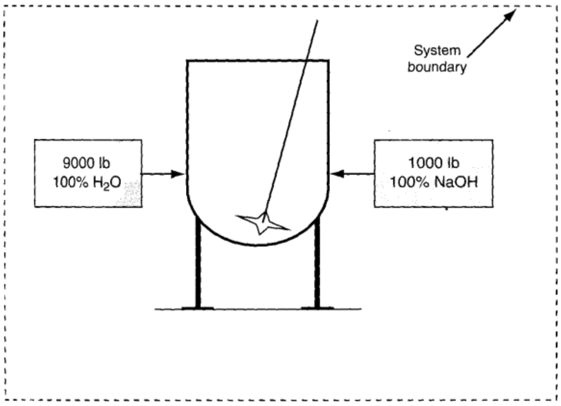
Material Balances for Batch and Semi-Batch Processes

كمية ثابتة

- A batch process is used to process a fixed amount of material each time it is operated. Initially, the material to be processed is charged into the system. After processing of the material is complete, the products are removed.

- Batch processes are used industrially for speciality processing applications (e.g., producing pharmaceutical products), which typically operate at relatively low production rates.

- Look at Figure11a that illustrates what occurs at the start of a batch process, and after thorough mixing, the final solution remains in the system (Figure 11b).



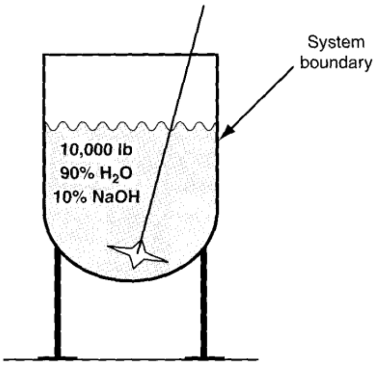


Figure 11b The final state of a batch mixing process.

Figure 11a The initial state of a batch mixing process.

عملية تشغيل افتراضية

♦ We can summarize the hypothetical operation of the batch as a flow system (open system) as follows (Figure 12):

Final conditions: All values = 0 Flows out:

NaOH = 1,000 lb

H_2O = 9,000 lb

Total = 10,000 lb Initial conditions: All value = 0

Flows in:

NaOH = 1,000 lb

H_2O = 9,000 lb

Total 10,000 lb

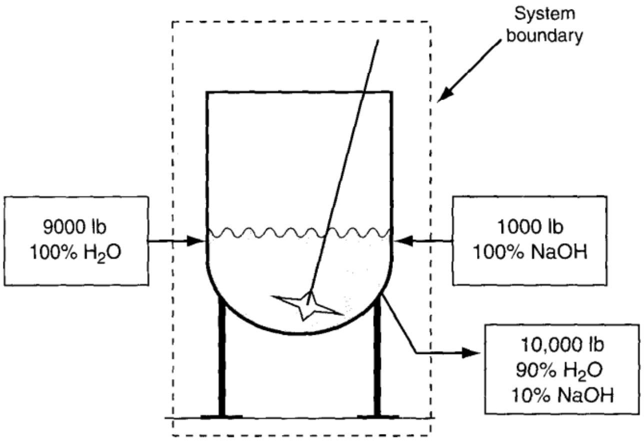


Figure 12 The batch process in Figure 11 represented as an open system.

المواد تدخل اثناء التشغيل

: In a semi-batch process material enters the process during its operation, but does not leave. Instead mass is allowed to accumulate in the process vessel. Product is withdrawn only after the process is over. لا تخرج الى بعد انتهاء العملية

A figure 13 illustrates a semi-batch mixing process. Initially the vessel is empty (Figure 13a). Figure13b shows

: the semi-batch system after 1 hour of operation. Semi-batch processes are open and unsteady – state.

Only flows enter the systems, and none leave, hence the system is an unsteady state – one that you can treat

: as having continuous flows, as follows:

Final conditions:

NaOH = 1,000 lb

H_2O = 9,000 lb

Total = 10,000 lb

Flows out: All values = 0

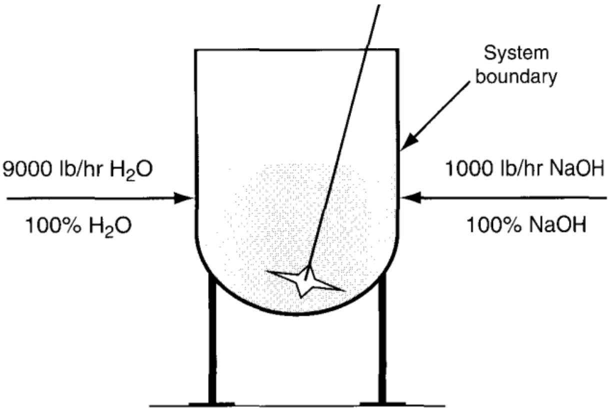
Flows in:

NaOH = 1,000 lb

H_2O = 9,000 lb

Total = 10,000 lb

Initial conditions: All values = 0



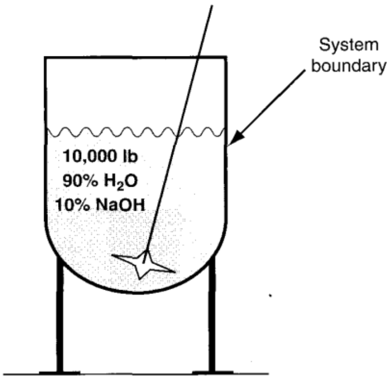


Figure 13b

Condition of a semi-batch mixing process Figure 6.13 Initial condition for the semi-batch mixing after 1 hour of operation. process. Vessel is empty.

Example 3

A measurement for water flushing of a steel tank originally containing motor oil showed that 0.15 percent by weight of the original contents remained on the interior tank surface. What is the fractional loss of oil before flushing with water, and the pounds of discharge of motor oil into the environment during of a 10,000 gal tank truck that carried motor oil? (The density of motor oil is about 0.80 g/cm^3).

Solution

Basis: 10,000 gal motor oil at an assumed 77°F

The initial mass of the motor oil in the tank was

(10000 gal)(3.785 lit/1 gal)(1000 cm^3/1 lit)(0.8 g/cm^3)(1 lb/454 g) = 66700 lb

The mass fractional loss is 0.0015. The oil material balance is

Initial   unloaded   residual discharged on cleaning

66,700   =   66,700 (0.9985)   +   66,700 (0.0015) Thus,

the discharge on flushing is 66,700 (0.00 15) = 100 lb.

Questions

1. Is it true that if no material crosses the boundary of a system, the system is a closed system?
2. Is mass conserved within an open process? 3. Can an accumulation be negative? What does a negative accumulation mean? ظروف
4. Under what circumstances can the accumulation term in the material balance be zero for a process?
5. Distinguish between a steady-state and an unsteady-state process.
6. What is a transient process? Is it different than an unsteady-state process?
7. Does Equation 6.4 apply to a system involving more than one component?
8. When a chemical plant or refinery uses various feeds and produces various products, does Equation 6.4 apply to each component in the plant?
9. What terms of the general material balance, Equation (6.5), can be deleted if
    a. The process is known to be a steady-state process.
    b. The process is carried out inside a closed vessel.
    c. The process does not involve a chemical reaction.
10. What is the difference between a batch process and a closed process?
11. What is the difference between a semi-batch process and a closed process?
12. What is the difference between a semi-batch process and an open process?

Answers:

1. Yes
2. Not necessarily – accumulation can occur
3. Yes; depletion الاستنزاف
4. No reaction (a) closed system, or (b) flow of a component in and out are equal.
5. In an unsteady-state system, the state of the system changes with time, whereas with a steady-state system, it does not.
6. A transient process is an unsteady-state process.

7. Yes

8. Yes

9. (a) Accumulation; (b) flow in and out; (c) generation and consumption

10. None

11. A flow in occurs

12. None, except in a flow process, usually flows occur both in and out

Problems

1. Here is a report from a catalytic polymerization unit:

Charge:	Pounds per hour	Propanes
and butanes	15,500	
Production:		
Propane and lighter	5,680	
Butane	2,080	
Polymer	missing	

What is the production in pounds per hour of the polymer?

2. A plant discharges 4,000 gal/min of treated wastewater that contains 0.25 mg/L of PCB, (polychloronated biphenyls) into a river that contains no measurable PCBs upstream of the discharge. If the river flow rate is 1,500 cubic feet per second, after the discharged water has thoroughly mixed with the river water, what is the concentration of PCBs in the river in mg/L?

$(3.785 \text{ lit}/1 \text{ gal})$ $\frac{1 \text{ L}}{3.531 \times 10^{-2} \text{ ft}^3}$

Answers:

1. 7,740 lb/hr

2. $1.49 * 10^{-3}$ mg/L.

2.2 General Strategy for Solving Material Balance Problems

Problem Solving

An orderly method of analyzing problems and presenting their solutions represents training in logical thinking that is of considerably greater value than mere knowledge of how to solve a particular type of problem.

The Strategy for Solving Problems

1. Read and understand the problem statement.

2. Draw a sketch of the process and specify the system boundary.

3. Place labels for unknown variables and values for known variables on the sketch.

4. Obtain any missing needed data.
5. Choose a basis.
6. Determine the number of unknowns.
7. Determine the number of independent equations, and carry out a degree of freedom analysis.
8. Write down the equations to be solved.
9. Solve the equations and calculate the quantities asked for.
10. Check your answer.

<u>Example 4</u>

A thickener in a waste disposal unit of a plant removes water from wet sewage sludge as shown in Figure 10. How many kilograms of water leave the thickener per 100 kg of wet sludge that enter the thickener? The process is in the steady state.

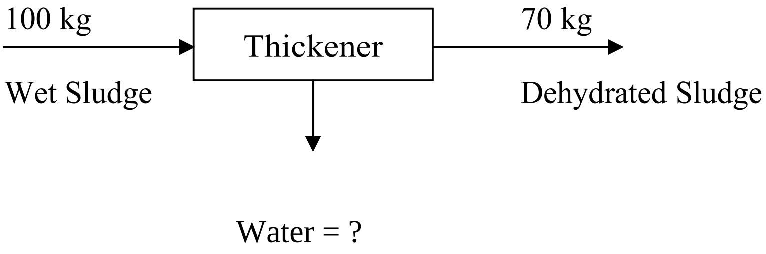


Figure 10

Solution

Basis: 100 kg wet sludge

The system is the thickener (an open system). No accumulation, generation, or consumption occurs. The total mass balance is

<u>In</u> = <u>Out</u>

100 kg = 70 kg + kg of water Consequently,

the water amounts to 30 kg.

Example 5

A continuous mixer mixes NaOH with H_2O to produce an aqueous solution of NaOH. Determine the composition and flow rate of the product if the flow rate of NaOH is 1000 kg/hr, and the ratio of the flow rate of the H_2O to the product solution is 0.9. For this process,

1. Sketch of the process is required.
2. Place the known information on the diagram of the process.
3. What basis would you choose for the problem?
4. How many unknowns exist?
5. Determine the number of independent equations.
6. Write the equations to be solved.
7. Solve the equations.
8. Check your answer.

Solution

1. The process is an open one, and we assume it to be steady state.

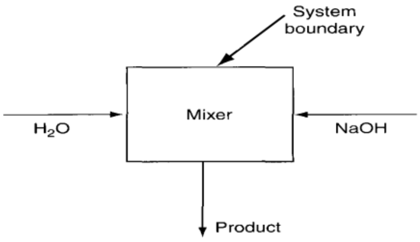
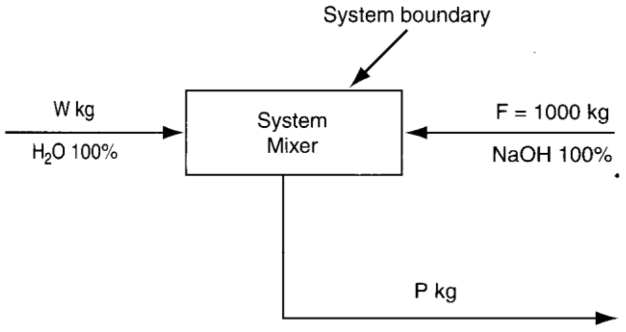


Figure E7.2

2. Because no contrary information is provided about the composition of the H_2O and NaOH streams, we will assume that they are 100% H_2O and NaOH, respectively.



Component	kg	ω (add if useful)
NaOH	P_{NaOH}	$\omega^P_{NaOH} = \frac{P_{NaOH}}{P}$
H_2O	P_{H_2O}	$\omega^P_{H_2O} = \frac{P_{H_2O}}{P}$
Total	P	1.00

3. Basis (1000 kg or 1 hour or 1000 kg/hr) (all are equivalent)

4. We do not know the values of four variables: W, P, P_{NaOH} and P_{H2O}.

5. You can write three material balances:

- one for the NaOH
- one for the H_2O
- one total balance (the sum of the two component balances)

Only two are independent.

Note: You can write as many independent material balances as there are species involved in the system. 6. Material balance: in = out or in – out = 0

$$\text{NaOH balance:} \quad 1000 = P_{NaOH} \quad \text{or} \quad 1000 - P_{NaOH} = 0 \qquad (1)$$

$$H_2O\text{ balance:} \quad W = P_{H_2O} \quad \text{or} \quad W - P_{H_2Q} = 0 \qquad (2)$$

$$\text{Given ratio:} \quad W = 0.9P \quad \text{or} \quad W - 0.9P = 0 \qquad (3)$$

$$\text{Sum of components in } P\text{: } P_{NaOH} + P_{H_2O} = P \text{ or } P_{NaOH} + P_{H_2O} - P = 0 \qquad (4)$$

Could you substitute the total mass balance 1000 + W = P for one of the two component mass balances? Of course In fact, you could calculate P by solving just two equations:

$$\text{Total balance:} \quad 1000 + W = P$$

$$\text{Given ratio:} \quad W = 0.9P$$

7. Solve equations:

W = 0.9 P substitute in total balance 1000 + 0.9 P = P

∴ P = 10000 kg & W = 0.9 * 10000 = 9000 kg (The basis is still 1 hr (F_{NaOH} = 1000 kg))

From these two values you can calculate the amount of H_2O and NaOH in the product

$$\text{From the } \begin{cases} \text{NaOH balance:} \\ \\ H_2O\text{ balance:} \end{cases} \text{ you get } \begin{cases} P_{NaOH} = 1000\text{ kg} \\ \\ P_{H_2O} = 9000\text{ kg} \end{cases}$$

Then

$$\omega^P_{NaOH} = \frac{1000\text{ kg NaOH}}{10{,}000\text{ kg Total}} = 0.1$$

$$\omega^P_{H_2O} = \frac{9{,}000\text{ kg }H_2O}{10{,}000\text{ kg Total}} = 0.9$$

Note

$$\boxed{\omega^P_{NaOH} + \omega^P_{H_2O} = 1}$$

8. The total balance would have been a redundant balance, and could be used to check the answers

$$P_{NaOH} + P_{H2O} = P$$

1,000 + 9,000 = 10,000

Note: After solving a problem, use a redundant equation to check your values.

Degree of Freedom Analysis

The phrase degrees of freedom have evolved from the design of plants in which fewer independent equations than unknowns exist. The difference is called the degrees of freedom available to the designer to specify flow rates, equipment sizes, and so on. You calculate the number of degrees of freedom (N_D) as follows:

Degrees of freedom = number of unknowns — number of independent equations

$$N_D = N_U - N_E$$

When you calculate the number of degrees of freedom you ascertain the solve ability of a problem. Three outcomes exist:

Case	N_D	Possibility of Solution
$N_U = N_E$	0	Exactly specified (determined); a solution exists
$N_U > N_E$	>0	Under specified (determined); more independent equations required
$N_U < N_E$	<0	Over specified (determined)

For the problem in Example 6,

$N_U = 4$

$N_E = 4$

So that

$N_D = N_U - N_E = 4 - 4 = 0$

And a unique solution exists for the problem.

Example 7

A cylinder containing CH_4, C_2H_6, and N_2 has to be prepared containing a CH_4 to C_2H_6 mole ratio of 1.5 to 1. Available to prepare the mixture is (l) a cylinder containing a mixture of 80% N_2 and 20% CH_4, (2) a cylinder containing a mixture of 90% N_2 and 10% C_2H_6, and (3) a cylinder containing pure N_2. What is the number of degrees of freedom, i.e., the number of independent specifications that must be made, so that you can determine the respective contributions from each cylinder to get the desired composition in the cylinder with the three components?

Solution

A sketch of the process greatly helps in the analysis of the degrees of freedom. Look at Figure 11.

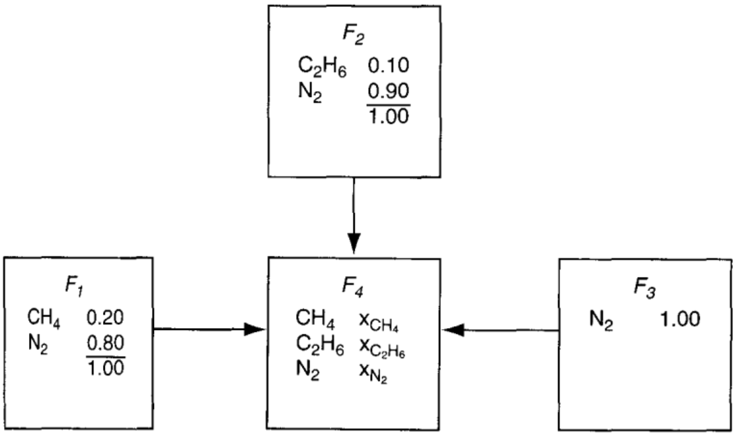


Figure 11

Do you count <u>seven unknowns</u> — three values of x_i and four values of F_i? How many independent equations can be written?

- ♦ Three material balances: CH_4, C_2H_6, and N_2
- ♦ One specified ratio: moles of CH_4 to C_2H_6 equal 1.5 or $(X_{CH4}/X_{C2H6}) = 1.5$
- ♦ One summation of mole fractions: $\sum x_i^{F4} = 1$

Thus, there are seven minus five equals two degrees of freedom ($N_D = N_U – N_E = 7 – 5 = 2$). If you pick a basis, such as $F_4 = 1$, one other value has to be specified to solve the problem to calculate composition of F_4.

<u>Example 8</u>

In the growth of biomass $CH_{1.8}O_{0.5}N_{0.16}S_{0.0045}P_{0.0055}$, with the system comprised of the biomass and the substrate, the substrate contains the carbon source for growth, $C_\alpha H_\beta O_\gamma$, plus NH_3, O_2, H_2O, CO_2, H_3PO_4, and H_2SO_4. The relations between the elements and the compounds in the system are:

	$CH_{1.8}O_{0.5}N_{0.16}S_{0.0045}P_{0.0055}$	$C_\alpha H_\beta O_\gamma$	NH_3	O_2	CO_2	H_2O	H_2SO_4	H_3PO_4
C	1	α	0	0	1	0	0	0
H	1.8	β	3	0	0	2	2	3
O	0.5	γ	0	2	2	1	4	4
N	0.16	0	1	0	0	0	0	0
S	0.0045	0	0	0	0	0	1	0
P	0.0055	0	0	0	0	0	0	1

How many degrees of freedom exist for this system (assuming that the values of α, β, and γ are specified)?

Solution

Based on the given data six element balances exist for the 8 species present, hence the system has two degrees of freedom.

Questions

1. What does the concept "solution of a material balance problem" mean?
2. (a) How many values of unknown variables can you compute from one independent material balance?

(b) From three independent material balance equations?

(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.

Dr.Ali H.Abbar

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

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.

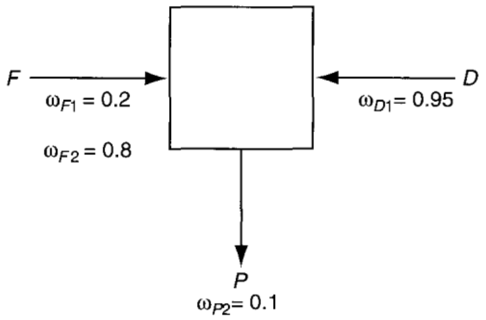


Figure SAT7.2P3

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.

2.3 Solving Material Balance Problems for Single Units without Reaction

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 9

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.

Dr.Ali H.Abbar

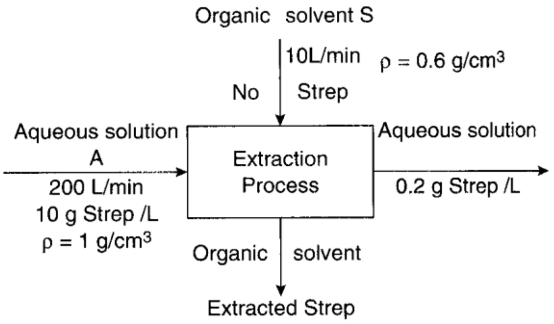


Figure E8.1

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:

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

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 10

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?

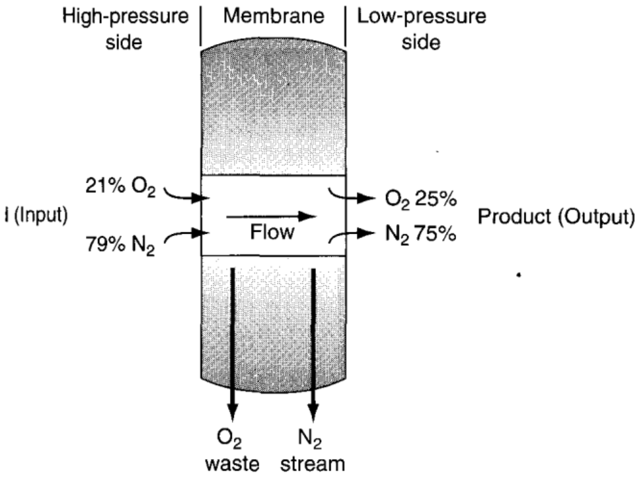
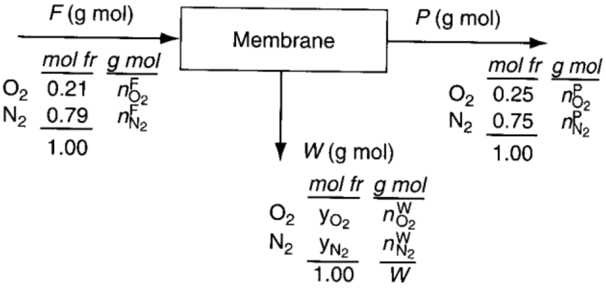

High-pressure side
Membrane
Low-pressure side
21% O_2
l (Input)
79% N_2
Flow
O_2 25%
N_2 75%
Product (Output)
O_2 waste
N_2 stream

Figure E8.2a

Solution

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



Basis: 100 g mol = F

Basis: F = 100

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

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

$y^P_{O_2} = n^P_{O_2}/P = 0.25 \qquad n^P_{O_2} = 0.25P$

$y^P_{N_2} = n^P_{N_2}/P = 0.75 \qquad n^P_{N_2} = 0.75P$

$W = 0.80(100) = 80$

Material balances: O_2 and N_2

Implicit equations: $\Sigma n^W_i = W$ or $\Sigma y^W_i = 1$

	In	Out		In	Out
O_2:	$0.21\,(100)$	$= 0.25P + y^W_{O_2}\,(80)$	or	$0.21\,(100)$	$= 0.25P + n^W_{O_2}$
N_2:	$0.79\,(100)$	$= 0.75P + y^W_{N_2}\,(80)$	or	$0.79\,(100)$	$= 0.75P + n^W_{N_2}$
	1.00	$= y^W_{O_2} + y^W_{N_2}$	or	80	$= n^W_{O_2} + n^W_{N_2}$

The solution of these equations is

$n^W_{O_2} = 16$ and $n^W_{N_2} = 64$, or $y^W_{O_2} = 0.20$ and $y^W_{N_2} = 0.80$, and $P = 20$ g mol.

Check: total balance 100 = 20 + 80 OK

™<u>Another method for solution</u>

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

$$0.21(100) = 0.25(20) + n^W_{O_2}$$

$n^W_{O_2} = 16$ g mol, and $n^W_{O_2} = 80 - 16 = 64$ g mol.

<u>Note (Example 10)</u>

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

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

Example 11

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.

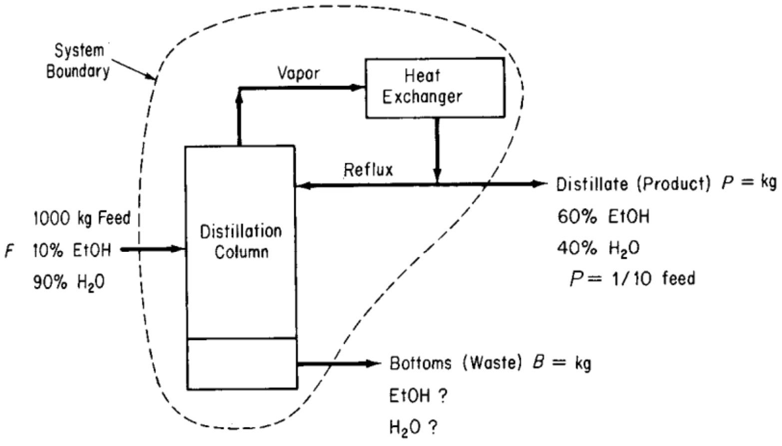


Figure E8.3

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: $\Sigma m^B_i = B$ or $\Sigma \omega^B_i = 1$

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

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

$$40 + 860 = 900 = B$$

Example 12

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.

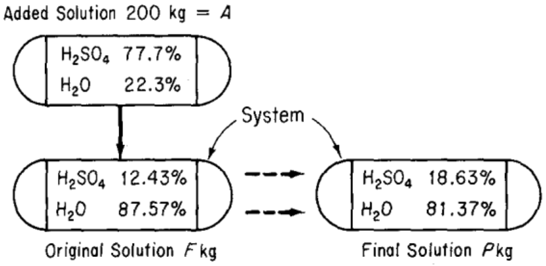


Figure E8.4

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 13

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.

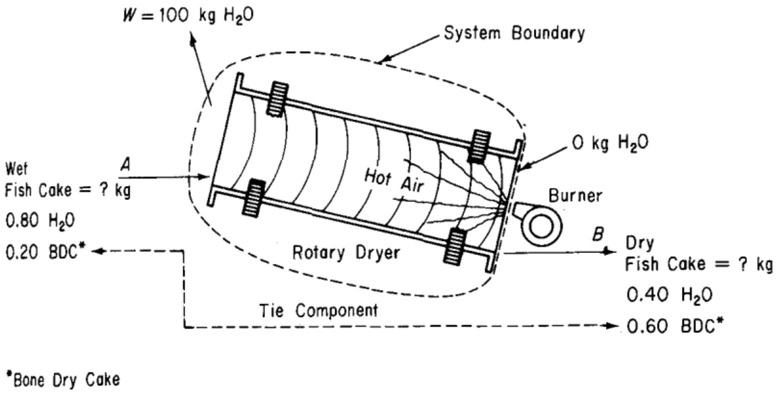


Figure E8.5

Solution

This is a steady-state process without reaction.

Basis: 100 kg of water evaporated = W

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

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.

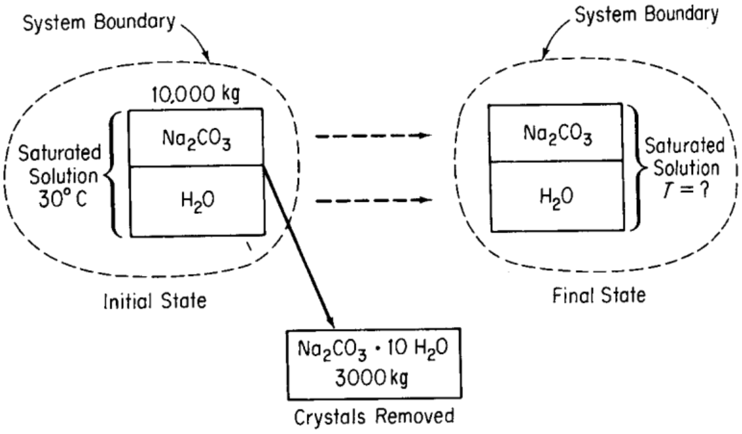
Example 14

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:

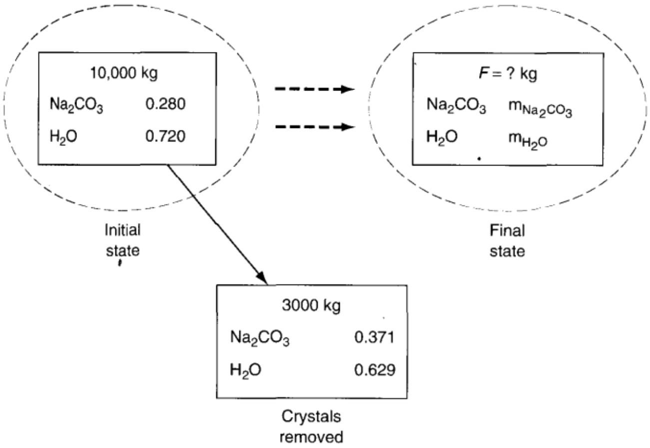
$$\frac{38.8 \text{ g } Na_2CO_3}{38.8 \text{ g } Na_2CO_3 + 100 \text{ g } H_2O} = 0.280 \text{ mass fraction } Na_2CO_3$$

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

$$\omega_i{}^I I = m_i^I,\ \omega_i{}^F F = m_i^F,\ \text{and}\ \omega_i{}^C C = m_i^C$$

Note that are redundant equations. C = Crystals Also redundant are equations such as $\Sigma\omega_i = 1$ and $\Sigma m_i = m_{total}$. 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, $\dfrac{1{,}687\ \text{kg}\ Na_2CO_3}{5{,}313\ \text{kg}\ H_2O} = \dfrac{31.8\ \text{g}\ Na_2CO_3}{100\ \text{g}\ H_2O}$

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 14

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

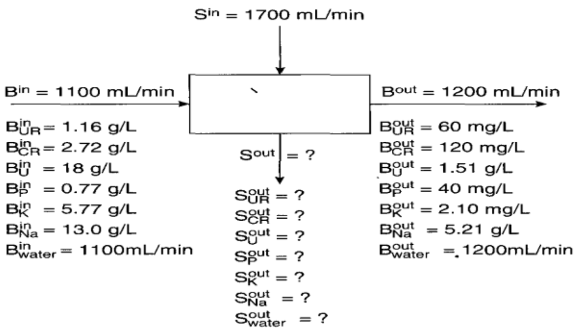


Figure E8.7b

- The entering solution is assumed to be essentially water.

The water balance in grams, assuming that I 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:

$$\begin{array}{lll}
 & & \underline{g/L} \\
\text{UR:} & 1.1(1.16) + 0 = 1.2(0.060) + 1.6\, S^{\text{out}}_{\text{UR}} & S^{\text{out}}_{\text{UR}} = 0.75 \\
\text{CR:} & 1.1(2.72) + 0 = 1.2(0.120) + 1.6\, S^{\text{out}}_{\text{CR}} & S^{\text{out}}_{\text{CR}} = 1.78 \\
 & & \\
\text{U:} & 1.1(18) + 0 = 1.2(1.51) + 1.6\, S^{\text{out}}_{\text{U}} & S^{\text{out}}_{\text{U}} = 11.2 \\
\text{P:} & 1.1(0.77) + 0 = 1.2(0.040) + 1.6\, S^{\text{out}}_{\text{P}} & S^{\text{out}}_{\text{P}} = 0.50 \\
\text{K:} & 1.1(5.77) + 0 = 1.2(0.120) + 16\, S^{\text{out}}_{\text{K}} & S^{\text{out}}_{\text{K}} = 3.8 \\
\text{Na:} & 1.1(13.0) + 0 = 1.2(3.21) + 1.6\, S^{\text{out}}_{\text{Na}} & S^{\text{out}}_{\text{Na}} = 6.53
\end{array}$$

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.

2.4 The Chemical Reaction Equation and Stoichiometry

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 15

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 16

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)

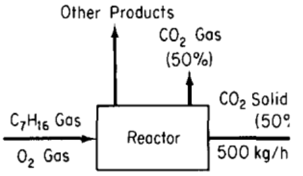


Figure E9.2

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 17

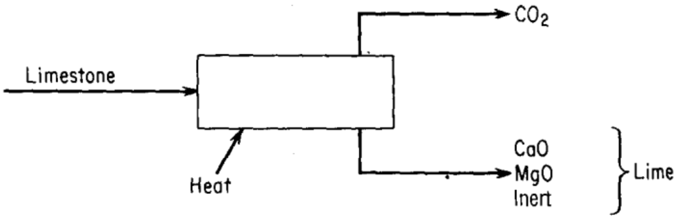
A limestone analyses (weight %): $CaCO_3$ 92.89%, $MgCO_3$ 5.41% and Inert 1.70% By heating the limestone you recover oxides known as lime.

(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 CO_2 is:

0.9280 lb mol CaO is equivalent to 0.9280 lb mol CO_2

0.0642 lb mol MgO is equivalent to 0.0642 lb mol CO_2

Total lb mol CO_2 = 0.9280 + 0.0642 = 0.992 lb mol 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 CO_2 from a total balance: 100 - 56.33 = 44.67.

Now, to calculate the quantities originally asked for:

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

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

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

Terminology for Applications of Stoichiometry

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:

$$\xi = \frac{n_i - n_{io}}{v_i} \quad \dots 9.1$$

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

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

Example 18

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:

$$n_i = \frac{90\text{ g NH}_3}{} \left| \frac{1\text{ g mol NH}_3}{17\text{ g NH}_3} \right. = 5.294\text{ g mol NH}_3$$

$$n_{i0} = \frac{5\text{ g NH}_3}{} \left| \frac{1\text{ g mole NH}_3}{17\text{ g NH}_3} \right. = 0.294\text{ g mol NH}_3$$

$$\xi = \frac{n_i - n_{i0}}{v_i} = \frac{(5.294 - 0.204)\text{g mol NH}_3}{2\text{ g mol NH}_3\text{/moles reacting}} = 2.50\text{ moles reacting}$$

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

$$N_2\text{:}\quad n_{i0} = \frac{100\text{ g N}_2}{} \left| \frac{1\text{ g mol N}_2}{28\text{ g N}_2} \right. = 3.57\text{ g mol N}_2$$

$$n_{N_2} = 3.57 + (-1)(2.5) = 1.07\text{ g mol N}_2$$

$$m_{N_2} = \frac{1.07\text{ g mol N}_2}{} \left| \frac{28\text{ g N}_2}{1\text{ g mol N}_2} \right. = 30\text{ g N}_2$$

$$H_2\text{:}\quad n_{i0} = \frac{50\text{ g H}_2}{} \left| \frac{1\text{ g mol H}_2}{2\text{ g H}_2} \right. = 25\text{ g mol H}_2$$

$$\mathrm{n}_{\mathrm{H2}}\, n_{N_2} = 25 + (-3)(2.5) = 17.5\text{ g mol H}_2$$

$$\mathrm{m}_{\mathrm{H2}}\, m_{N_2} = \frac{17.5\text{ g mol H}_2}{} \left| \frac{2\text{g H}_2}{1\text{ g mol H}_2} \right. = 35\text{ g H}_2$$

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

$$n_i = n_{i0} + \sum_{k=1}^{R} v_{ki}\,\xi_k \qquad \dots 9.3$$

Where R is the total number of independent reactions.

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.

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

™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, ξ^{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,

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

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

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

$$\begin{array}{cccc} & \underline{\textit{Ratio in feed}} & & \underline{\textit{Ratio in chemical equation}} \\ \dfrac{B}{A}: & \dfrac{3.2}{1.1} = 2.91 & < & \dfrac{3}{1} = 3 \\ \dfrac{C}{A}: & \dfrac{2.4}{1.1} = 2.18 & > & \dfrac{2}{1} = 2 \end{array}$$

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 19

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

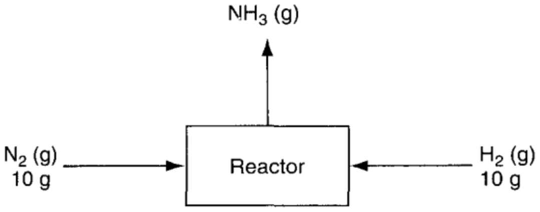
a. What is the maximum number of grams of NH_3 that can be produced?

b. What is the limiting reactant?

c. What is the excess reactant?

Dr.Ali H.Abbar

Solution



	$N_2(g)$ +	$3H_2(g)$ →	$2NH_3(g)$
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

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

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

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

For example, for the reaction equation described in Example 16, 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

$$\frac{14.4 \text{ kg } CO_2}{} \left| \frac{1 \text{ kg mol } CO_2}{44.0 \text{ kg } CO_2} \right| \frac{1 \text{ kg mol } C_7H_{16}}{7 \text{ kg mol } CO_2} = 0.0468 \text{ kg mol } C_7H_{16}$$

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

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).

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

$$= \frac{\xi}{\xi^{max}}$$

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. 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 20

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

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

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

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

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

Example 21

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

$$C_2H_6 \rightarrow 2\ C + 3\ H_2 \qquad (a)$$
$$\searrow C_2H_4 + H_2 \qquad (b)$$

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 22

The two reactions of interest for this example are

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

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

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_5C1	$C_3H_6Cl_2$	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_5C1?

e. What was the selectivity of C_3H_5C1 relative to $C_3H_6Cl_2$?

f. What was the yield of C_3H_5C1 expressed in g of C_3H_5C1 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.

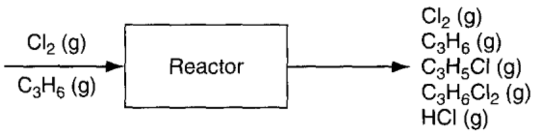


Figure E9.8

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

(a)

$$\frac{4.6 \text{ g mol } C_3H_5C1}{} \left| \frac{1 \text{ g mol } Cl_2}{1 \text{ g mol } C_3H_5Cl} \right. = 4.6 \text{ g mol } Cl_2 \text{ reacts}$$

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.l 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

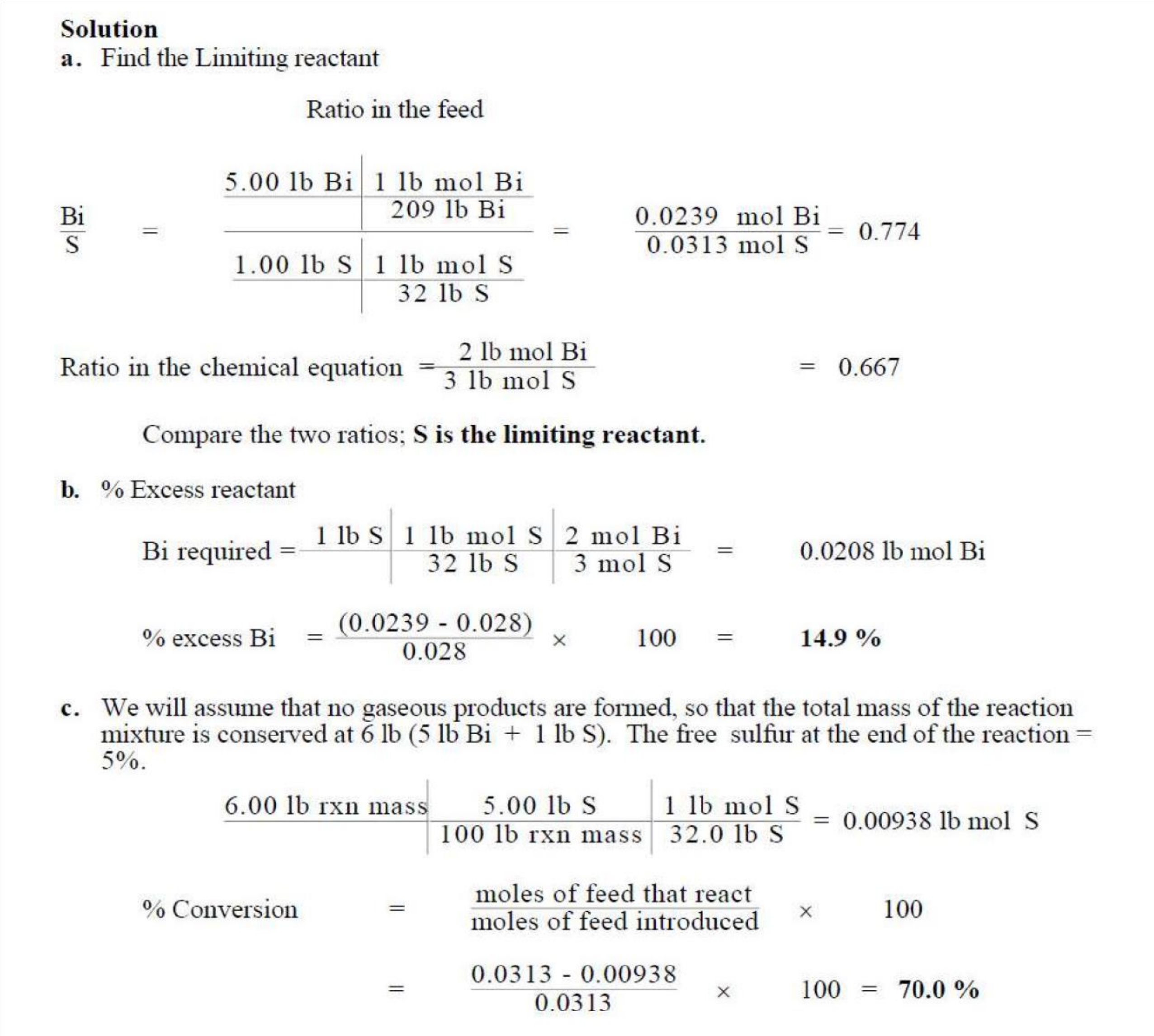
$$\xi_2 = \frac{n_i - n_{io}}{v_i} = \frac{24.5 - 0}{1} = 24.5$$

Example 23

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

$$\frac{Bi}{S} = \frac{\dfrac{5.00\text{ lb Bi}}{}\Big|\dfrac{1\text{ lb mol Bi}}{209\text{ lb Bi}}}{\dfrac{1.00\text{ lb S}}{}\Big|\dfrac{1\text{ lb mol S}}{32\text{ lb S}}} = \frac{0.0239\text{ mol Bi}}{0.0313\text{ mol S}} = 0.774$$

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

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

b. % Excess reactant

$$\text{Bi required} = \frac{1\text{ lb S}}{}\Big|\frac{1\text{ lb mol S}}{32\text{ lb S}}\Big|\frac{2\text{ mol Bi}}{3\text{ mol S}} = 0.0208\text{ lb mol Bi}$$

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

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%.

$$\frac{6.00\text{ lb rxn mass}}{}\Big|\frac{5.00\text{ lb S}}{100\text{ lb rxn mass}}\Big|\frac{1\text{ lb mol S}}{32.0\text{ lb S}} = 0.00938\text{ lb mol S}$$

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

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

Questions

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

Answers:

Q.3 Reactant present in the least stoichiometric quantity.

Q.4 All other reactants than the limiting reactant.

Q.5 For a species in

Open system:

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

Closed system:

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

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.

2.5 Material Balances for Processes Involving Reaction

Species Material Balances

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.

$$\begin{Bmatrix}\text{moles of}\\ i \text{ at } t_2\\ \text{in the}\\ \text{system}\end{Bmatrix} - \begin{Bmatrix}\text{moles of}\\ i \text{ at } t_1\\ \text{in the}\\ \text{system}\end{Bmatrix} = \begin{Bmatrix}\text{moles of } i\\ \text{entering}\\ \text{the system}\\ \text{between } t_2 \text{ and } t_1\end{Bmatrix} - \begin{Bmatrix}\text{moles of } i\\ \text{leaving}\\ \text{the system}\\ \text{between } t_2 \text{ and } t_1\end{Bmatrix} + \begin{Bmatrix}\text{moles of } i\\ \text{generated}\\ \text{by reaction}\\ \text{between } t_2 \text{ and } t_1\end{Bmatrix} - \begin{Bmatrix}\text{moles of } i\\ \text{consumed}\\ \text{by reaction}\\ \text{between } t_2 \text{ and } t_1\end{Bmatrix} \qquad (1)$$

Note that we have written Equation (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:

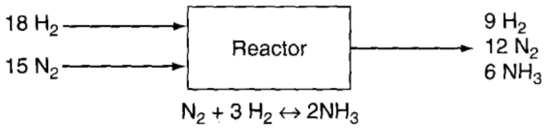


Figure 10.1. A reactor to produce NH_3.

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

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

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

$$\nu_{NH_3} = 2$$

$$\nu_{H_2} = -3$$

$$\nu_{N_2} = -1$$

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

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

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

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

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

Component	*Out*	*In*	=	*Generation or Consumption*
i	n_i^{out}	$-n_i^{in}$	=	$\nu_i\,\xi$
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

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

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

Example 24

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.

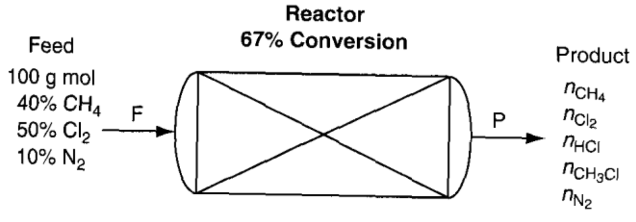


Figure E10.1

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 g mol.

Example 25

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

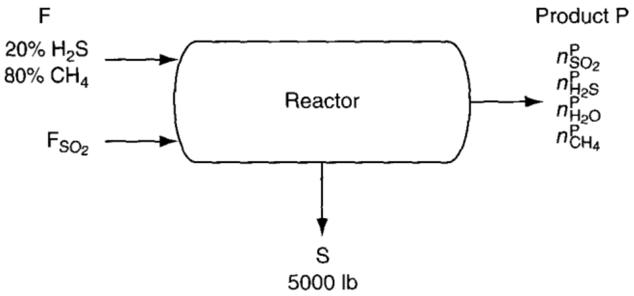


Figure E10.2

Basis is 5000 lb S (156.3 lb mol S)

Basis: S = 5000 lb (156.3 lb mol)

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

Specifications: 4 (3 independent)

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

$$n^P_{H_2O} = 2(52.1) = 104.2 \text{ lb mol } H_2O$$

$$n^P_{H_2S} = \frac{1}{10} n^P_{H_2O} = 10.4 \text{ lb mol } H_2S$$

Next, Equation (g) gives

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

$$f = \frac{-(-2)\xi}{0.2F} = \frac{(2)(52.1)}{(0.2)(573)} = 0.91$$

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 jth reaction in the minimal set.

R is the number of independent chemical reaction equations (the size of the minimal set).

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 26

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).

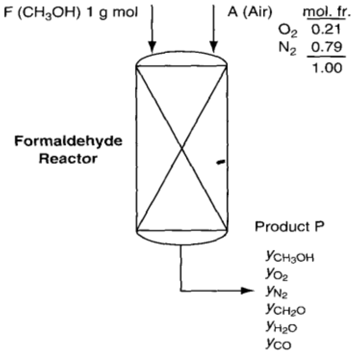


Figure E10.3

Basis: l gmol F The

limiting reactant is CH_3OH.

Use the fraction conversion, Equation 10.3:

$$\xi_1 = \frac{-0.90}{-1}(1) = 0.9 \text{ g moles}$$

reacting The yield is related to ξ_i as follows

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

By reaction 1:

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

By reaction 2:

The yield is

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

ξ_2 = 0.1 5 g moles reacting

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

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

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

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

$$\Sigma y_i^P = 1$$

Implicit equation:

Calculate P using Equation 10.5:

$$P = \sum_{i=1}^{S} n_i^{in} + \sum_{i=1}^{S}\sum_{j=1}^{R} v_{i_j}\,\xi_j$$

$$= 1 + 4.76 + \sum_{i=1}^{6}\sum_{j=1}^{2} v_{i_j}\,\xi_j$$

$$= 5.76 + [(-1) + (-{}^1\!/_2) + (1) + 0 + (1) + 0]\,0.9$$

$$+ [0 + (-{}^1\!/_2) + (-1) + 0 + (1) + (1)]\,0.15 = 6.28 \text{ g mol}$$

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 27

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 propenoic 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) percents of ethanol and propenoic 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

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

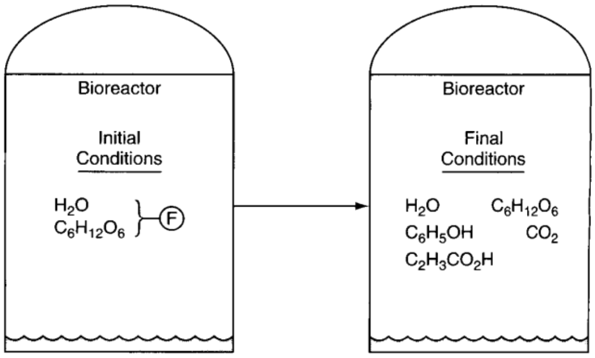


Figure E10.4

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)

$$n_{H_2O}^{Initial} = 195.3 \text{ or } n_{C_6H_{12}O_6}^{Initial} = 2.665$$

(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.

ξ_1 = 1.364 kg moles reacting ξ_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 3977 kg is close enough to 4000 kg of feed to validate the results of the calculations.

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]

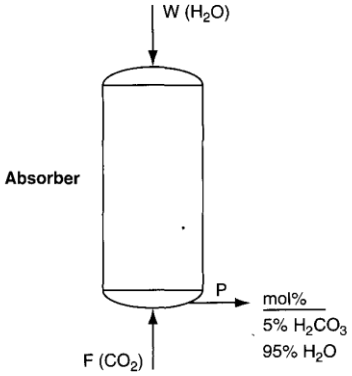


Figure 10.2 Schematic of the CO_2 absorber.

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

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

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

Example 28

Solution of Examples 24 and 26 Using Element Balances: All of the given data for this example is the same as in Examples 24 and 25

Solution

1. Example 24

The element material balances are:

$$\text{C:}\quad 100\,(0.40) = n^{\text{out}}_{CH_4}(1) + n^{\text{out}}_{CH_3Cl}(1)$$

$$\text{H:}\quad 100\,(0.40)(4) = n^{\text{out}}_{CH_4}(4) + n^{\text{out}}_{HCl}(1) + n^{\text{out}}_{CH_3Cl}(3)$$

$$\text{Cl:}\quad 100\,(0.50)(2) = n^{\text{out}}_{Cl_2}(2) + n^{\text{out}}_{HCl}(1) + n^{\text{out}}_{CH_3Cl}(1)$$

$$\text{2N:}\quad 100\,(0.10)(1) = n^{\text{out}}_{N_2}(1)$$

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

2. Example 25

The element balances are:

$$\text{C:}\quad 1(1) + 4.76(0) = P[y^P_{CH_3OH}(1) + y^P_{CH_2O}(1) + y^P_{CO}(1)]$$

$$\text{H:}\quad 1(4) + 4.76(0) = P[y^P_{CH_3OH}(4) + y^P_{CH_2O}(2) + y^P_{H_2O}(2)]$$

$$\begin{aligned}\text{O:}\quad 1(1) + 1.00 &= P[y^P_{CH_3OH}(1) + y^P_{O_2}(2) + y^P_{CH_2O}\,(1)\\ &\quad + y^P_{H_2O}(1) + y^P_{CO}(1)]\end{aligned}$$

$$\text{2N:}\quad 1(0) + 3.76 = P[y^P_{N_2}(1)]$$

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, and P. , y_i^P

---

n 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 29

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

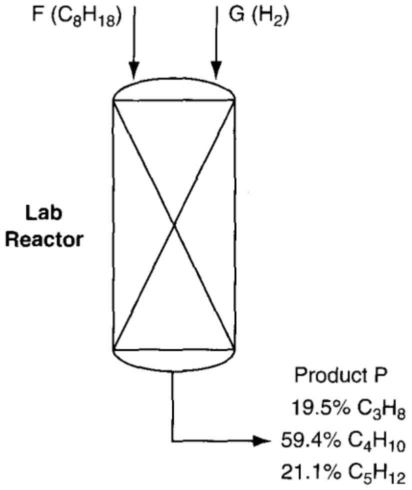


Figure E10.6

Basis: P= 100 g mol

Element balances: 2 H, C The element balances:

$$C: F(8) + G(0) = 100[(0.195)(3) + (0.594)(4) + (0.211)(5)]$$

$$H: F(18) + G(2) = 100[(0.195)(8) + (0.594)(10) + (0.211)(12)]$$

And the solution is F = 50.2 g mol G = 49.8 g mol

The ratio $$\frac{H_2 \text{ consumed}}{C_8H_{18} \text{ reacted}} = \frac{49.8 \text{ g mol}}{50.2 \text{ g mol}} = 0.992$$

Material Balances Involving Combustion

a Combustion is the reaction of a substance with oxygen with the associated release of energy and generation of product gases such as H_2O, CO_2, CO, and SO_2.

a Most combustion processes use air as the source of oxygen. For our purposes you can assume that air contains 79% N_2 and 21% O_2.

Special terms:

1. Flue or stack gas: All the gases resulting from combustion process including the water vapor, sometimes known as a wet basis.
2. Orsat analysis or dry basis: All the gases resulting from combustion process not including the water vapor. Orsat analysis refers to a type of gas analysis apparatus in which the volumes of the respective gases are measured over and in equilibrium with water; hence each component is saturated with water vapor. The net result of the analysis is to eliminate water as a component being measured (show Figure 10.4).

3. Complete combustion: the complete reaction of the hydrocarbon fuel producing CO_2, SO_2, and H_2O.
4. Partial combustion: the combustion of the fuel producing at least some CO. Because CO itself can react with oxygen, the production of CO in a combustion process does not produce as much energy as it would if only CO_2 were produced.
5. Theoretical air (or theoretical oxygen): The minimum amount of air (or oxygen) required to be brought into the process for complete combustion. Sometimes this quantity is called the required air (or oxygen).
6. Excess air (or excess oxygen): In line with the definition of excess reactant given in Chapter 9, excess air (or oxygen) would be the amount of air (or oxygen) in excess of that required for complete combustion as defined in (5).

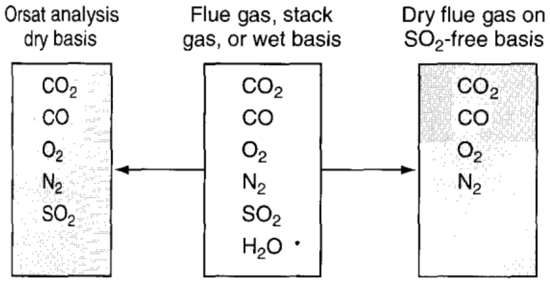


Figure 10.4 Comparison of a gas analysis on different bases.

Note: The calculated amount of excess air does not depend on how much material is actually burned but what is possible to be burned. Even if only partial combustion takes place, as, for example, C burning to both CO and CO_2, the excess air (or oxygen) is computed as if the process of combustion went to completion and produced only CO_2.

The percent excess air is identical to the percent excess O_2:

$$\%\text{ excess air} = \frac{\text{excess air}}{\text{required air}}\times 100 = \frac{\text{excess } O_2/0.21}{\text{required } O_2/0.21}\times 100 \qquad \dots 10.6$$

Note that the ratio 1/0.2 1 of air to O_2 cancels out in Equation 10.6. Percent excess air may also be computed as

$$\%\text{ excess air} = \frac{O_2 \text{ entering process} - O_2 \text{ required}}{O_2 \text{ required}}\times 100 \qquad \dots 10.7$$

Or

$$\%\text{ excess air} = \frac{\text{excess } O_2}{O_2 \text{ entering} - \text{excess } O_2}\times 100 \qquad \dots 10.8$$

Example 30

Fuels other than gasoline are being eyed for motor vehicles because they generate lower levels of pollutants than does gasoline. Compressed propane is one such proposed fuel. Suppose that in a test 20 kg of C_3H_8 is burned with 400 kg of air to produce 44 kg of CO_2 and 12 kg of CO. What was the percent excess air?

Solution

This is a problem involving the following reaction $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

Basis: 20 kg of C_3H_8

n Since the percentage of excess air is based on the complete combustion of C_3H_8 to CO_2 and H_2O, the fact that combustion is not complete has no influence on the calculation of “excess air.”

The required O_2 is

$$\frac{20 \text{ kg } C_3H_8}{} \left| \frac{1 \text{ kg mol } C_3H_8}{44.09 \text{ kg } C_3H_8} \right| \frac{5 \text{ kg mol } O_2}{1 \text{ kg mol } C_3H_8} = 2.27 \text{ kg mol } O_2$$

The entering O_2 is

$$\frac{400 \text{ kg air}}{} \left| \frac{1 \text{ kg mol air}}{29 \text{ kg air}} \right| \frac{21 \text{ kg mol } O_2}{100 \text{ kg mol air}} = 2.90 \text{ kg mol } O_2$$

The percentage of excess air is $\%\,\text{excess air} = \frac{\quad_2 \qquad\qquad\qquad _2\quad}{O_2\text{required}} \times 100$

$$\%\text{ excess air} = \frac{2.90 \text{ lb mol } O_2 - 2.27 \text{ lb mol } O_2}{2.27 \text{ lb mol } O_2} \left| \frac{100}{} \right. = 28\%$$

O enteringprocess−O required

Note:

In calculating the amount of excess air, remember that the excess is the amount of air that enters the combustion process over and above that required for complete combustion.

For example, suppose that a gas containing 80% C_2H_6 and 20% O_2 is burned in an engine with 200% excess air. Eighty percent of the ethane goes to CO_2, 10% goes to CO, and 10% remained unburned. What is the amount of the excess air per 100 moles of the gas?

Solution

First, you can ignore the information about the CO and the unburned ethane because the basis of the calculation of excess air is complete combustion. Specifically C goes to CO_2; S to SO_2, H_2 to H_2O, CO goes to CO_2 and so on. Second, the oxygen in the fuel cannot be ignored. Based on the reaction

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

Basis: 100 moles of gas

- 80 moles of C_2H_6 require 3.5(80) = 280 moles of O_2 for complete combustion.

- The gas contains 20 moles of O_2, so that only 280 – 20 = 260 moles of O_2 are needed in the entering air for complete combustion.
- Thus, 260 moles of O_2 are the required O_2 and the calculation of the 200% excess O_2 (air) is based on 260, not 280, moles of O_2:

Entering with air	Moles O_2
Required O_2:	260
Excess O_2:	(2)(260) = 520
Total O_2:	780

Example 31

Figure El0.8 is a sketch of a fuel cell in which a continuous flow of methane (CH_4) and air (O_2 plus N_2) produce electricity plus CO_2 and H_2O. Special membranes and catalysts are needed to promote the reaction of CH_4. Based on the data given in Figure El0.8, you are asked to calculate the composition of the products in P.

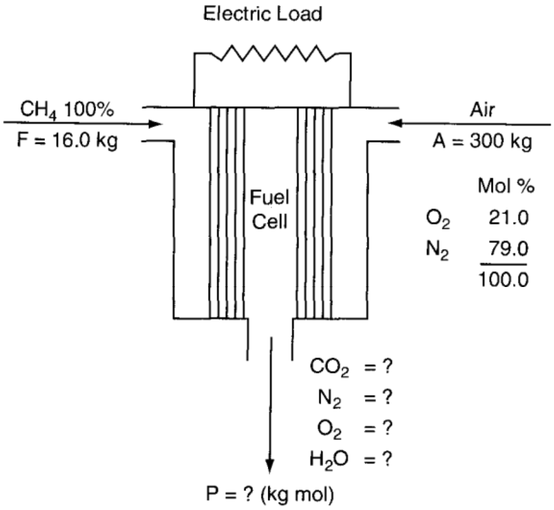


Figure E10.8

Solution

Assume a complete reaction occurs because no CH_4 appears in P. The system is the fuel cell (open, steady state). The necessary preliminary conversions as follows:

$$\frac{300\ \text{kg A}}{}\,\Bigg|\,\frac{1\ \text{kg mol A}}{29.0\ \text{kg A}} = 10.35\ \text{kg mol A in}$$

$$\frac{16.0\ \text{kg CH}_4}{}\,\Bigg|\,\frac{1\ \text{kg mol CH}_4}{16.0\ \text{kg CH}_4} = 1.00\ \text{kg mol CH}_4\ \text{in}$$

$$\frac{10.35\ \text{kg mol A}}{}\,\Bigg|\,\frac{0.21\ \text{kg mol O}_2}{1\ \text{kg mol A}} = 2.17\ \text{kg mol O}_2\ \text{in}$$

$$\frac{10.35\ \text{kg mol A}}{}\,\Bigg|\,\frac{0.79\ \text{kg mol N}_2}{1\ \text{kg mol A}} = 8.18\ \text{kg mol N}_2\ \text{in}$$

Basis: 16.0 kg CH_4 entering = 1 kg mol CH_4

Specifications and calculated quantities: 2 $\quad n^A_{O_2} = 2.17,\ n^A_{N_2} = 8.18$

Implicit equation: $\quad \Sigma n^P_i = P$

The element material balances are (in moles):

	Out		In
C:	$n^P_{CO_2}(1)$	=	1(1)
H:	$n^P_{H_2O}(2)$	=	1(4)
O:	$n^P_{CO_2}(2) + n^P_{O_2}(2) + n^P_{H_2O}(1)$	=	2.17(2)
2N:	$n^P_{N_2}$	=	8.18

The species material balances are:

Compound	Out		In		$v_i\xi$		g mol
CH_4:	$n^P_{CH_4}$	=	1.0	−	1×1	=	0
O_2:	$n^P_{O_2}$	=	2.17	−	2×1	=	0.17
N_2:	$n^P_{N_2}$	=	8.18	−	0×1	=	8.18
CO_2:	$n^P_{CO_2}$	=	0	+	1×1	=	1.0
H_2O:	$n^P_{H_2O}$	=	0	+	2×1	=	2.0

The solution of either set of equations gives

$$n^P_{CH_4} = 0,\ n^P_{O_2} = 0.17,\ n^P_{N_2} = 8.18,\ n^P_{CO_2} = 1.0,\ n^P_{H_2O} = 2.0,\ P = 11.35$$

The mole percentage composition of P is

$$y_{O_2} = 1.5\%,\ y_{N_2} = 72.1\%,\ y_{CO_2} = 8.8\%,\ \text{and}\ y_{H_2O} = 17.6\%$$

Problems

1. Hydrofluoric acid (HF) can be manufactured by treating calcium fluoride (CaF_2) with sulfuric acid (H_2SO_4). A sample of fluorospar (the raw material) contains 75% by weight CaF_2 and 25% inert (nonreacting) materials. The pure sulfuric acid used in the process is in 30% excess of that theoretically required. Most of the manufactured HF leaves the reaction chamber as a gas, but a solid cake that contains 5% of all the HF formed, plus $CaSO_4$, inerts, and unreacted sulfuric acid is also removed from the reaction chamber. Assume complete conversion of the CaF_2 occurs. How many kilograms of cake are produced per 100 kg of fluorospar charged to the process?
2. Corrosion of pipes in boilers by oxygen can be alleviated through the use of sodium sulfite. Sodium sulfite removes oxygen from boiler feedwater by the following reaction:

   $$2Na_2SO_3 + O_2 \rightarrow 2NaSO_4$$

   How many pounds of sodium sulfite are theoretically required (for complete reaction) to remove the oxygen from 8,330,000 lb of water (10^6 gal) containing 10.0 parts per million (ppm) of dissolved oxygen and at the same time maintain a 35% excess of sodium sulfite?
3. Consider a continuous, steady-state process in which the following reactions take place:

   $$C_6H_{12} + 6H_2O \rightarrow 6CO + 12H_2$$
   $$C_6H_{12} + H_2 \rightarrow C_6H_{14}$$

   In the process 250 moles of C_6H_{12} and 800 moles of H_2O are fed into the reactor each hour. The yield of H_2 is 40.0% and the selectivity of H_2 relative to C_6H_{14} is 12.0. Calculate the molar flow rates of all five components in the output stream.

4. Consider a system used in the manufacture of electronic materials (all gases except Si)

   SiH_4, Si_2H_4, Si_2H_6, H_2, Si How
   many independent element balances can you make for this system?

5. Methane burns with O_2 to produce a gaseous product that contains CH_4, O_2, CO_2, CO, H_2O, and H_2. How many independent element balances can you write for this system?
6. Solve the problems (1, 2 & 3) using element balances.
7. Pure carbon is burned in oxygen. The flue gas analysis is: CO_2 75 mo1%, CO l4 mol% & O_2 11 mol%. What was the percent excess oxygen used?
8. Toluene, C_7H_8, is burned with 30% excess air. A bad burner cause 15% of the carbon to form soot (pure C) deposited on the walls of the furnace, what is the Orsat analysis of the gases leaving the furnace?
9. A synthesis gas analyzing CO_2: 6.4%, O_2: 0.2%, CO: 40.0% and H_2: 50.8% (the balance is N_2) is burned with excess dry air. The problem is to determine the composition of the flue gas. How many degrees of freedom exist in this problem, that is, how many additional variables must be specified?
10. A coal analyzing 65.4% C, 5.3% H, 0.6% S, 1.1% N, 18.5% O, and 9.1% ash is burned so that all combustible is burnt out of the ash. The flue gas analyzes 13.00% CO_2, 0.76% CO, 6.17% O_2, 0.87% H_2, and 79.20% N_2. All of the sulfur burns to SO_2, which is included in the CO_2 in the gas analysis (i.e., $CO_2 + SO_2 = 13\%$).

    Calculate:
    a. Pounds of coal fired per 100 lb mol of dry flue gas as analyzed;
    b. Ratio of moles of total combustion gases to moles of dry air supplied;
    c. Total moles of water vapor in the stack gas per 100 lb of coal if the entering air is dry; d. Percent excess air.
11. A hydrocarbon fuel is burnt with excess air. The Orsat analysis of the flue gas shows 10.2% CO_2, 1.0% CO, 8.4% O_2, and 80.4% N_2. What is the atomic ratio of H to C in the fuel?

Answers:

1. 186 kg
2. 887 lb
3. (a) C_6H_{12} = 139 mol/hr; (b) H_2O = 453 mol/hr; (c) CO = 347 mol/hr; (d) H_2 = 640 mol/hr; (e) C_6H_{14} = 53.3 mol/hr.

4. Two
5. Three
6. See the answers to the problems (1, 2 &3).
7. 4.5%
8. 9.1% CO_2, 8.9% O_2, 82% N_2
9. 1
10. (a) 252; (b)1.063; (c) 2.31; (d) 33.8%
11. 0.81

2.6 Material Balance Problems Involving Multiple Units

- A process flowsheet (flowchart) is a graphical representation of a process. A flowsheet describes the actual process in sufficient detail that you can use it to formulate material (and energy) balances.

Figure 1l.1a illustrates a serial combination of mixing and splitting stages. In a <u>mixer</u>, two or more entering streams of different compositions are combined. In a <u>splitter</u>, two or more streams exit, all of which have the same composition. In a <u>separator</u>, the exit streams can be of different compositions.

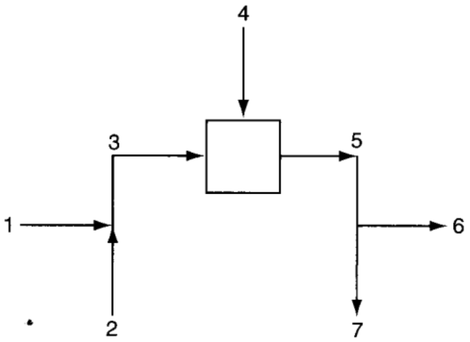


Figure 11.1a serial mixing and splitting in a system without reaction. Streams 1 plus 2 mix to form Stream 3, and Stream 5 is split into Streams 6 and 7.

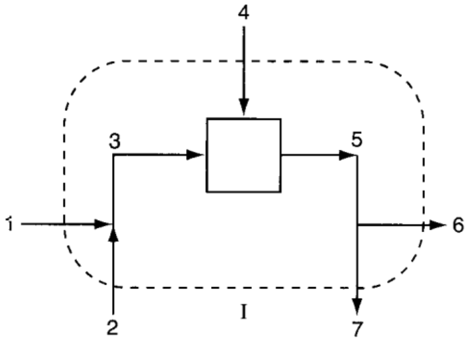


Figure 11.1b the dashed line I designates the boundary for overall material balances made on the process in Figure l1.1a.

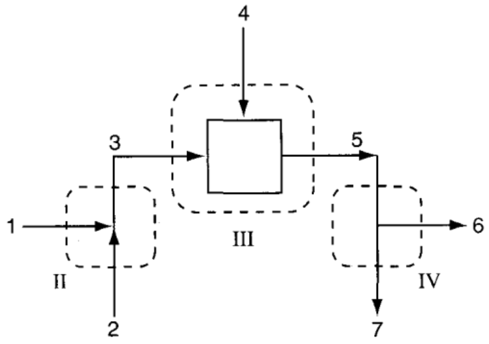


Figure 11.1c Dashed lines II, III and IV designate the boundaries for material balances around each of the individual units comprising the overall process.

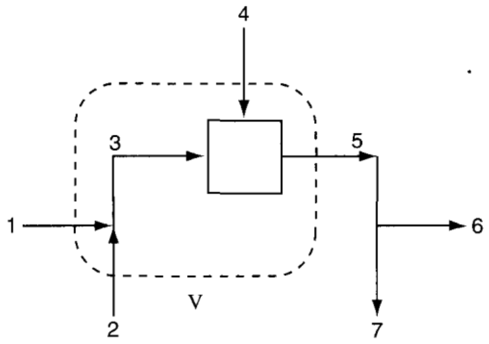


Figure 11.1d the dashed line V designates the boundary for material balances around a system comprised of the mixing point plus the unit portrayed by the box.

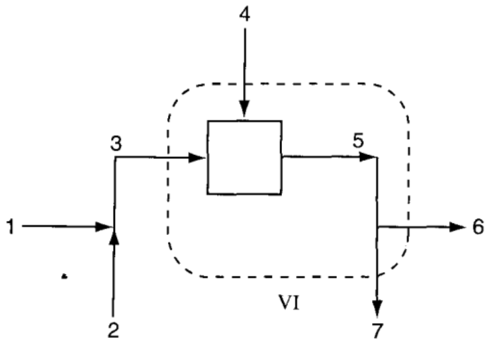


Figure 11.1e the dashed line VI designates the boundary for material balances about a system comprised of the unit portrayed by the box plus the splitter.

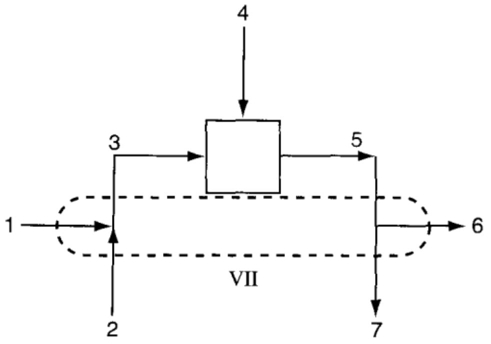


Figure 11.1f the dashed line VII designates the boundary for material balances about a system comprised of the mixer plus the splitter.

Example 32

Acetone is used in the manufacture of many chemicals and also as a solvent. In its latter role, many restrictions are placed on the release of acetone vapor to the environment. You are asked to design an acetone recovery system having the flow sheet illustrated in Figure El1.1. All the concentrations shown in El1.1 of both the gases and liquids are specified in weight percent in this special case to make the calculations simpler. Calculate, A, F, W, B, and D per hour.

G = 1400 kg/hr.

Solution

This is an open, steady-state process without reaction. Three subsystems exist.

Pick 1 hr as a basis so that G = 1400 kg.

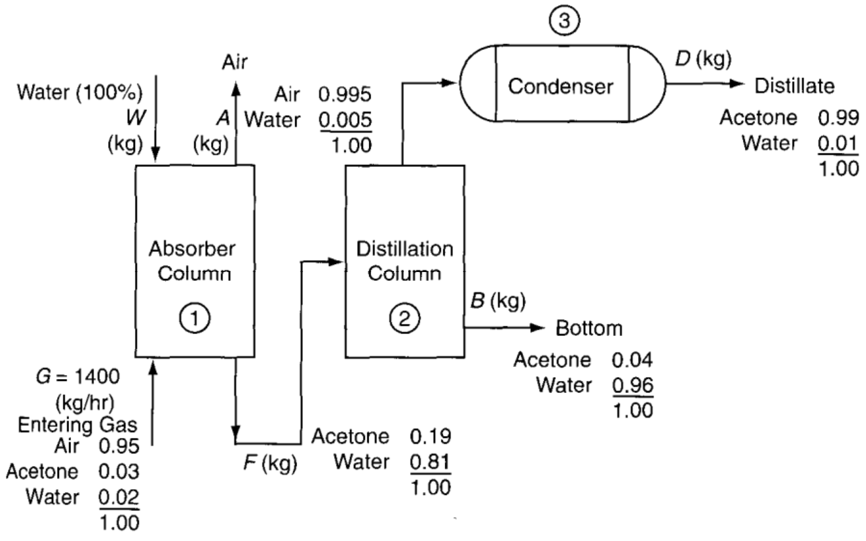


Figure E11.1

The mass balances for Unit 1 (Absorber Column)

$$\begin{array}{llcllll}
 & \underline{\textit{In}} & & \underline{\textit{Out}} & & & \\
\text{Air:} & 1400\,(0.95) & = & & & A(0.995) & \text{(a)} \\
\text{Acetone:} & 1400\,(0.03) & = & F(0.19) & & & \text{(b)} \\
\text{Water:} & 1400\,(0.02) + W(1.00) & = & F(0.81) & + & A(0.005) & \text{(c)}
\end{array}$$

Solve Equations (a), (b), and (c) to get A =1336.7 kg/hr, F = 221.05 kg/hr and W = 157.7 kg/hr (Check)

Use the total balance (Absorber Column).

$$\begin{array}{rcl}
\mathrm{G} + \mathrm{W} & = & \mathrm{A} + \mathrm{F} \\
1400 & & 1336 \\
\underline{157.7} & & \underline{221.05} \\
1557.7 & \cong & 1557.1
\end{array}$$

The mass balances for the combined Units 2 plus 3 (Distillation & Condenser) are:

$$\begin{array}{lll}
\text{Acetone:} & 221.05(0.19) = D(0.99) + B(0.04) & \text{(d)} \\
\text{Water:} & 221.05(0.81) = D(0.01) + B(0.96) & \text{(e)}
\end{array}$$

Solve Equations (d) and (e) simultaneously to get D = 34.90kg/hr and B = 186.1 kg/hr

(Check) Use the total balance (Distillation & Condenser)

$$F = D + B \text{ or } 221.05 \cong 34.90 + 186.1 = 221.0$$

Note

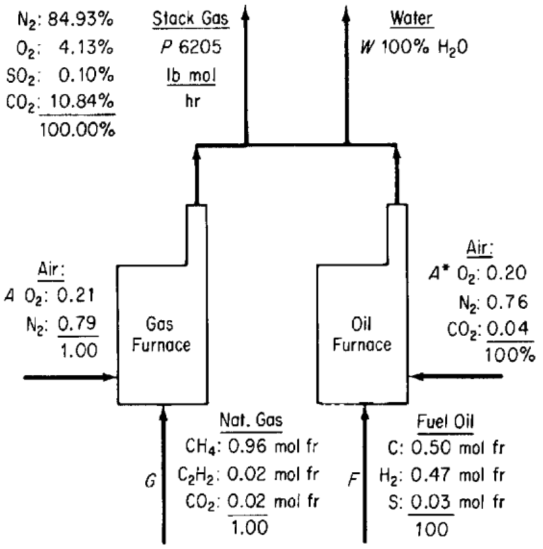
As a matter of interest, what other mass balances could be written for the system and substituted for any one of the Equations (a) through (e)? Typical balances would be the overall balances

$$\begin{array}{llclclcll}
 & \underline{\textit{In}} & & & \underline{\textit{Out}} & & & & \\
\text{Air:} & G\,(0.95) & = & A(0.995) & & & & & \text{(f)} \\
\text{Acetone:} & G(0.03) & = & & & D(0.99) & + & B(0.04) & \text{(g)} \\
\text{Water:} & G\,(0.02) + W & = & A(0.005) & + & D(0.01) & + & B(0.96) & \text{(h)} \\
\text{Total} & G + W & = & A & + & D & + & B & \text{(i)}
\end{array}$$

Example 33

In the face of higher fuel costs and the uncertainty of the supply of a particular fuel, many companies operate two furnaces, one fired with natural gas and the other with fuel oil. The gas furnace uses air while the oil furnace uses an oxidation stream that analyzes: O_2, 20%; N_2, 76%; and CO_2, 4%. The stack gases go up a common stack, See Figure El1.2.

Figure E11.2



The reserve of fuel oil was only 560 bbl. How many hours could the company operate before shutting down if no additional fuel oil was attainable? How many lb mol/hr of natural gas were being consumed? The minimum heating load for the company when translated into the stack gas output was 6205 lb mol/hr of dry stack gas. The molecular weight of the fuel oil was 7.91 lb/lb mol, and its density was 7.578 lb/gal.

Solution

This is an open, steady-state process with reaction. Two subsystems exist.

Basis: 1 hr, so that P = 6205 lb mol

The overall balances for the elements are (in pound moles)

$$\begin{array}{lllcl}
 & \multicolumn{2}{c}{\textit{In}} & & \textit{Out} \\
\text{2H:} & G(1.94) & +\ F(0.47) & = & W(1) \\
\text{2N:} & A(0.79) & +\ A^{*}(0.76) & = & 6205(0.8493) \\
\text{2O:} & A(0.21) & +\ A^{*}(0.20+0.04) & & 6205(0.0413+0.001+0.1084) \\
 & & +\ G(0.02) & = & +W(^{1}\!/_{2}) \\
\text{S:} & F(0.03) & & = & 6205(0.0010) \\
\text{C:} & G(0.96) & +\ (2)(0.02)+0.02 & & \\
 & & +\ F(0.50)+0.04A^{*} & = & 6205(0.1084)
\end{array}$$

Solve the S balance for F; the sulfur is a tie component. Then solve for the other four balances simultaneously for G. The results are:

F = 207 lb mol/hr and G = 499 lb mol/hr

Finally, the fuel oil consumption is

$$\frac{207\text{ lb mol}}{\text{hr}}\left|\frac{7.91\text{ lb}}{\text{lb mol}}\right|\frac{\text{gal}}{7.578\text{ lb}}\left|\frac{\text{bbl}}{42\text{ gal}}\right. = 5.14\text{ bbl/hr}$$

If the fuel oil reserves were only 560 bbl,

$$\frac{560\text{ bbl}}{5.14\dfrac{\text{bbl}}{\text{hr}}} = 109\text{ hr}$$

Example 34

Figure E11.3 shows the process and the known data. You are asked to calculate the compositions of every flow stream, and the fraction of the sugar in the cane that is recovered.

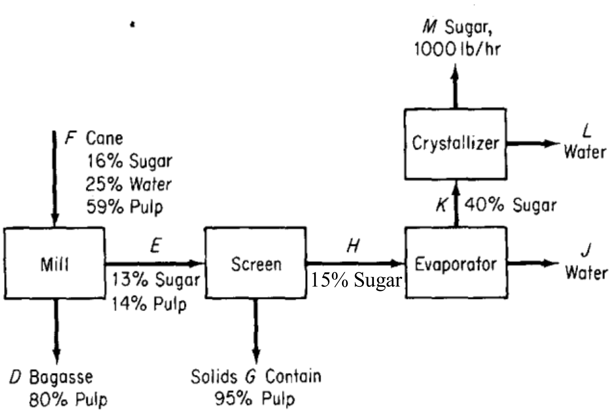


Figure E11.3

Solution

Basis: 1 hour (M= l000lb) Let

S = sugar, P = pulp, and W = water.

For the crystallizer the equations are (using $\omega_W^K = 1 - 0.40 = 0.60$)

Sugar: K (0.40) = L (0) + 1000

Water: K (0.60) = L + 0

From which you get K = 2500 lb and L = 1500 lb.

Check using the total flows: 2500 = 1500 + 1000 = 2500

Using same method for solution: evaporator, screen, and lastly solve the equations for the mill.

The results for all of the variables are:

lb	*mass fraction*
$D = 16{,}755$	$\omega_S^D = 0.174$
$E = 7{,}819$	$\omega_W^D = 0.026$
$F = 24{,}574$	$\omega_W^E = 0.73$
$G = 1{,}152$	$\omega_S^G = 0.014$
$H = 6{,}667$	$\omega_W^G = 0.036$
$J = 4{,}167$	$\omega_W^H = 0.85$
$K = 2{,}500$	$\omega_W^K = 0.60$
$L = 1{,}500$	
$M = 1000$	

The fraction of sugar recovered = [product (sugar) / in (sugar)]

= [1000/(24,574)*(0.16)] = 0.25

Problems

1. A two-stage separations unit is shown in Figure SAT11P1. Given that the input stream Fl is 1000 lb/hr, calculate the value of F2 and the composition of F2.

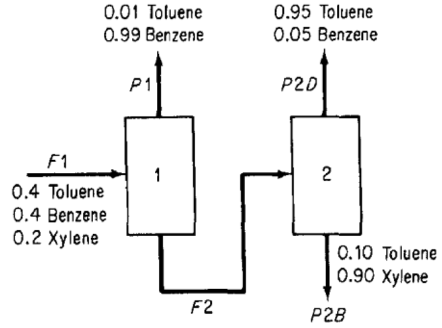


Figure SAT11P1

2. A simplified process for the production of SO_3 to be used in the manufacture of sulfuric acid is illustrated in Figure SAT11P2. Sulfur is burned with 100% excess air in the burner, but for the reaction $S + O_2 \rightarrow SO_2$, only 90% conversion of the S to SO_2 is achieved in the burner. In the converter, the conversion of SO_2 to SO_3 is 95% complete. Calculate the kg of air required per 100 kg of sulfur burned, and the concentrations of the components in the exit gas from the burner and from the converter in mole fractions.

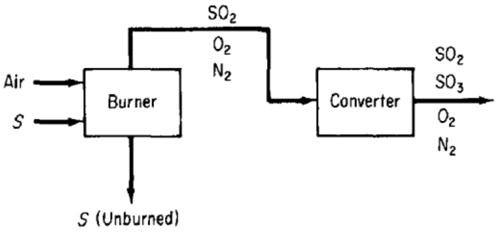


Figure SAT11P2

3. In the process for the production of pure acetylene, C_2H_2 (see Figure SAT11P3), pure methane (CH_4), and pure oxygen are combined in the burner, where the following reactions occur:

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \quad (1)$$

$$CH_4 + 1\tfrac{1}{2}O_2 \rightarrow 2H_2O + CO \quad (2)$$

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \quad (3)$$

   a. Calculate the ratio of the moles of O_2 to moles of CH_4 fed to the burner.

b. On the basis of 100 lb mol of gases leaving the condenser, calculate how many pounds of water are removed by the condenser.

c. What is the overall percentage yield of product (pure) C_2H_2, based on the carbon in the natural gas entering the burner?

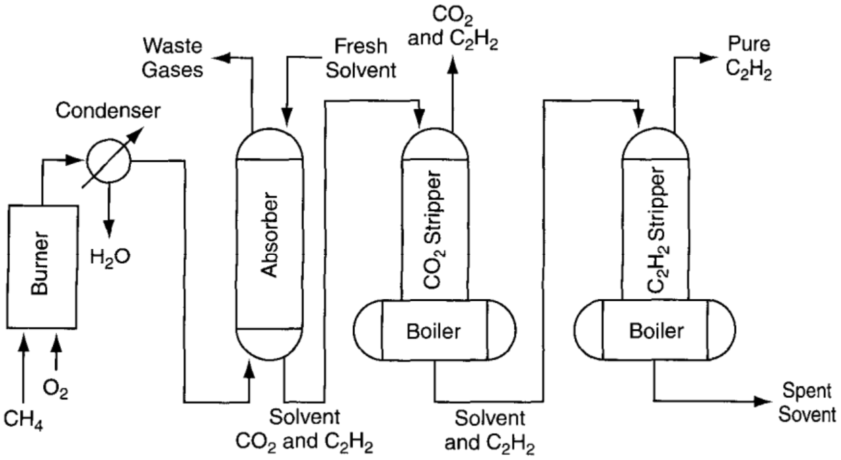


Figure SAT11P3

The gases from the burner are cooled in the condenser that removes all of the water. The analysis of the gases leaving the condenser is as follows:

	Mol %
C_2H_2	8.5
H_2	25.5
CO	58.3
CO_2	3.7
CH_4	4.0
Total	100.0

These gases are sent to an absorber where 97% of the C_2H_2 and essentially all the CO_2 are removed with the solvent. The solvent from the absorber is sent to the CO_2 stripper, where all the CO_2 is removed. The analysis of the gas stream leaving the top of the CO_2 stripper is as follows:

	Mol %
C_2H_2	7.5
CO_2	92.5
Total	100.0

The solvent from the CO_2 stripper is pumped to the C_2H_2 stripper, which removes all the C_2H_2 as a pure product.

Answers:

1. Assume that the compositions in the figure are mass fractions. Then:

	lb	**mass fraction**
Toluene	396	0.644
Benzene	19.68	0.032
Xylene	200	0.325

2. 863 lb air/lb S

	Converter	**Burner**
SO_2	0.5%	9.5%
SO_3	9.4	—
O_2	7.4	11.5
N_2	82.7	79.0

3. (a) 1.14; (b) 2240 lb; (c) 9.9%.

2.7 Recycle, Bypass, Purge, and the Industrial Application of Material Balances

Introduction

- Recycle is fed back from a downstream unit to an upstream unit, as shown in Figure 12.lc. The stream containing the recycled material is known as a recycle stream.
- Recycle system is a system that includes one or more recycle streams.
- Because of the relatively high cost of industrial feedstocks, when chemical reactions are involved in a process, recycle of unused reactants to the reactor can offer significant economic savings for high-volume processing systems. Heat recovery within a processing unit (energy recycle) reduces the overall energy consumption of the process.

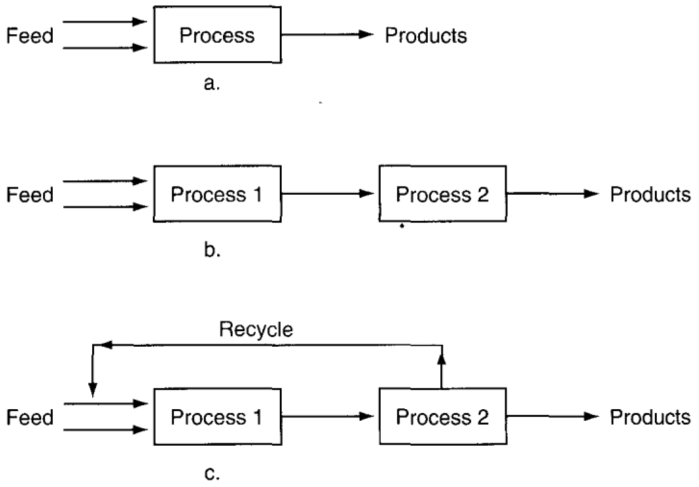


Figure 12.1: Figure 12.la shows a single unit with serial flows. Figure 12.b shows multiple units but still with serial flows. Figure 12.lc shows the addition of recycle.

Recycle without Chemical Reaction

- ™ Recycle of material occurs in a variety of processes that do not involve chemical reaction, including distillation, crystallization, and heating and refrigeration systems.
- ™ Examine Figure 12.2. You can write material balances for several different systems, four of which are shown by dashed lines in Figure 12.2 (Overall balance 1, Mixer balance 2, Process balance 3 & Separator balance 4).

- ™ The fresh feed enters the overall system and the overall or net product is removed.
- ™ The total (gross) feed enters the process and the gross product is removed.
- ™ In addition, you can make balances (not shown in Figure 12.2) about combinations of subsystems, such as the process plus the separator (3 plus 4), or the mixing point plus the process (2 plus 3).

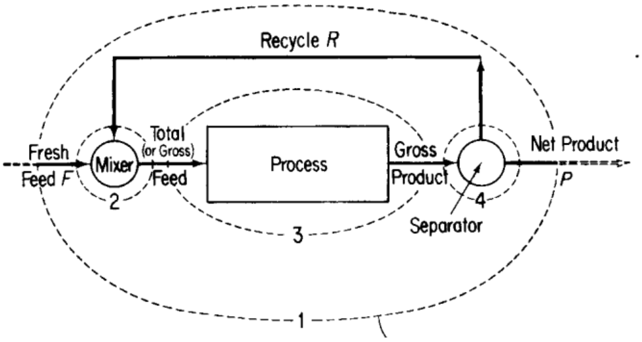


Figure 12.2 Process with recycle (the numbers designate possible system boundaries for the material balances).

Example 35

Figure E12.la is a schematic of a process for the production of flake NaOH, which is used in households to clear plugged drains in the plumbing (e.g., Drano).

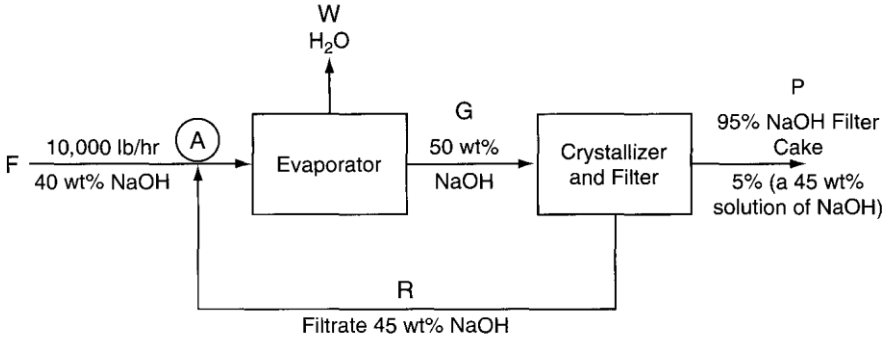


Figure E12.1a

The fresh feed to the process is 10,000 lb/hr of a 40% aqueous NaOH solution. The fresh feed is combined with the recycled filtrate from the crystallizer, and fed to the evaporator where water is removed to produce a 50% NaOH solution, which in turn is fed to the crystallizer. The crystallizer produces a filter cake that is 95% NaOH crystals and 5% solution that itself consists of 45% NaOH. The filtrate contains 45% NaOH.

a. You are asked to determine the flow rate of water removed by the evaporator, and the recycle rate for this process.

b. Assume that the same production rate of NaOH flakes occurs, but the filtrate is not recycled. What would be the total feed rate of 40% NaOH have to be then? Assume that the product solution from the evaporator still contains 50% NaOH.

Solution

Open, steady-state process.

a. Basis: 10,000 lb fresh feed (equivalent to 1 hour) The unknowns are W, G, P, and R.

Overall NaOH balance

$$(0.4)(10{,}000) = 0.95\ P + (0.45)\ (0.05)\ P$$

$$P = 4113\ \text{lb}$$

Overall H_2O balance

$$(0.6)\ (10{,}000) = W + [(0.55)(0.05)](4113)$$

$$W = 5887\ \text{lb}$$

(or use the overall total balance 10,000 = 4113 + W)

The total amount of NaOH exiting with P is $[(0.95) + (0.45)(0.05)](4113) = 4000$ lb

NaOH balance on the crystallizer $0.5\ G = 4000 + 0.45\ R$

H_2O balance on the crystallizer $0.5\ G = 113 + 0.55\ R$

(or use the total balance G = R + 4113)

$$R = 38{,}870\ \text{lb}$$

b. Figure E12.lb.

Chemical Engineering Principles-I Dr.Ali H.Abbar

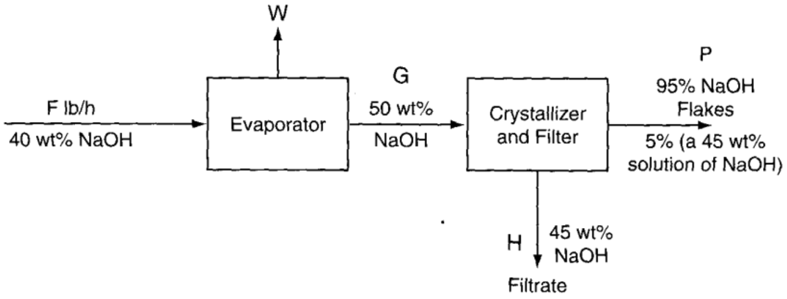


Figure E12.1b

The basis is now P = 4113 lb (the same as 1 hour) The unknowns are now F, W, G, and H.

NaOH balance on the crystallizer

$$0.5\ G = [(0.95) + (0.05)\ (0.45)]\ (4113) + 0.45\ H$$

H_2O balance on the crystallizer

$$0.5G = [(0.05)\ (0.55)\ (4113)] + 0.55\ H$$

$$H = 38{,}870\ \text{lb}$$

Overall NaOH balance

$$0.40\ F = 0.45(38{,}870) + 4000$$

$$F = 53{,}730\ \text{lb}$$

: Note that without recycle, the feed rate must be 5.37 times larger than with recycle to produce the same amount of product.

Recycle with Chemical Reaction

: The most common application of recycle for systems involving chemical reaction is the recycle of reactants, an application that is used to increase the overall conversion in a reactor. Figure 12.3 shows a simple example for the reaction

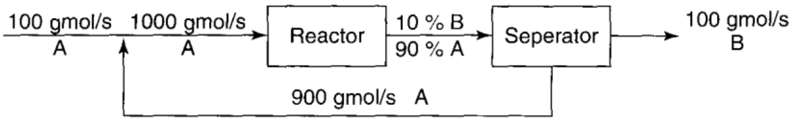


Figure 12.3 A simple recycle system with chemical reaction.

If you calculate the extent of reaction for the overall process in Figure 12.3 based on B

$$\xi_{\text{overall}} = \frac{100 - 0}{1} = 100 \text{ moles reacting}$$

If you use material balances to calculate the output P of the reactor (on the basis of 1 second) you get A = 900 g mol B = 100 g mol

And the extent of reaction based on B for the reactor by itself as the system is

$$\xi_{\text{reactor}} = \frac{100 - 0}{1} = 100 \text{ moles reacting}$$

In general, the extent of reaction is the same regardless of whether an overall material balance is used or a material balance for the reactor is used.

- Two types of conversion when reactions occur:

1. Overall fraction conversion:

$$\frac{\text{mass (moles) of reactant in the fresh feed-mass (moles) of reactant in the output of the overall process}}{\text{mass (moles) of reactant in the fresh feed}}$$

2. Single - pass (“once - through”) fraction conversion:

$$\frac{\text{mass (moles) of reactant fed into the reactor-mass (moles) of reactant exiting the reactor}}{\text{mass (moles) of reactant fed into the reactor}}$$

For the simple recycle reactor in Figure 12.3, the overall conversion is

$$\frac{100 - 0}{100} \times 100 = 100\%$$

And the single-pass conversion is

$$\frac{1000 - 900}{1000} \times 100 = 10\%$$

When the fresh feed consists of more than one reactant, the conversion can be expressed for a single component, usually the limiting reactant, or the most important (expensive) reactant.

♦ The overall conversion and the single-pass conversion can be expressed in terms of the extent of reaction, ξ.

$$\text{Overall conversion of species A} = f_{\text{OA}} = \frac{-v_{\text{A}}\xi}{n_{\text{A}}^{\text{fresh feed}}} \tag{12.1}$$

$$\text{Single-pass conversion} = f_{\text{SP}} = \frac{-v_{\text{A}}\xi}{n_{\text{A}}^{\text{reactor feed}}} \tag{12.2}$$

$$\frac{f_{\text{SP}}}{f_{\text{OA}}} = \frac{n_{\text{A}}^{\text{fresh feed}}}{n_{\text{A}}^{\text{fresh feed}} + n_{\text{A}}^{\text{recycle}}} \tag{12.3}$$

Example 36

Cyclohexane (C_6H_{12}) can be made by the reaction of benzene (Bz) (C_6H_6) with hydrogen according to the following reaction:

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$$

For the process shown in Figure El2.2, determine the ratio of the recycle stream to the fresh feed stream if the overall conversion of benzene is 95%, and the single-pass conversion is 20%. Assume that 20% excess hydrogen is used in the fresh feed, and that the composition of the recycle stream is 22.74 mol % benzene and 77.26 mol % hydrogen.

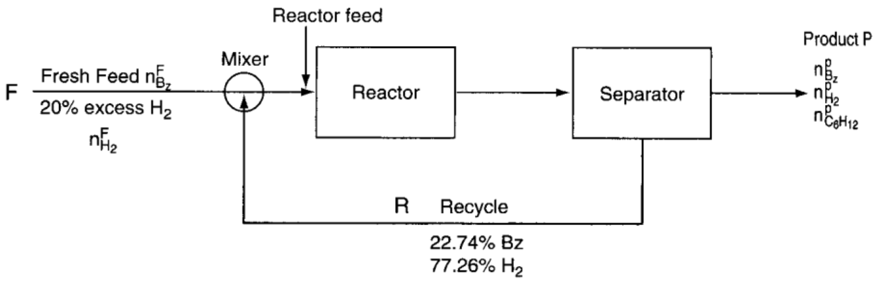


Figure E12.2 Schematic of a recycle reactor.

Solution

The process is open and steady state.

Basis = 100 mol (g mol or lb mol) of fresh benzene feed

Excess H_2 = (in – required)/ required (for complete reaction) In H_2 (Feed):

$$n^F_{H_2} = 100(3)(1 + 0.20) = 360 \text{ mol}$$

The total fresh feed = 100 + 360 = 460 mol.

From Equation (12.1) for benzene (ν_{Bz} = - 1)

$$0.95 = \frac{-(-1)\xi}{100}$$

ξ = 95 reacting moles.

The unknowns are R, $n^P_{B_z}$, $n^P_{H_2}$, and $n^P_{C_6H_{12}}$.

The species overall balances are

$$n_i^{out} = n_i^{in} + \nu_i \xi_{overall}$$

$$\begin{aligned}
\text{Bz:}\quad & n^P_{Bz} = 100 + (-1)(95) = 5 \text{ mol}\\
H_2\text{:}\quad & n^P_{H_2} = 360 + (-3)(95) = 75 \text{ mol}\\
C_6H_{12}\quad & n^P_{C_6H_{12}} = 0 + (1)(95) = \underline{95 \text{ mol}}\\
& P = 175 \text{ mol}
\end{aligned}$$

The amount of the Bz feed to the <u>reactor</u> is 100 + 0.2274 R, and ξ = 95. Thus, for benzene

$$0.20 = \frac{-(-1)95}{100 + 0.2274R}$$

and R = 1649 mol

Finally, the ratio of recycle to fresh feed is

$$\frac{R}{F} = \frac{1649 \text{ mol}}{460 \text{ mol}} = 3.58$$

<u>Example 37</u>

Immobilized glucose isomerase is used as a catalyst in producing fructose from glucose in a fixed-bed reactor (water is the solvent). For the system shown in Figure El2.3a, what percent conversion of glucose results on one pass through the reactor when the ratio of the exit stream to the recycle stream in mass units is equal to 8.33? The reaction is

$$\underset{\text{Glucose}}{C_{12}H_{22}O_{11}} \rightarrow \underset{\text{Fructose}}{C_{12}H_{22}O_{11}}$$

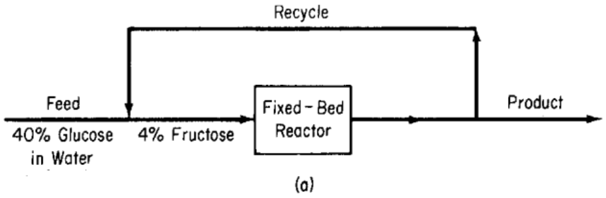


Figure E12.3a

Solution

The process is an open, steady-state process with a reaction occurring and a recycle.

: Figure E12.3b includes all the known and unknown values of the variables using appropriate notation (W stands for water, G for glucose, and F for fructose).

: Note that the recycle stream and product stream have the same composition, and consequently the same mass symbols are used in the diagram for each stream.

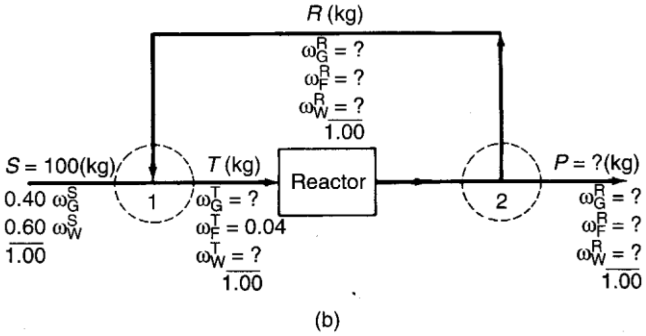


Figure E12.3b

Pick as a basis S = 100 kg

Overall balances

Total: $P = S = 100$ kg

Consequently,

$$R = \frac{100}{8.33} = 12.0 \text{ kg} \quad [P/R = 8.33]$$

Overall no water is generated or consumed, hence

Water: $$100(0.60) = P\omega_W^R = 100\omega_W^R$$
$$\omega_W^R = 0.60$$

Mixing point 1

$$\textit{Total:}\quad 100 + 12 = T = 112$$

$$\textit{Glucose:}\quad 100(0.40) + 12\omega_G^R = 112\omega_G^T$$

$$\textit{Fructose:}\quad 0 + 12\omega_F^R = 112(0.04)$$

Or $\omega_F^R = 0.373$

Also, because $\omega_F^R + \omega_G^R + \omega_W^R = 1$,

$$\omega_G^R = 1 - 0.373 - 0.600 = 0.027$$

Next from the glucose balance $\omega_G^T = 0.360$

Reactor plus Separator 2

Total: T = 12 + 100 = 112 (a redundant equation)

$$\textit{Glucose:}\quad \omega_G^T T - (R + P)(\omega_G^R) = (f)(\omega_G^T T)$$

$$(0.360)(112) - (112)(0.027) = f(0.360)(112)$$
$$40.3 - 3.02 = f(40.32)$$
$$f = 0.93$$

Check by using Equation 12.2 and the extent of reaction

$$\xi = \frac{3.02 - 40}{-1} = 37 \quad f = \frac{-(-1)(37)}{40} = 0.93$$

Example 38

Reactors that involve biological materials (bioreactors) use living organisms to produce a variety of products. Bioreactors are used for producing ethanol, antibiotics, and proteins for dietary supplements and medical diagnosis. Figure E12.4 shows a recycle bioreactor in which the overall conversion of the proprietary component in the fresh feed to product is 100%. The conversion of the proprietary component to product per pass in the reactor is 40%. Determine the amount of recycle and the mass percent of component in the recycle stream if the product stream contains 90% product, and the feed to the reactor contains 3 wt % of the component.

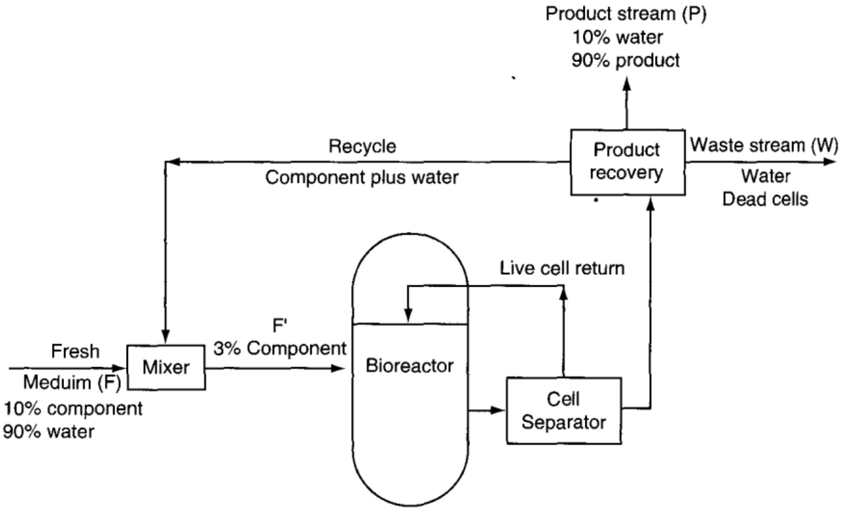


Figure E12.4

Assume that the component and the product have essentially the same molecular weight, and that the waste contains only water and dead cells.

Solution

Basis = 100 kg of fresh feed (F).

Overall balances

Total balance: 100 = P + W

Component balance: 0.10 (100) = 0.90 P

P = 11.1 kg W = 88.9 kg

The reactor plus the product recovery unit balance

$$\begin{array}{cccccc} \textit{Accumulation} & \textit{Input} & \textit{Output} & \textit{Generation} & \textit{Consumption} \\ 0 & = [100\,(0.10) + R\omega] & -\ R\omega & +\quad 0 & -0.40\,[100\,(0.10) + R\omega] \end{array}$$

$R\omega = 15$ kg of component in the recycle stream

Component balance: $100\,(0.10) + 15 = 0.03\,F' \longrightarrow F' = 833$ kg

$R + 100 = F' \longrightarrow R = 833 - 100 = 733$ kg

$$\omega = \frac{15}{733} = 0.0205$$

Mixer balance Total

balance:

Bypass and Purge

a. A bypass stream—a stream that skips one or more stages of the process an goes directly to another downstream stage (Figure 12.4).

A bypass stream can be used to control the composition of a final exit stream from a unit by mixing the bypass stream and the unit exit stream in suitable proportions to obtain the desired final composition.

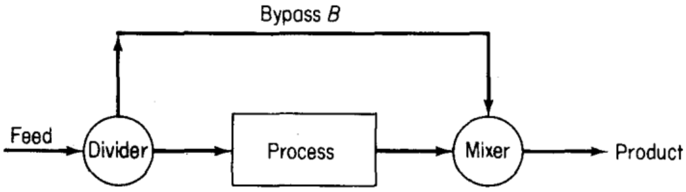


Figure 12.4 A process with a bypass stream.

b. A purge stream—a stream bled off from the process to remove an accumulation of inert or unwanted material that might otherwise build up in the recycle stream (Figure 12.5).

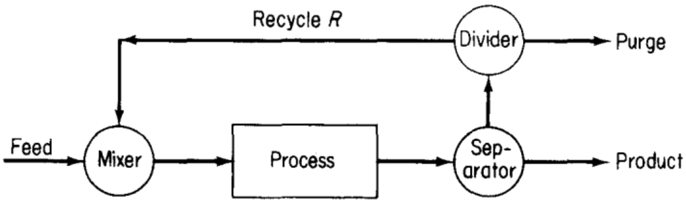


Figure 12.5 A process with a recycle stream with purge.

Example 39

In the feedstock preparation section of a plant manufacturing natural gasoline, isopentane is removed from butane-free gasoline. Assume for purposes of simplification that the process and components are as shown in Figure E12.5. What fraction of the butane-free gasoline is passed through the isopentane tower? The process is in the steady state and no reaction occurs.

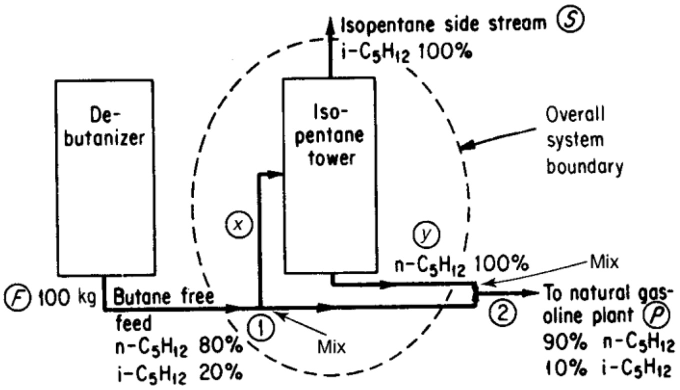


Figure E12.5

Solution

Basis: 100 kg feed

Overall balances

Total material balance:

$$\frac{In}{100} = \frac{Out}{S + P} \qquad \text{(a)}$$

Component balance for n-C_5 (tie component)

$$\frac{In}{100(0.80)} = \frac{Out}{S(0) + P(0.90)} \qquad \text{(b)}$$

Consequently,

$$P = 100\left(\frac{0.80}{0.90}\right) = 88.9 \text{ kg}$$

$$S = 100 - 88.9 = 11.1 \text{ kg}$$

Balance around isopentane tower:

Let x be the kg of butane-free gas going to the isopentane tower, and y be the kg of the n-C_5H_{12} stream leaving the isopentane tower.

Total material balance:

$$\frac{In}{x} = \frac{Out}{11.1 + y} \qquad \text{(c)}$$

Component balance for n-C_5 $x(0.80) = y$ (d)

Consequently, combining (c) and (d) yields $x = 55.5$ kg, or the desired fraction is 0.55.

Another approach to this problem is to make a balance at mixing points 1 and 2.

Balance around mixing point 2:

Material into junction = Material out

Total material: $(100 - x) + y = 88.9$ (e)

Component (iso-C_5): $(100 - x)(0.20) + 0 = 88.9(0.10)$ (f) Solving yields $x = 55.5$ kg as before

Example 40

Figure E12.6 illustrates a steady-state process for the production of methanol. All of the compositions are in mole fractions or percent. The stream flows are in moles.

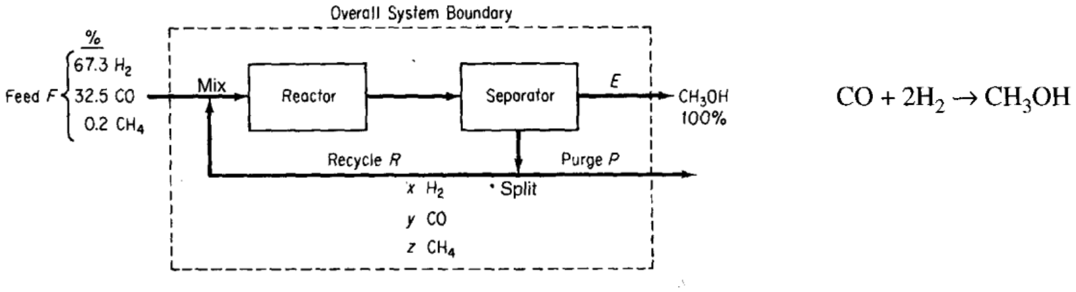


Figure E12.6

Note in Figure E12.6 that some CH_4 enters the process, but does not participate in the reaction. A purge stream is used to maintain the CH_4 concentration in the exit from the separator at no more than 3.2 mol%, and prevent hydrogen buildup as well. The once-through conversion of the CO in the reactor is 18%.

Compute the moles of recycle, CH_3OH, and purge per mole of feed, and also compute the purge gas composition.

Solution

The mole fraction of the components in the purge stream have been designated as x, y, and z for H_2, CO, and CH_4, respectively.

Basis: F = 100 mol The variables whose values are unknown are x, y, z, E, P, and R.

The implicit mole fraction balance in the recycle stream

$$z = 0.032 \qquad \text{(a)}$$

$$x + y + z = 1 \qquad \text{(b)}$$

The overall element balances are (in moles):

$$\begin{aligned} &2H: && 67.3 + 0.2(2) = E(2) + P(x + 2z) && \text{(c)}\\ &C: && 32.5 + 0.2 \quad = E(1) + P(y + z) && \text{(d)}\\ &O: && 32.5 \quad = E(1) + P(y) && \text{(e)} \end{aligned}$$

Reactor plus the Separator

$$\text{CO:} \quad \frac{In}{[32.5 + Ry]} - \frac{Out}{[y(R + P)]} = \frac{Consumed}{(32.5 + Ry)(0.18)} \qquad \text{(f)}$$

Equation (a) can be substituted into Equations (b) through (f), and the resulting five equations solved by successive substitution or by using a computer program. The resulting values obtained are (in moles)

E	CH_3OH	31.25
P	purge	6.25
R	recycle	705
x	H_2	0.768
y	CO	0.200
z	CH_4	0.032

Problems

1. How many recycle streams occur in Figure SAT12.1PI?

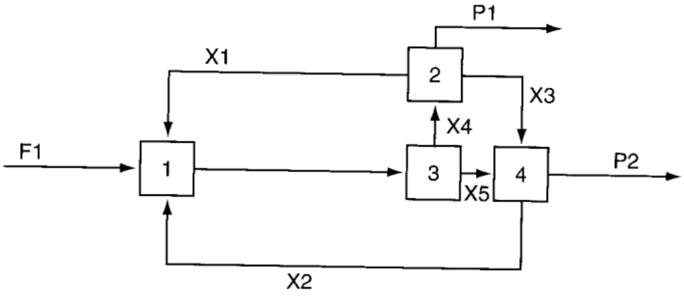


Figure SAT12.1P1

2. The Hooker Chemical Corporation operates a process in Michigan for the purification of HCl. Figure SATI2.1P2 shows the flow sheet for the Hooker process. The streams from the bottoms of the five towers are liquid. The streams from the tops of the towers are gases. HCl is insoluble in the HCB (hexachlorobutadiens).

   The various stream compositions are shown in Figure SAT12.1P2.
   How many recycle streams are there in the Hooker process?

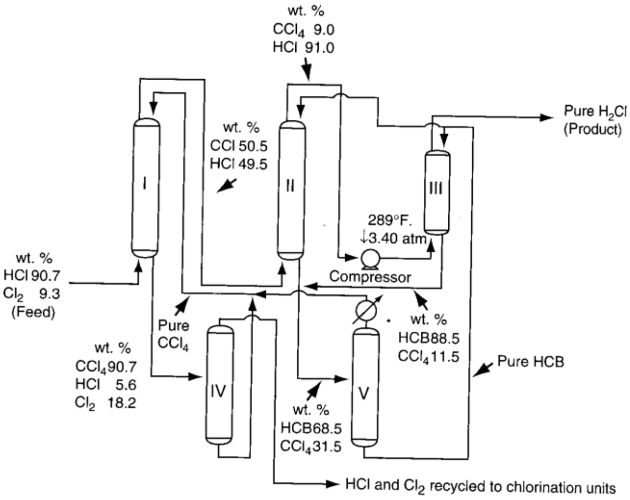


Figure SAT12.1P2

3. A ball mill grinds plastic to make a very fine powder. Look at Figure SAT12.2P1.

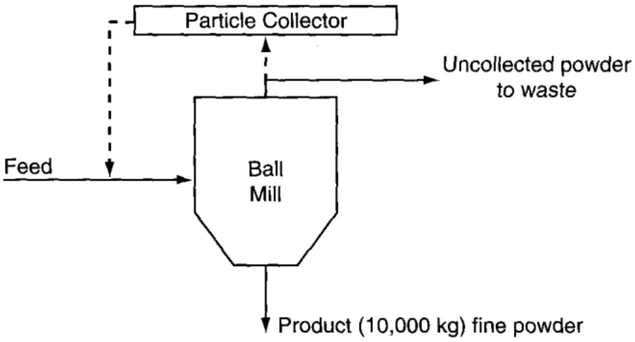


Figure SAT12.2P1

At the present time 10,000 kg of powder are produced per day. You observe that the process (shown by the solid lines) is inefficient because 20% of the feed is not recovered as powder—it goes to waste.

You make a proposal (designated by the dashed lines) to recycle the uncollected material back to the feed so that it can be remilled. You plan to recycle 75% of the 200 kg of uncollected material back to the feed stream. If the feed costs $1.20/kg, how much money would you save per day while producing 10,000 kg of fine powder?

4. Sea water is to be desalinized by reverse osmosis using the scheme indicated in Figure SATI2.2P2. Use the data given in the figure to determine: (a) the rate of waste brine removal (B); (b) the rate of desalinized water (called potable water) production (P); (c) the fraction of the brine leaving the reverse osmosis cell (which acts in essence as a separator) that is recycled.

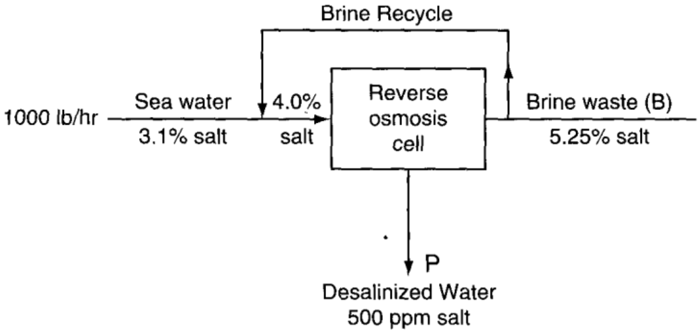


Figure SAT12.2P2

5. A material containing 75% water and 25% solid is fed to a granulator at a rate of 4000 kg/hr. The feed is premixed in the granulator with recycled product from a dryer, which follows the granulator (to reduce the water concentration of the overall material fed into the granulator to 50% water, 50% solid). The product that leaves the dryer is 16.7% water. In the dryer, air is passed over the solid being dried. The air entering the dryer contains 3% water by weight (mass), and the air leaving the dryer contains 6% water by weight (mass).
   a. What is the ratio of the recycle to the feed entering the granulator?
   b. What is the rate of air flow to the dryer on a dry basis?

6. Benzene, toluene, and other aromatic compounds can be recovered by solvent extraction with sulfur dioxide (SO_2). Figure SAT12.2P4 is the process schematic. As an example, a catalytic reformate stream containing 70% benzene and 30% nonbenzene material is passed through the countercurrent extractive recovery scheme shown in Figure SAT12.2P4. 1000 lb of reformate and 3000 lb of SO_2 are fed to the system per hour. The benzene product stream contains 0.15 lb of SO_2 per lb of benzene. The raffinate stream contains all the initially charged nonbenzene material as well as 0.25 lb of benzene per lb of nonbenzene material. The remaining component in the raffinate stream is SO_2. How many lb of benzene are extracted in the product stream on an hourly basis? How many lb of raffinate are produced per hour?

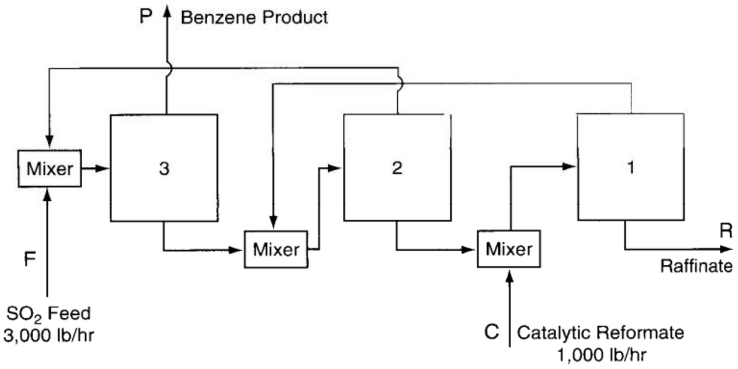


Figure SAT12.2P4

7. A catalytic dehydrogenation process shown in Figure SAT12.3Pl, produces 1, 3 butadiene (C_4H_6) from pure normal butane (C_4H_{10}). The product stream contains 75 mol/hr of H_2 and 13 mol/hr of C_4H_{10} as well as C_4H_6. The recycle stream is 30% (mol) C_4H_{10} and 70% (mol) C_4H_6, and the flow is 24 mol/hr.

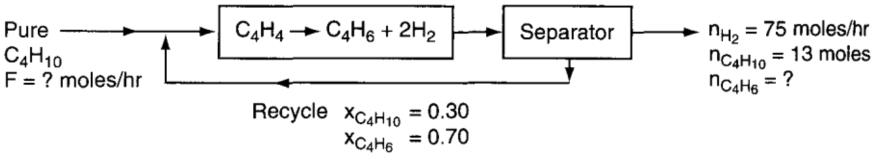


Figure SAT12.3P1

(a) What are the feed rate, F, and the product flow rate of C_4H_6 leaving the process?

(b) What is the single-pass conversion of butane in the process?

8. Pure propane (C_3H_8) from El Paso is dehydrogenated catalytically in a continuous process to obtain propylene (C_3H_6). All of the hydrogen formed is separated from the reactor exit gas with no loss of hydrocarbon. The hydrocarbon mixture is then fractionated to give a product stream containing 88 mole % propylene and 12 mole % propane. The other stream, which is 70 mole % propane and 30 mole % propylene, is recycled. The one-pass conversion in the reactor is 25%, and 1000 kg of fresh propane are fed per hour. Find (a) the kg of product stream per hour, and (b) the kg of recycle stream per hour.

9. Ethyl ether is made by the dehydration of ethyl alcohol in the presence of sulfuric acid at 140°C:

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

Figure SAT12.3P3 is a simplified process diagram. If 87% conversion of the alcohol fed to the reactor occurs per pass in the reactor, calculate: (a) kilograms per hour of fresh feed, and (b) kilograms per hour of recycle.

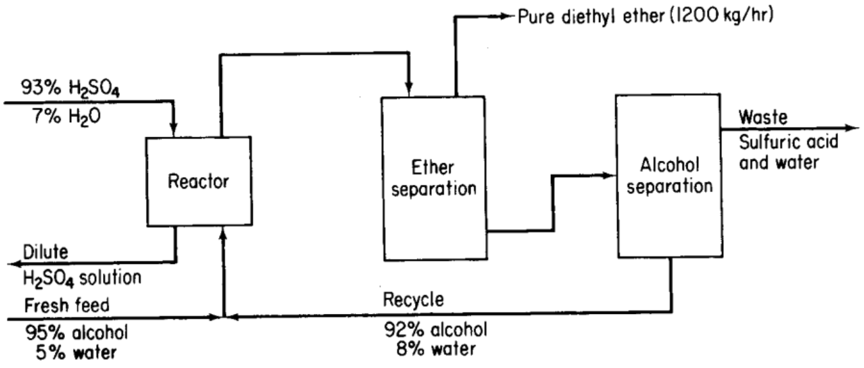


Figure SAT12.3P3

10. In the famous Haber process (Figure SAT12.4P1) to manufacture ammonia, the reaction is carried out at pressures of 800 to 1000 atm and at 500 to 600°C using a suitable catalyst. Only a small fraction of the material entering the reactor reacts on one pass, so recycle is needed. Also, because the nitrogen is obtained from the air, it contains almost 1% rare gases (chiefly argon) that do not react. The rare gases would continue to build up in the recycle until their effect on the reaction equilibrium would become adverse. Therefore, a small purge stream is used.

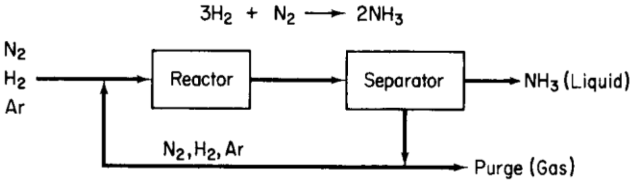


Figure SAT12.4P1

The fresh feed of gas composed of 75.16% H_2, 24.57% N_2, and 0.27% Ar is mixed with the recycled gas and enters the reactor with a composition of 79.52% H_2. The gas stream leaving the ammonia separator contains 80.0 1% H_2 and no ammonia. The product ammonia contains no dissolved gases. Per 100 moles of fresh feed:

a. How many moles are recycled and purged?
b. What is the percent conversion of hydrogen per pass?

11. Figure SAT12.4P2 shows a simplified process to make ethylene dichloride ($C_2H_4C1_2$). The feed data have been placed on the figure. Ninety percent conversion of the C_2H_4 occurs on each pass through the reactor. The overhead stream from the separator contains 98% of the Cl_2 entering the separator, 92% of the entering C_2H_4, and 0.1% of the entering $C_2H_4C1_2$. Five percent of the overhead from the separator is purged. Calculate (a) the flow rate and (b) the composition of the purge stream.

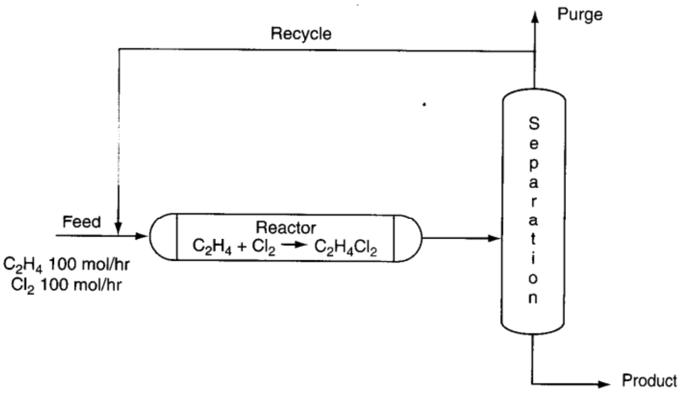


Figure SAT12.4P2

Answers:

1. 2
2. 5
3. $2250
4. (a) 591 lb/hr; (b) 409 lb/hr; (c) 0.55
5. (a) ratio = 3000 kg of recycle/hr and feed = 7000 kg/hr; (b) air = 85,100 kg/hr
6. (a) benzene extracted: P = 625 lb/hr; (b) raffinate produced: R = 3,281 lb/hr
7. (a) mol/hr C_4H_6 = 37.5 and F = 50.5 mol/hr; (b) 0.65
8. (a) 960 kg/hr; (b) 3659 kg/hr
9. (a) 1570 kg/hr; (b) 243 kg/hr

10. (a) 890 recycled and 3.2 purged; (b) 9.2% conversion (errors can be caused by loss of significant figures)

11. (a) 1.49 mol/hr; (b) Cl_2: 0.658; C_2H_4: 0.338; $C_2H_4C1_2$: 0.0033.

Dr.Ali H.Abbar

Chapter Three

Gases, Vapors, Liquids, and Solids

: Property is meaning any measurable characteristic of a substance, such as pressure, volume, or temperature, or a characteristic that can be calculated or deduced, such as internal energy.

: State and Equilibrium A system will possess a unique set of properties, such as temperature, pressure, density, and so on, at a given time, and thus is said to be in a particular state. A change in the state of the system results in a change in at least one of its properties.

: By equilibrium we mean a state in which there is no tendency toward spontaneous change. When a system is in equilibrium with another system, or the surroundings, it will not change its state unless the other system, or the surroundings, also changes.

: A phase is defined as a completely homogeneous and uniform state of matter. Liquid water would be a phase; ice would be another phase. Two immiscible liquids in the same container, such as mercury and water, would represent two different phases because the liquids have different properties.

3.1 Ideal Gas Law Calculations

The Ideal Gas Law

Under conditions such that the average distance between the molecules in a substance is great enough to neglect the effect of the intermolecular forces and the volume of the molecules themselves, a gas can be termed an ideal gas. More properly, an ideal gas is an imaginary gas that obeys exactly the following relationship

$$pV = nRT \qquad (1)$$

Where p = absolute pressure of the gas V =
total volume occupied by the gas n =
number of moles of the gas
R = ideal gas constant in appropriate units
T = absolute temperature of the gas Sometimes
the ideal gas law is written as

$$p\hat{V} = RT \qquad (1a)$$

Where $\hat{V}$ is the specific volume (volume per mole or mass) of the gas.

Table 1 Common Standard Conditions for the Ideal Gas

System	T	P	$\hat{V}$
SI	273.15K	101.325 kPa	22.415 m^3/kg mol
Universal scientific	0.0°C	760 mm Hg	22.415 liters/g mol
Natural gas industry	60.0°F (15.0°C)	14.696 psia (101.325 kPa)	379.4 ft^3/lb mol
American engineering	32°F	1 atm	359.05 ft^3/lb mol

40 kg CO_2	1 kg mol CO_2	22.42 m^3 CO_2
	44 kg CO_2	1 kg mol CO_2

Example 1

Calculate the volume, in cubic meters, occupied by 40 kg of CO_2 at standard conditions.

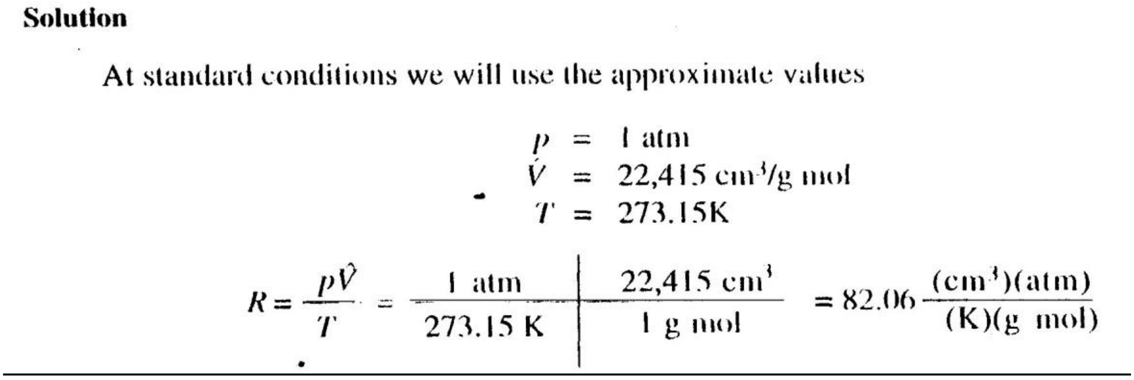
Solution

Basis: 40 kg of CO_2

$= 20.4\ m^3\ CO_2$ atS.C.

Example 2

Find the value for the universal gas constant R for the following combinations of units: For 1 g mol of ideal gas when the pressure is in atm, the volume in cm^3, and the temperature in K.



Solution

At standard conditions we will use the approximate values

$$p = 1\ \text{atm}$$
$$\hat{V} = 22{,}415\ \text{cm}^3/\text{g mol}$$
$$T = 273.15\text{K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1\ \text{atm}}{273.15\ \text{K}}\,\Big|\,\frac{22{,}415\ \text{cm}^3}{1\ \text{g mol}} = 82.06\,\frac{(\text{cm}^3)(\text{atm})}{(\text{K})(\text{g mol})}$$

In many processes going from an initial state to a final state, you can use the ratio of ideal gas law in the respective states and eliminate R as follows (the subscript 1 designates the initial state, and the subscript 2 designates the final state)

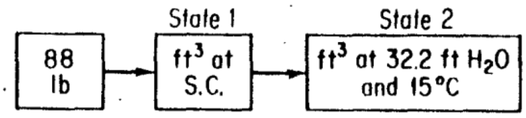
$$\frac{p_1 V_1}{p_2 V_2} = \frac{n_1 R T_1}{n_2 R T_2}$$

or

$$\left(\frac{p_1}{p_2}\right)\left(\frac{V_1}{V_2}\right) = \left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right) \qquad \ldots\ 3.2(2)$$

Example 3

Calculate the volume occupied by 88 lb of CO_2 at a pressure of 32.2 ft of water and at 15°C Solution



The final volume can be calculated via Equation 13.2 in which both R and n_1/n_2 cancel out:

$$V_2 = V_1 \left(\frac{p_1}{p_2}\right)\left(\frac{T_2}{T_1}\right)$$

Assume that the pressure is absolute pressure.

At S.C. (state 1)	At state 2
$p = 33.91\ \text{ft H}_2\text{O}$	$p = 32.2\ \text{ft H}_2\text{O}$
$T = 273\ \text{K}$	$T = 273 + 15 = 288\ \text{K}$

Basis: 88 lb of CO_2

$$\begin{array}{l|l|l|l|l} 88\ \text{lb CO}_2 & & 359\ \text{ft}^3 & 288 & 33.91 \\ \hline & 44\ \text{lb CO}_2 & 1\ \text{lb mol} & 273 & 32.2 \\ & 1\ \text{lb mol CO}_2 & & & \end{array} = \begin{array}{l} 798\ \text{ft}^3\ \text{CO}_2 \\ \text{at } 32.2\ \text{ft H}_2\text{O and } 15^{\circ}\text{C} \end{array}$$

Calculation of V_1

Another solution

The same results can be obtained by using Eq. 1

$$R = \frac{p\hat{V}}{T}$$

At S.C.,

$$p = 33.91 \text{ ft } H_2O \qquad V = 359 \text{ ft}^3/\text{lb mol} \qquad T = 273\text{K}$$

$$R = \begin{array}{c|c} 33.91 & 359 \\ \hline & 273 \end{array} = 44.59 \, \frac{(\text{ft } H_2O)(\text{ft}^3)}{(\text{lb mol})(\text{K})}$$

Basis: 88 lb of CO_2

$$V = \frac{nRT}{p} = \begin{array}{c|c|c} 88 \text{ lb } CO_2 & 44.59 \, (\text{ft } H_2O)(\text{ft}^3) & 288 \text{ K} \\ \hline \frac{44 \text{ lb } CO_2}{\text{lb mol } CO_2} & (\text{lb mol})(\text{K}) & 32.2 \text{ ft } H_2O \end{array}$$

$$= 798 \text{ ft}^3 \; CO_2 \text{ at } 32.2 \text{ ft } H_2O \text{ and } 15°\text{C}$$

The Gas Density

The density of a gas is defined as the mass per unit volume and can be expressed in kilograms per cubic meter, pounds per cubic foot, grams per liter, or other units

Example 4

What is the density of N_2 at 27°C and 100 kPa in SI units?

Solution

Basis: 1 m^3 of N_2 at 27°C and 100 kPa

$$\begin{array}{c|c|c|c|c} 1 \text{ m}^3 & 273 \text{ K} & 100 \text{ kPa} & 1 \text{ kg mol} & 28 \text{ kg} \\ \hline & 300 \text{ K} & 101.3 \text{ kPa} & 22.4 \text{ m}^3 & 1 \text{ kg mol} \end{array} = 1.123 \text{ kg}$$

density = 1.123 kg/m^3 of N_2 at 27°C (300 K) and 100 kPa

The Gas Specific Gravity

The specific gravity of a gas is usually defined as the ratio of the density of the gas at a desired temperature and pressure to that of air (or any specified reference gas) at a certain temperature and pressure.

Example 5

What is the specific gravity of N_2 at 80°F and 745 mm Hg compared to air at 80°F and 745 mm Hg?

Solution

Basis: 1 ft^3 of air at 80°F and 745 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 745 & & 29 \\ \hline & 540 & 760 & 359 & \end{array} = 0.0721\ lb/ft^3 \text{ at } 80°F \text{ and } 745\ mm\ Hg$$

Basis: 1 ft^3 of N_2 at 80°F and 745 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 745 & & 28 \\ \hline & 540 & 760 & 359 & \end{array} = 0.0697\ lb/ft^3 \text{ at } 80°F \text{ and } 745\ mm\ Hg$$

$$(sp.\ gr.)_{N_2} = \frac{0.0697}{0.0721} = 0.967\ \frac{lb\ N_2/ft^3 \text{ at } 80°F,\ 745\ mm\ Hg}{lb\ air/ft^3 \text{ air at } 80°F,\ 745\ mm\ Hg}$$

Note: for gases at the same temperature and pressure, the specific gravity is just the ratio of the respective molecular weights. Let A be one gas and B be another.

$$p\hat{V} = RT \qquad \text{or} \qquad p\frac{1}{\rho} = RT$$

Thus $$sp.gr. = \frac{\rho_A}{\rho_B} = \left(\frac{p_A}{p_B}\right)\left(\frac{mol.wt._A}{mol.wt._B}\right)\left(\frac{T_B}{T_A}\right) \qquad (3)$$

Ideal Gas Mixtures and Partial Pressure

The partial pressure of gas; i defined by Dalton, p_i, namely the pressure that would be exerted by a single component in a gaseous mixture if it existed by itself in the same volume as occupied by the mixture and at the same temperature of the mixture is

$$p_i V_{total} = n_i RT_{total} \qquad \text{... 3.4} \qquad (4)$$

Where p_i is the partial pressure of component i. If you divide Eq. (4) by Eq. (1), you find that

$$\frac{p_i V_{total}}{p_{total} V_{total}} = \frac{n_i R T_{total}}{n_{total} R T_{total}}$$

or

$$p_i = p_{total} \frac{n_i}{n_{total}} = p_{total}\, y_i \qquad (5)\ 3.5$$

Where y_i is the mole fraction of component i. Can you show that Dalton's law of the summation of partial pressures is true using Eq. 13.5?

$$p_1 + p_2 + \ldots + p_n = p_t \qquad (6)\ \ldots 3.6$$

Although you cannot measure the partial pressure directly with an instrument, you can calculate the value from Eqs. 5 and/or 6.

Example 6

A flue gas analyzes 14.0% CO_2, 6.0% O_2, and 80.0% N_2. It is at 400°F and 765.0 mm Hg pressure. Calculate the partial pressure of each component.

Solution

Use Eq, (13.5) $p_i = p_t\, y_i$

Basis: 1.00 kg (or lb) mol flue gas

Component	kg (or lb) mol	p (mm Hg)
CO_2	0.140	107.1
O_2	0.060	45.9
N_2	0.800	612.0
Total	1.000	765.0

On the basis of 1.00 mole of flue gas, the mole fraction y of each component, when multiplied by the total pressure, gives the partial pressure of that component.

Real Gas Relationships

: We have said that at room temperature and pressure many gases can be assumed to act as ideal gases.

: However, for some gases under normal conditions, and for most gases under conditions of high pressure, values of the gas properties that you might obtain using the ideal gas law would be at wide variance with the experimental evidence. . You might wonder exactly how the behavior of real gases compares with that calculated from the ideal gas laws.

: In Fig. 3.2 you can see how the ($p\hat{V}$)product of several gases deviates from that predicted by the ideal gas laws as the pressure increases substantially. Thus it is clear that we need some way of computing the p-V-T properties of a gas that is not ideal, i.e. the real gas.

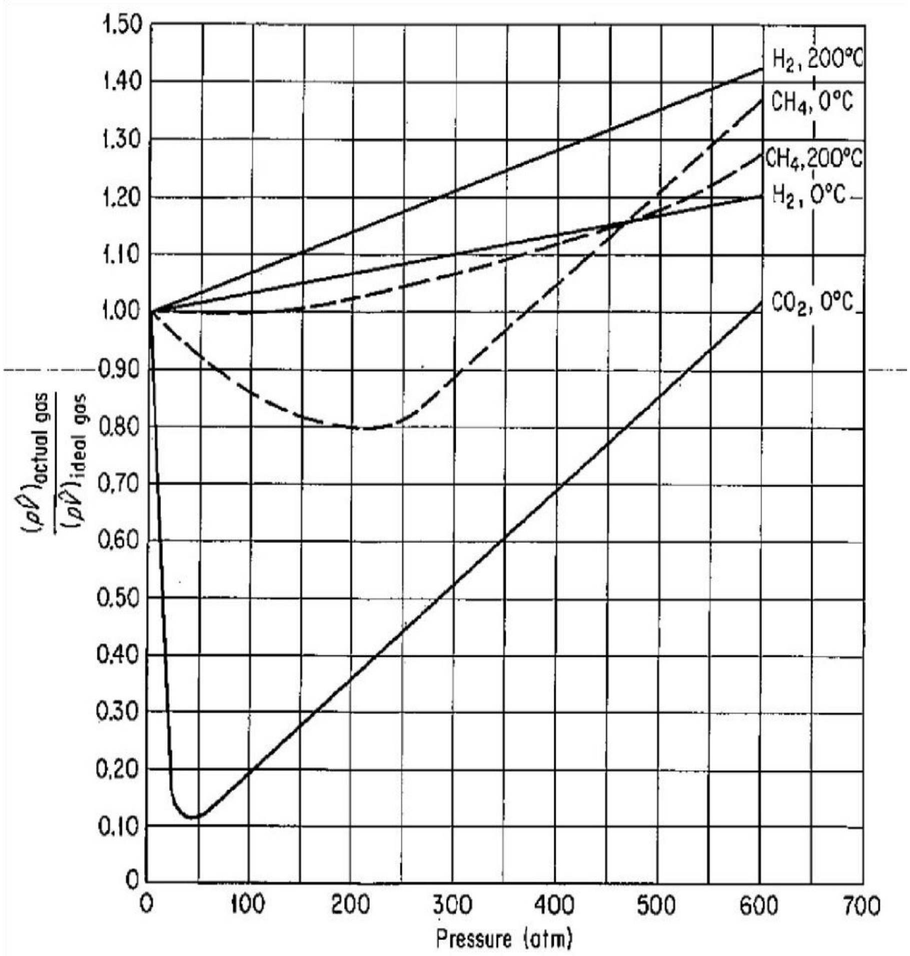


Figure 1 Deviation of real gases from the ideal gas law at high pressures.

Three methods of getting or predicting real gas properties in lieu of having experimental data:

1. Compressibility charts
2. Equations of state
3. Estimated properties

Critical State, Reduced Parameters, and Compressibility

- The critical state for the gas-liquid transition is the set of physical conditions at which the density and other properties of the liquid and vapor become identical.
- The law of corresponding states expresses the idea that in the critical state all substances should behave alike.
- Refer to Figure 2 in which the states of water are illustrated. As the temperature increases, the density of the liquid and vapor approach each other until finally at 374.14 °C, the values are the same.

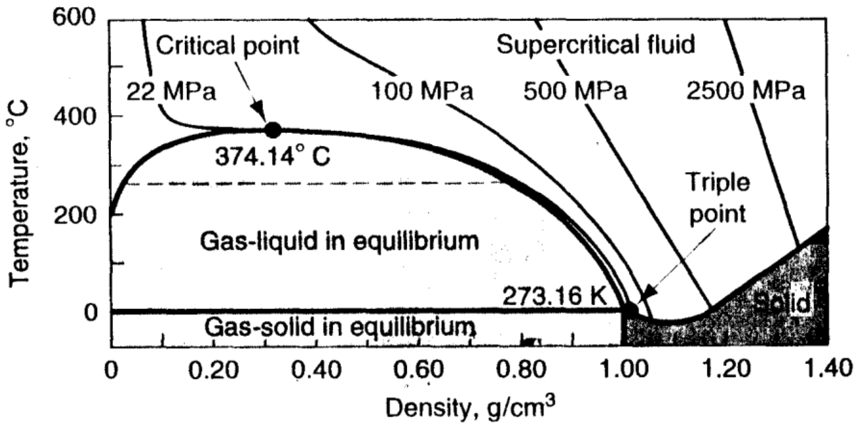


Figure 2 The regions of existence of solid, liquid, gaseous, and supercritical water. At the triple point solid, liquid, and gas are all in equilibrium.

™A supercritical fluid, that is, a compound in a state above the critical point, combines some of the properties of both gases and liquids.

™Another set of terms with which you should immediately become familiar are the reduced parameters. These are corrected, or normalized, conditions of temperature, pressure, and volume and are expressed mathematically as

$$T_r = \frac{T}{T_c}$$

$$p_r = \frac{p}{p_c}$$

$$V_r = \frac{V}{V_c}$$

Compressibility Factor (z)

One common way is to modify the ideal gas law by inserting an adjustable coefficient z, the compressibility factor, a factor that compensates for the nonideality of the gas. Thus, the ideal gas law becomes a real gas law, a generalized equation of state.

$$p\,V = z\,n\,R\,T \tag{7}$$

™Figure 3 shows the generalized compressibility charts or z – factor chart prepared by Nelson and Obert. These charts are based on 30 gases.

Figure 3 (e) is a unique chart that, by having several parameters plotted simultaneously on it, helps you avoid trial-anderror solutions or graphical solutions of real gas problems. One of these helpful parameters is the ideal reduced volume defined as

$$V_{r_i} = \frac{\hat{V}}{\hat{V}_{c_i}}$$

V_{c_i} the ideal critical volume (not the experimental value of the critical volume), or

$$\hat{V}_{c_i} = \frac{RT_c}{p_c}$$

Both V_{r_i} and $\hat{V}_{c_i}$ are easy to calculate since T_c and p_c are presumed known.

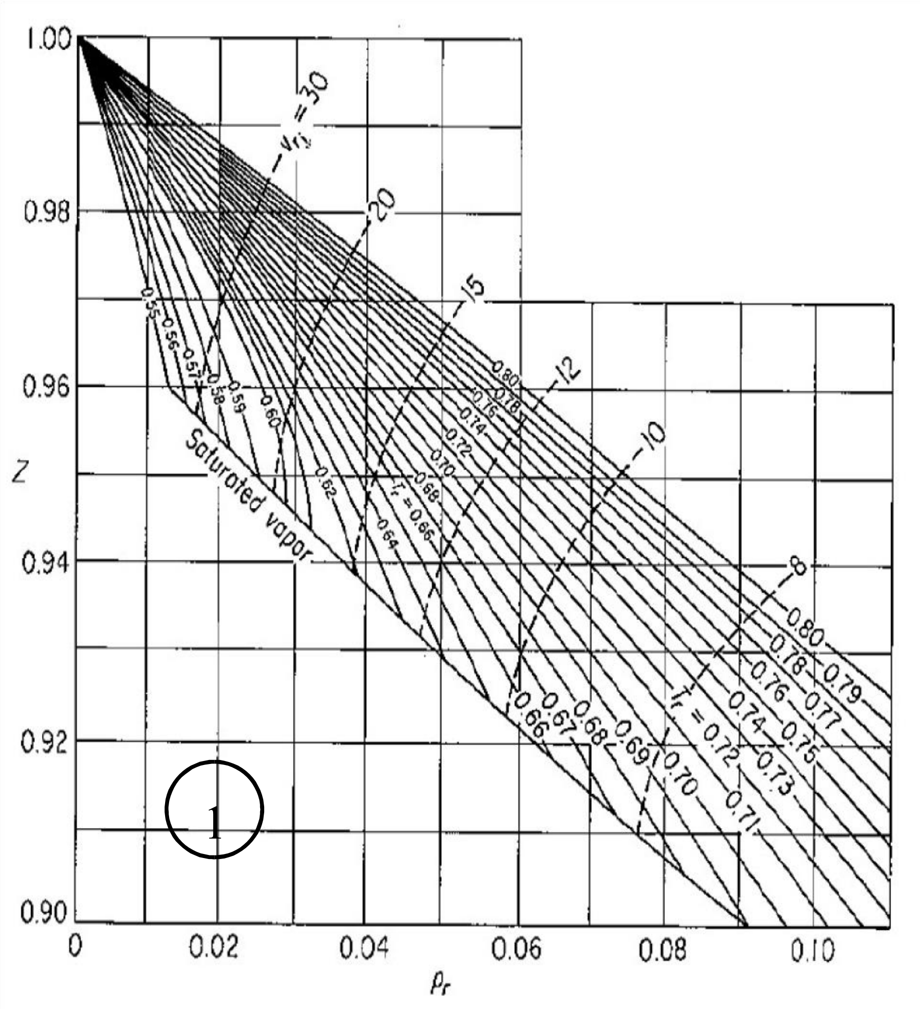


Figure 3(a) Generalized Compressibility Chart, Very Low Reduced Pressure.

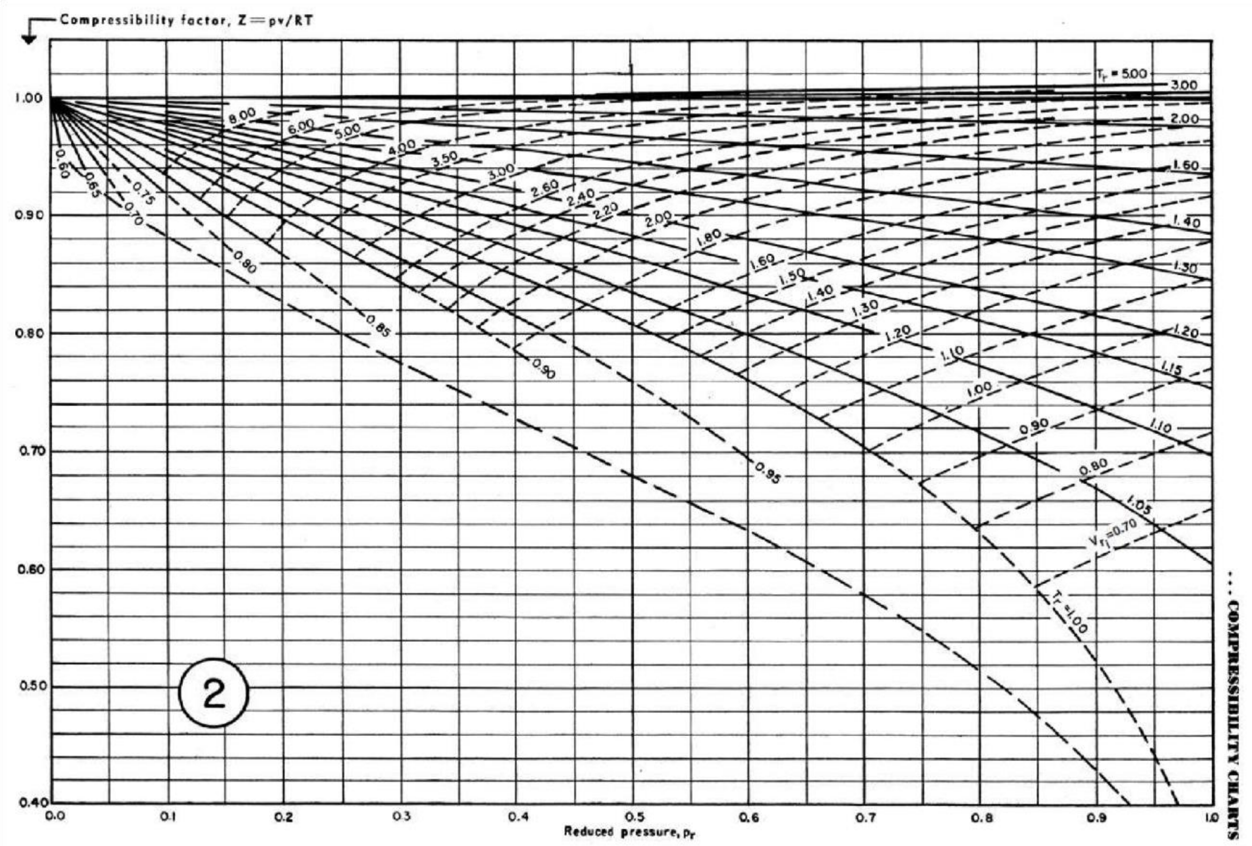


Figure 3(b) Generalized Compressibility Chart, Low Pressure .

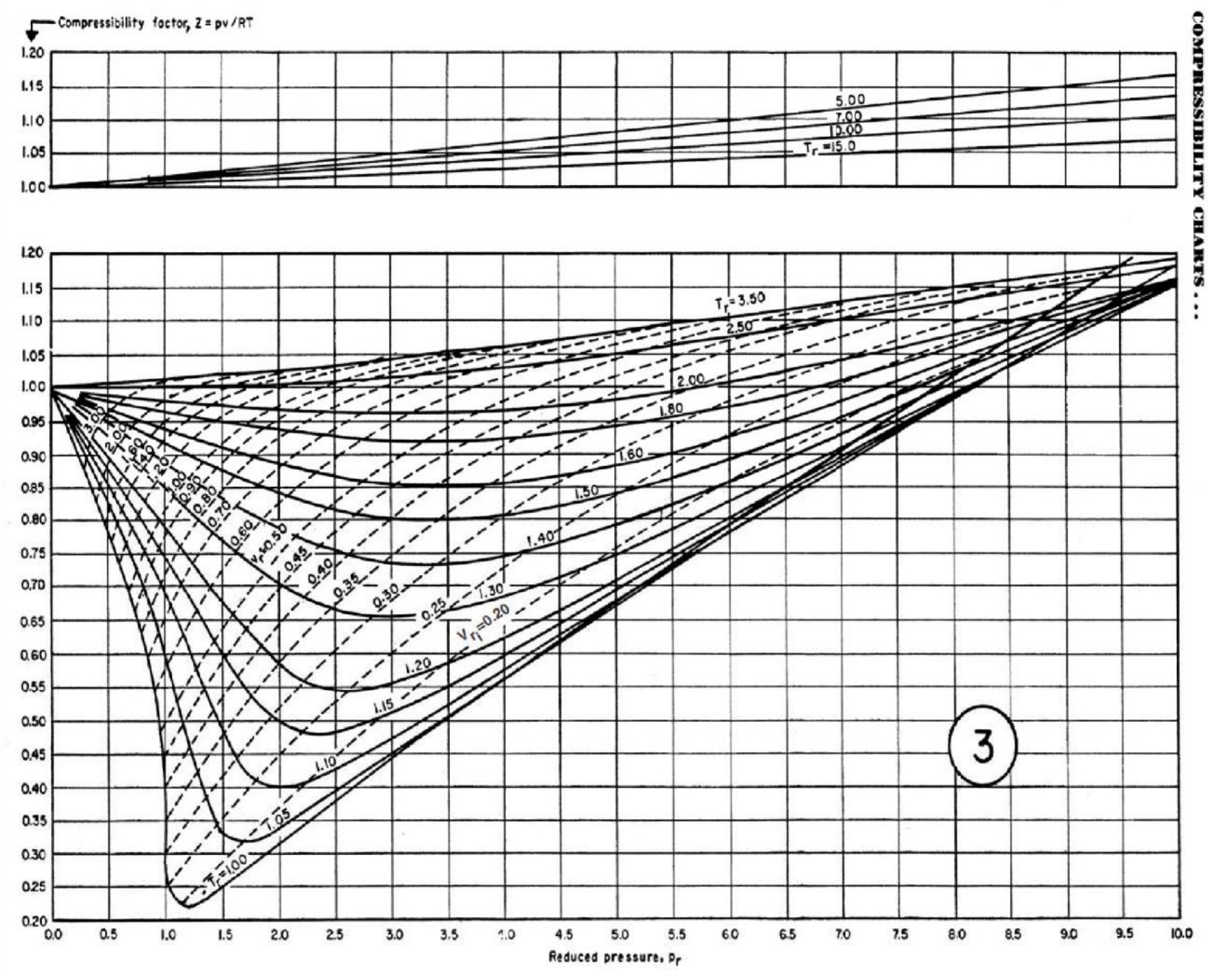


Figure 3(c) Generalized Compressibility Chart, Medium Pressure.

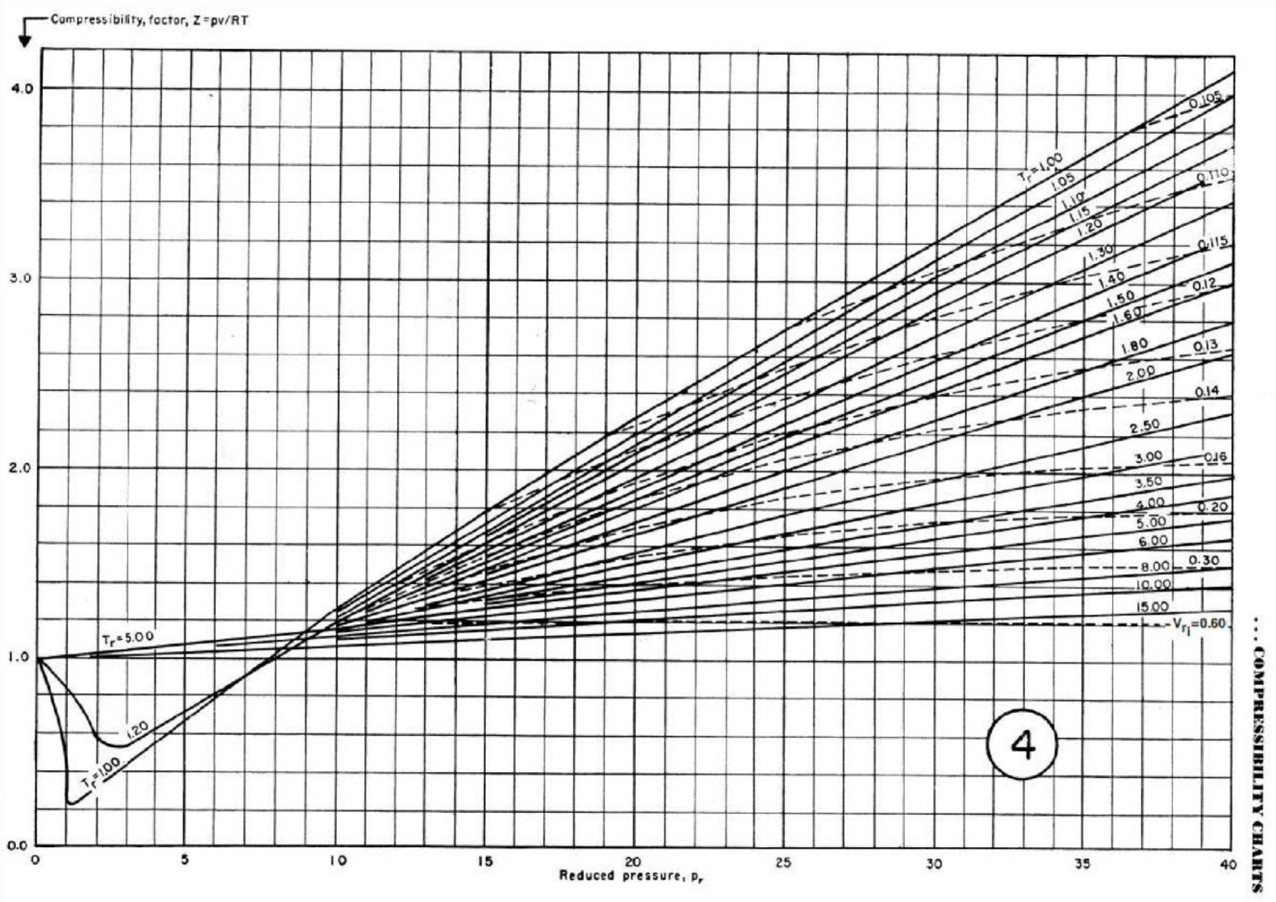


Figure 3(d) Generalized Compressibility Chart, High Pressure.

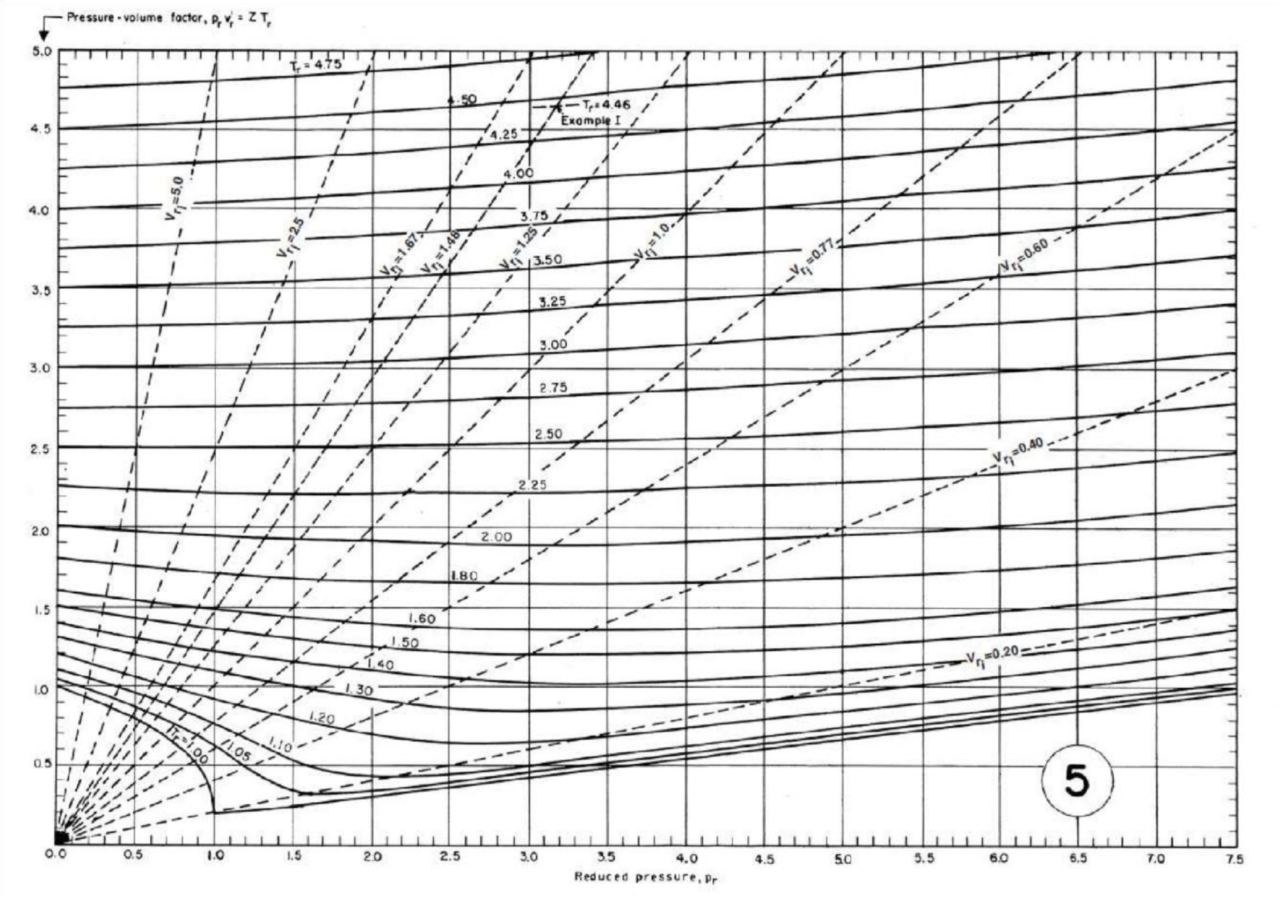


Figure 3 (e) Generalized Compressibility Chart, with Special Scales.

Note

The value z = 1 represents ideality, and the value z = 0.27 is the compressibility factor at the critical point.

Example 7

In spreading liquid ammonia fertilizer, the charges for the amount of NH_3 are based on the time involved plus the pounds of NH_3 injected into the soil. After the liquid has been spread, there is still some ammonia left in the source tank (volume = 120 ft^3), but in the form of a gas. Suppose that your weight tally, which is obtained by difference, shows a net weight of 125 lb of NH_3 left in the tank as a gas at 292 psig. Because the tank is sitting in the sun, the temperature in the tank is 125°F. Your boss complains that his calculations show that the specific volume of the gas is 1.20 ft^3/lb and hence that there are only 100 lb of NH_3 in the tank. Could he be correct? See Figure E 3.7.

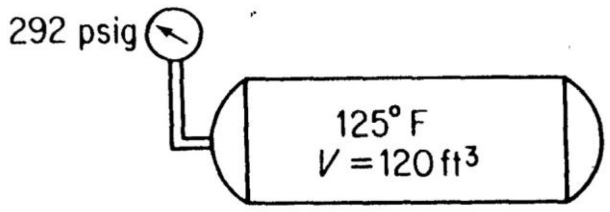


Figure E 3.7

Figure E3.9

Solution

Apparently, your boss used the ideal gas law in getting his figure of 1.20 ft^3/lb of NH_3 gas:

$$R = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(^\circ\text{R})} \qquad p = 292 + 14.7 = 306.7 \text{ psia}$$

$$T = 125^\circ\text{F} + 460 = 585^\circ\text{R} \qquad n = \frac{1 \text{ lb}}{17 \text{ lb/lb mol}}$$

$$\hat{V} = \frac{RT}{p} = \frac{\frac{1}{17}(10.73)(585)}{306.7} = 1.20 \text{ ft}^3/\text{lb}$$

However, he should have used the compressibility factor, because NH_3 does not behave as an ideal gas under the observed conditions of temperature and pressure. Let us again compute the mass of gas in the tank this time using

$$pV = znRT$$

From Appendix D:

$$T_c = 405.5K \simeq 729.9R$$

$$p_c = 111.3 \text{ atm} \simeq 1636 \text{ psia}$$

Then, since z is a function of T_r and p_r,

$$T_r = \frac{T}{T_c} = \frac{585^\circ \text{R}}{729.9^\circ \text{R}} = 0.801$$

$$p_r = \frac{p}{p_c} = \frac{306.7 \text{ psia}}{1636 \text{ psia}} = 0.187$$

From the Nelson and Obert chart, Fig. 13.3 (b), you can read z = 0.855. Now $\hat{V}$ can be calculated as

$$\hat{V} = \begin{array}{c|c} 1.20 \text{ ft}^3 \text{ ideal} & 0.855 \\ \hline \text{lb} & 1 \end{array} = 1.03 \text{ ft}^3/\text{lb } NH_3$$

$$\begin{array}{c|c} 1 \text{ lb } NH_3 & 120 \text{ ft}^3 \\ \hline 1.03 \text{ ft}^3 & \end{array} = 117 \text{ lb } NH_3$$

Note : Certainly 117 lb is a more realistic figure than 100 lb, and it is easily possible to be in error by 8 lb if the residual weight of NH_3 in the tank is determined by difference. As a matter of interest you might look up the specific volume of NH_3 at the conditions in the tank in a handbook. You would find that $\hat{V} = 0.973$ ft^3/lb, and hence the compressibility factor calculation yielded a volume with an error of only about 4%.

Example 13.8

Liquid oxygen is used in the steel industry, in the chemical industry, in hospitals, as rocket fuel, and for wastewater treatment as well as many other applications. In a hospital a tank of 0.0284-m^3 volume is filled with 3.500 kg of liquid O_2 that vaporized at -25°C. Will the pressure in the tank exceed the safety limit of the tank (l0^4 kPa)?

Solution

$$\text{Basis: } 3.500 \text{ kg } O_2$$

We know from Appendix D that

$$T_c = 154.4 \text{ K}$$

$$p_c = 49.7 \text{ atm} \rightarrow 5{,}035 \text{ kPa}$$

$$\hat{V}\ (\textit{molal volume}) = \frac{0.0284 \text{ m}^3}{3.500 \text{ kg}}\left|\frac{32 \text{ kg}}{1 \text{ kg mol}}\right. = 0.260 \text{ m}^3/\text{kg mol}$$

Note that the *molal volume must* be used in calculating V_{r_i} Since $\hat{V}_{c_i}$ is a volume per mole.

$$\hat{V}_{c_i} = \frac{RT_c}{p_c} = \frac{8.313\ (\text{m}^3)\ (\text{kPa})}{(\text{kg mol})(\text{K})}\left|\frac{154.4 \text{ K}}{5{,}035 \text{ kPa}}\right. = 0.255\frac{\text{m}^3}{\text{kg mol}}$$

Then

$$V_{r_i} = \frac{\hat{V}}{\hat{V}_{c_i}} = \frac{0.260}{0.255} = 1.02$$

Now we know two parameters, V_{r_i} and,

$$T_r = \frac{248 \text{ K}}{154.4 \text{ K}} = 1.61$$

From the Nelson and Obert chart [Fig. 3 (e)],

$$p_r = 1.43$$

Then

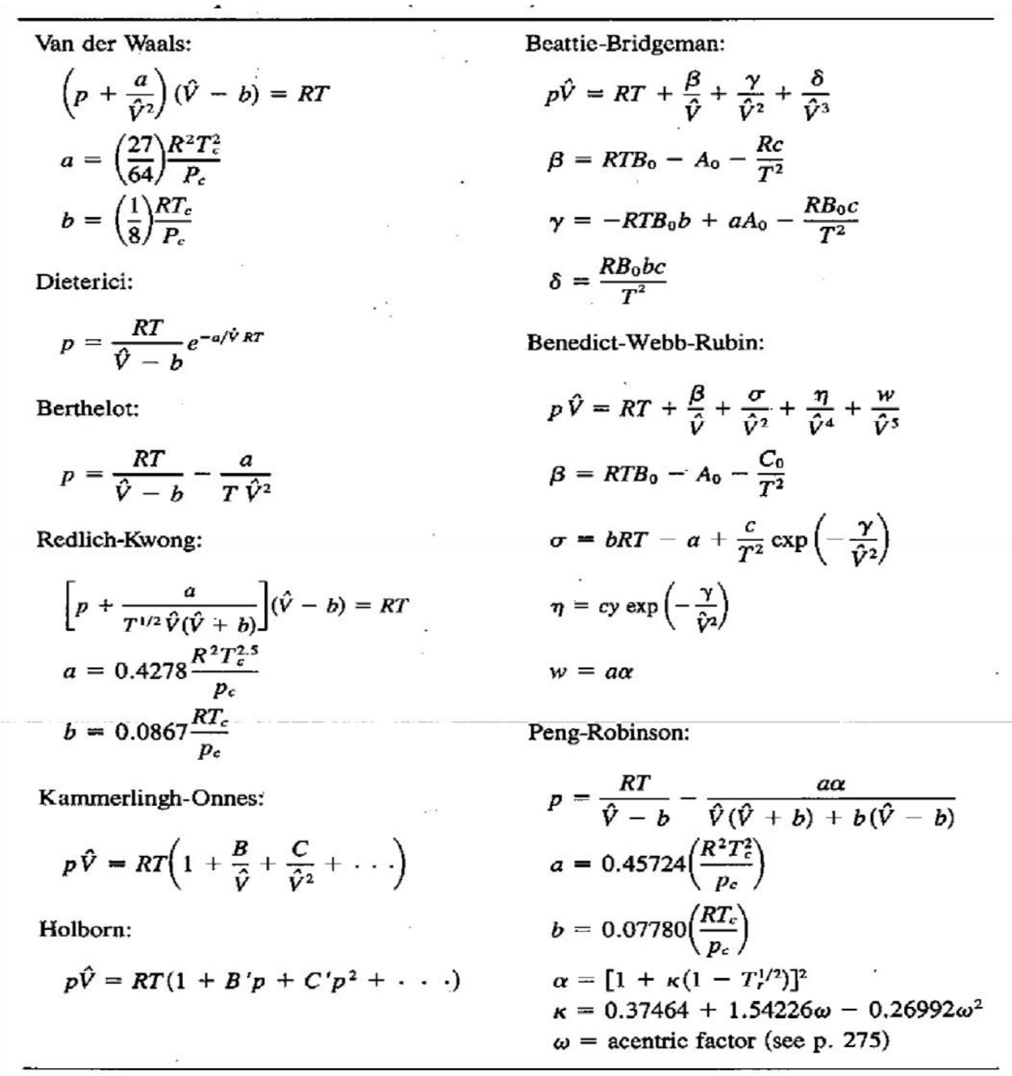
$$\begin{aligned} p &= p_r p_c \\ &= 1.43\ (5{,}035) = 7200 \text{ kPa} \end{aligned}$$

The pressure of 100 atm will not be exceeded. Even at room temperature the pressure will be less than 10^4 kPa.

13.2.2 Equations of State

- ™ Equations of state relate the p-V-T properties of a pure substance (or mixtures) by theoretical or empirical relations.
- ™ The simplest example of an equation of state is the ideal gas law itself. Table 13.2 lists a few of the commonly used equations of state (from among the hundreds that have been proposed) that involve two or more coefficients.

TABLE 3.2 Equations of State (for 1 Mole)*



Van der Waals:

$$\left(p + \frac{a}{\hat{V}^2}\right)(\hat{V} - b) = RT$$

$$a = \left(\frac{27}{64}\right)\frac{R^2T_c^2}{P_c}$$

$$b = \left(\frac{1}{8}\right)\frac{RT_c}{P_c}$$

Dieterici:

$$p = \frac{RT}{\hat{V} - b}e^{-a/\hat{V}RT}$$

Berthelot:

$$p = \frac{RT}{\hat{V} - b} - \frac{a}{T\hat{V}^2}$$

Redlich-Kwong:

$$\left[p + \frac{a}{T^{1/2}\hat{V}(\hat{V} + b)}\right](\hat{V} - b) = RT$$

$$a = 0.4278\frac{R^2T_c^{2.5}}{p_c}$$

$$b = 0.0867\frac{RT_c}{p_c}$$

Kammerlingh-Onnes:

$$p\hat{V} = RT\left(1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \cdots\right)$$

Holborn:

$$p\hat{V} = RT(1 + B'p + C'p^2 + \cdots)$$

Beattie-Bridgeman:

$$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\gamma}{\hat{V}^2} + \frac{\delta}{\hat{V}^3}$$

$$\beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = -RTB_0b + aA_0 - \frac{RB_0c}{T^2}$$

$$\delta = \frac{RB_0bc}{T^2}$$

Benedict-Webb-Rubin:

$$p\hat{V} = RT + \frac{\beta}{\hat{V}} + \frac{\sigma}{\hat{V}^2} + \frac{\eta}{\hat{V}^4} + \frac{w}{\hat{V}^5}$$

$$\beta = RTB_0 - A_0 - \frac{C_0}{T^2}$$

$$\sigma = bRT - a + \frac{c}{T^2}\exp\left(-\frac{\gamma}{\hat{V}^2}\right)$$

$$\eta = c\gamma\exp\left(-\frac{\gamma}{\hat{V}^2}\right)$$

$$w = a\alpha$$

Peng-Robinson:

$$p = \frac{RT}{\hat{V} - b} - \frac{a\alpha}{\hat{V}(\hat{V} + b) + b(\hat{V} - b)}$$

$$a = 0.45724\left(\frac{R^2T_c^2}{p_c}\right)$$

$$b = 0.07780\left(\frac{RT_c}{p_c}\right)$$

$$\alpha = [1 + \kappa(1 - T_r^{1/2})]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

ω = acentric factor (see p. 275)

- Van der Waals equation can easily be solved explicitly for (p) as follows:

$$p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

However, if you want to solve for V (or n), you can see that the equation becomes cubic in V (or n):

$$f(V) = V^3 - \left(nb + \frac{nRT}{p}\right)V^2 + \frac{n^2a}{p}V - \frac{n^3ab}{p} = 0$$

And can have multiple roots. We want a positive real root. Computer programs can solve nonlinear equations and can be used to solve for V if you have a reasonable initial guess for V, say from the ideal gas law.

Example 13.9

A cylinder 0.150 m^3 in volume containing 22.7 kg of propane C_3H_8 stands in the hot sun. A pressure gauge shows that the pressure is 4790 kPa gauge. What is the temperature of the propane in the cylinder? Use van der Waals equation.

Solution

Basis: 22.7 kg of propane

The van der Waals constants obtained from any suitable handbook

$$a = 9.24 \times 10^6 \text{ atm}\left(\frac{\text{cm}^3}{\text{g mol}}\right)^2$$

$$b = 90.7\,\frac{\text{cm}^3}{\text{g mol}}$$

$$p + \left(\frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

All the additional information you need is as follows:

$$p = \frac{(4790 + 101)\text{kPa}}{} \left| \frac{1 \text{ atm}}{101.3 \text{ kPa}} \right. = 48.3 \text{ atm abs}$$

$$R \text{ in the proper units is} = \frac{82.06(\text{cm}^3)(\text{atm})}{(\text{g mol})(\text{K})}$$

$$n = \frac{22.7}{44 \text{ kg/kg mol}} = 0.516 \text{ kg mol propane}$$

$$\left[48.3 + \frac{(0.516\times 10^3)^2(9.24\times 10^6)}{(0.150\times 10^6)^2}\right][0.150\times 10^6$$
$$-(0.516\times 10^3)(90.7)] = (0.516\times 10^3)(82.06)(T_K)$$

$$T = 384 \text{ K}$$

3.2.3 Gaseous Mixtures

In Kay's method, pseudocritical values for mixtures of gases are calculated on the assumption that each component in the mixture contributes to the pseudocritical value in the same proportion as the number of moles of that component. Thus the pseudocritical values are computed as follows:

$$p'_c = p_{c_A} y_A + p_{c_B} y_B + \cdots \qquad (8a) \; ...3.8\text{ a}$$

$$T'_c = T_{c_A} y_A + T_{c_B} y_B + \cdots \qquad (8b) \; ...3.8\text{ b}$$

Where p'$_c$ = pseudocritical pressure and T'$_c$ = pseudocritical temperature. (It has also been found convenient in some problems to calculate similarly a weighted pseudo-ideal-critical volume V'$_{ci}$.)

Then the respective pseudo-reduced values are

$$p'_r = \frac{p}{p'_c}$$

$$T'_r = \frac{T}{T'_c}$$

Example 10

A gaseous mixture has the following composition (in mole percent):

Methane, CH_4 20

Ethylene, C_2H_4 30 Nitrogen, N_2 50 at 90 atm pressure and 100°C. Compare the volume per mole as computed by the methods of:

(a) the perfect gas law

(b) the pseudoreduced technique (Kay's method)

Solution

Basis: 1 g mol of gas mixture

Additional data needed are:

Component	T_c (K)	p_c (atm)
CH_4	191	45.8
C_2H_4	283	50.5
N_2	126	33.5

$$R = 82.06\,\frac{(\text{cm}^3)(\text{atm})}{(\text{g mol})(\text{K})}$$

(a) Perfect gas law:

$$\hat{V} = \frac{RT}{p} = \frac{1(82.06)(373)}{90} = 340 \text{ cm}^3 \text{ at 90 atm and 373 K}$$

(b) According to Kay's method, we first calculate the pseudocritical values for the mixture

$$p_c' = p_{c_A}y_A + p_{c_B}y_B + p_{c_C}y_C = (45.8)(0.2) + (50.5)(0.3) + (33.5)(0.5)$$

$$= 41.2 \text{ atm}$$

$$T_c' = T_{c_A}y_A + T_{c_B}y_B + T_{c_C}y_C = (191)(0.2) + (283)(0.3) + (126)(0.5)$$

$$= 186 \text{ K}$$

Then we calculate the pseudo-reduced values for the mixture

$$p_r' = \frac{p}{p_c'} = \frac{90}{41.2} = 2.18, \qquad T_r' = \frac{T}{T_c'} = \frac{373}{186} = 2.01$$

With the aid of these two parameters we can find from Figure 3.3d Figure P3.3(c) that $z = 0.965$. Thus

$$\hat{V} = \frac{zRT}{p} = \frac{0.965(1)(82.06)(373)}{90} = 328 \text{ cm}^3 \text{ at 90 atm and 373 K}$$

Dr.Ali H.Abbar

Note

In instances in which the temperature or pressure of a gas mixture is unknown, to avoid a trial – and – error solution using the generalized compressibility charts, you can compute the pseudocritical ideal volume and a pseudoreduced ideal reduced volume V_{ri} thus

$$\hat{V}'_{c_i} = \frac{RT'_c}{p'_c} \qquad \text{and} \qquad \hat{V}'_{r_i} = \frac{\hat{V}}{\hat{V}_{c_i}}$$

$\hat{V}'_{r_i}$ can be used in lieu of p'_r or T'_r in the compressibility charts.

Vapor Pressure and Liquids

: The terms vapor and gas are used very loosely. From now on, the word vapor will be reserved to describe a gas below its critical point in a process in which the phase change is of primary interest, while the word gas or noncondensable gas will be used to describe a gas above the critical point or a gas in a process in which it cannot condense.

: If the vapor and liquid of a pure component are in equilibrium, then the equilibrium pressure is called the vapor pressure (see Figure 13.4).

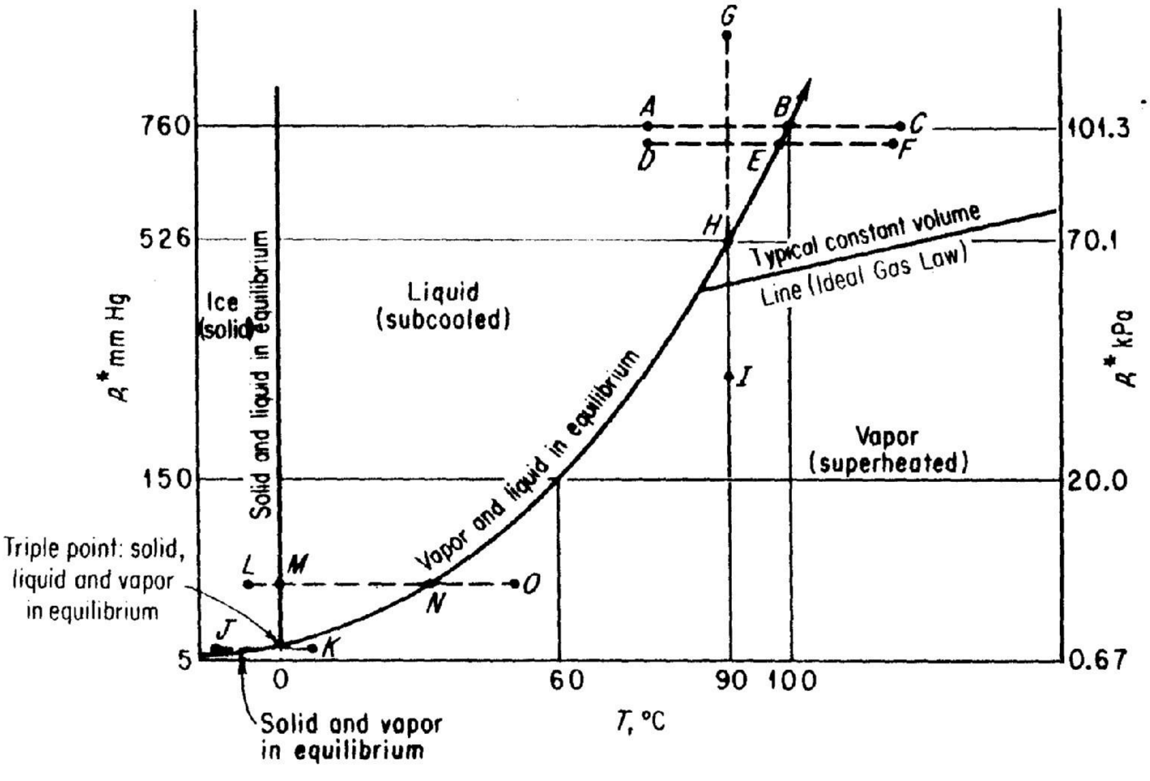


Figure 13.4 Vapor-pressure curve for water.

™ Any substance has an infinite number of boiling points, but by custom we say the <u>“normal” boiling point</u> is the temperature at which boiling takes place under a pressure of 1 atm (101.3 kPa, 760 mm Hg). (see Figure 13.5)

™When the solid passes directly into the vapor phase without first melting to become a liquid (line J-K as opposed to line L-M-N-O in Figure 13.4) it is said to sublime.

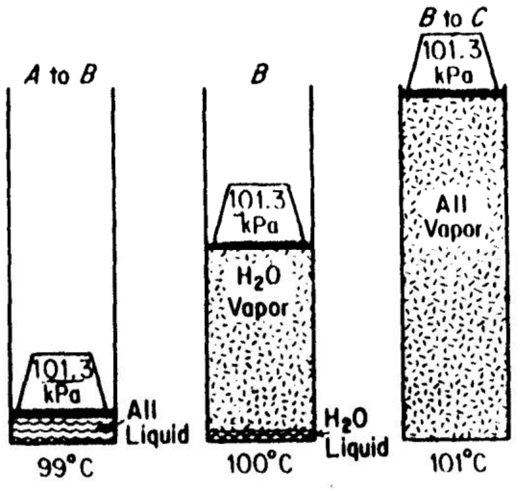


Figure 3.5 Transformation of liquid water into vapor at constant pressure. The 101.3 kPa exerted by the piston includes the force of the atmosphere above the piston.

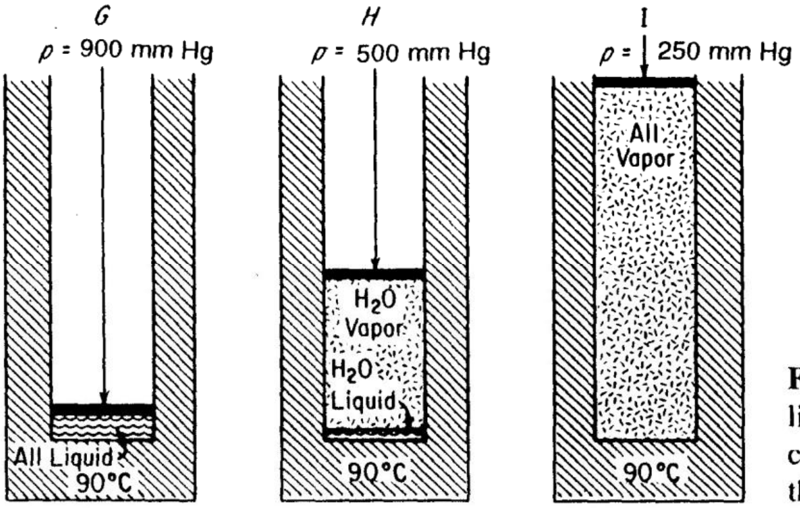


Figure 3.6 Transformation of liquid water into water vapor at a constant temperature by changing the imposed pressure.

™Another new term you will find used frequently is the word quality. A wet vapor consists of saturated vapor and saturated liquid in equilibrium. The mass fraction of vapor is known as the quality (x).

Change of Vapor Pressure with Temperature

You can see from Figure 13.4 that the function of p* versus T is not a linear Function (except as an approximation over a very small temperature range).

We will use the Antoine equation — it has sufficient accuracy for our needs:

$$\ln p^{*} = A - \frac{B}{\quad} \tag{9}$$

$$C+T$$

Where A, B, C = constants different for each substance T = temperature, K

Example 11

Calculate the vapor pressure of benzene at 50°C using the Antoine Equation. Also estimate the normal boiling point of benzene (the vapor pressure at 1 atm).

Solution

Antoine Equation $\ln(p^*) = A - \dfrac{B}{C + T}$

From Appendix G in the text the coefficients are

Benzene: $A = 15.9008$ $T = K$
$B = 2788.51$ $p^* = \text{mmHg}$
$C = -52.36$

a. Vapor Pressure of benzene at 50°C

$$\ln(p^*) = 15.9008 - \frac{2788.51}{-52.36 + (50 + 273)}$$

$$p^* = \mathbf{270\ mmHg\ abs}$$

b. At the boiling point the vapor pressure is 1 atm (760 mmHg abs.)

$$\ln(760) = 15.9008 - \frac{2788.51}{-52.36 + T}$$

Solving, T = **353.3K**

Liquid Properties

Often making density a linear function of temperature that is independent of pressure provides sufficiently accurate predictions

$$\rho = \rho_0 - \beta (T - T_0)$$ **...3.10** (10)

Where ρ_o and β are constants and ρ is the density of the liquid. Most liquids can be considered to be incompressible, that is, their density is independent of pressure.

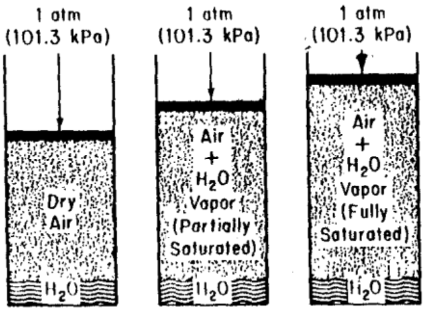
For compounds with like molecular structures, such as hydrocarbons of similar molecular weight, called ideal liquids, the density of a liquid mixture can be approximated by assuming that the weighted specific volumes are additive:

$$\hat{V}_{\text{average}} = x_1\hat{V}_1 + x_2\hat{V}_2 + \cdots x_n\hat{V}_n = \sum_{i=1}^{n} x_i\hat{V}_i$$ (11) **... 3.11**

Where n is the number of components in the mixture. For nonideal liquids or solids dissolved in liquids, experimental data or estimation techniques described in many of the references, as the specific volumes are not additive.

Saturation

Figure below shows that the volume of the air plus the water vapor increases until the air is saturated with water vapor, after which stage the volume remains constant.



Evaporation of water at constant pressure and temperature of 65°C

Assuming that the ideal gas law applies to both air and water vapor with excellent precision, we can say that the following relations hold at saturation:

$$\frac{p_{\text{air}}V}{p_{H_2O}V} = \frac{n_{\text{air}}RT}{n_{H_2O}RT}$$

or

$$\frac{p_{\text{air}}}{p_{H_2O}} = \frac{n_{\text{air}}}{n_{H_2O}} = \frac{p_{\text{air}}}{p_{\text{total}} - p_{\text{air}}}$$

in a volume V at temperature T.

Example 12

What is the minimum number of cubic meters of dry air al 20°C and 100 kpa necessary to evaporate 6.0 kg of ethyl alcohol if the total pressure remains constant al 100 kpa and the temperature remains 20°C? Assume that the air is blown through the alcohol to evaporate it in such a way that the exit pressure of the air alcohol mixture is at 100 kPa.

(Given: p^*_{alcohol} at 20°C = 5.93 kPa,   mol. wt. ethyl alcohol = 46.07).

Solution

See Figure E13.12. Assume that the process is isothermal.

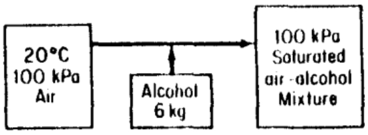


Figure E13.12

Basis: 6 kg of alcohol

$$\frac{p^*_{\text{alcohol}}}{p_{\text{air}}} = \frac{n_{\text{alcohol}}}{n_{\text{air}}}$$

$$p_{\text{air}} = p_{\text{total}} - p^*_{\text{alcohol}} = (100 - 5.93)\ \text{kPa} = 94.07\ \text{kPa}$$

$$\begin{array}{c|c|c}\text{6.0 kg alcohol} & \text{1 kg mol alcohol} & \text{94.07 kg mol air} \\ \hline & \text{46.07 kg alcohol} & \text{5.93 kg mol alcohol}\end{array} = 2.07\ \text{kg mol air}$$

$$V_{\text{air}} = \begin{array}{c|c|c}\text{2.07 kg mol air} & 8.314\ (\text{kPa})(\text{m}^3) & 293\ \text{K} \\ \hline & (\text{kg mol})(\text{K}) & 100\ \text{kPa}\end{array} = 50.3\ \text{m}^3 \text{ at } 20°\text{C and } 100\ \text{kPa}$$

♣ Another way to view this problem is to say that the final volume contains

V m^3 of alcohol at 5.93 kPa and 20°C

V m^3 of air at 94.07 kPa and 20°C

V m^3 of air plus alcohol at 100 kPa and 20°C

Thus, the volume could be calculated from the information about the alcohol

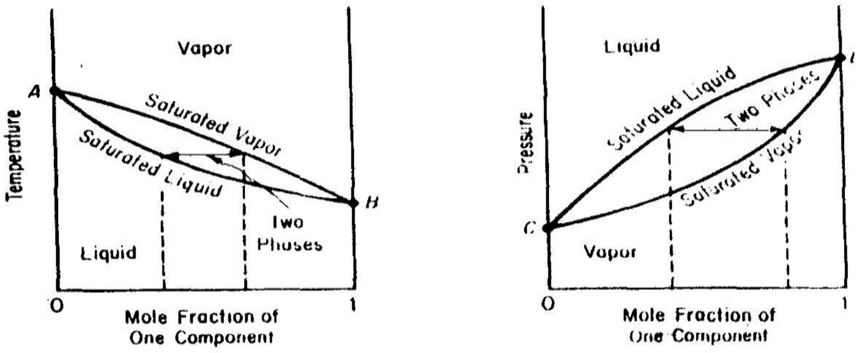
$$V_{\text{alcohol}} = \frac{\left(\frac{6}{46.07}\right) \left| \; 8.314 \; \right| \; 293}{\;\; \left| \;\; \right| \; 5.93} = 53.5 \text{ m}^3 \text{ at } 20°\text{C and } 5.93 \text{ kPa}$$

$$= V_{\text{air}} \text{ at } 94.07 \text{ kPa and } 20°\text{C}$$

$$V_{\text{air}} = \frac{53.5 \text{ m}^3 \; \left| \; 94.07 \right.}{\left| \; 100 \right.} = 50.3 \text{ m}^3 \text{ at } 100 \text{ kPa and } 20°\text{C}$$

Vapor-Liquid Equilibria for Multicomponent Systems

In two-phase vapor-liquid mixture at equilibrium, a component in one phase is in equilibrium with the same component in the other phase. The equilibrium relationship depends on the temperature, pressure, and composition of the mixture. Figure 13.7 illustrates two cases, one at constant pressure and the other at constant temperature.



(a) Constant Pressure (b) Constant Temperature

Figure 13.17 Vapor-liquid equilibrium for a binary mixture. The dashed lines show the equilibrium compositions.

Henry's law. Used primarily for a component whose mole fraction approaches zero, such as a dilute gas dissolved in as liquid:

$$p_i = H_i \, x_i \qquad (12)$$

Where p_i is the pressure in the gas phase of the dilute component at equilibrium at some temperature, and H_i is the Henry's law constant. Note that in the limit where $x_i \equiv 0$, $p_i \equiv 0$. Values of H can be found in several handbooks. Note that

$$y_i = \frac{p_i}{p_{tot}} = \frac{H_i x_i}{p_{tot}}$$

And since Hi, is roughly independent of p_{tot}, the higher the total pressure, the larger x_i.

Raoult's law. Used primarily for a component whose mole fraction approaches unity or for solutions of components quite similar in chemical nature, such as straight chain hydrocarbons. Let the subscript i denote the component, p_i be the partial pressure of component i in the gas phase, y_i be the gas-phase mole fraction, and x_i be the liquid-phase mole fraction. Then:

Note that in the limit where $x_i \equiv 1$, $p_i \equiv p_i^*$.

$$p_i = p_i^* x_i \qquad \text{...3.13} \quad (13)$$

Note that in the limit where $x_i \equiv 1$, $p_i \equiv p_i^*$.

Equilibrium constant K_i is defined using Eq. (13.13) as follows by assuming that Dalton's law applies to the gas phase ($p_i = p_t\, y_i$):

$$K_i = \frac{y_i}{x_i} = \frac{p_i^*}{p_{tot}} \qquad \text{...3.14} \quad (14)$$

Equation (14) gives reasonable estimates of K_i values at low pressures for components well below their critical temperatures, but yields values too large for components above their critical temperatures, at high pressures, and/or for polar compounds.

Bubble Point Temperature

Bubble point: The temperature at which a liquid just starts to vaporize (See Figure 13.4).

♣ To calculate the bubble point temperature (given the total pressure and liquid composition), you can write Eq. (13.14) as $y_i = K_i\, x_i$ and you know that $\sum y_i = 1$ in the vapor phase.

$$1 = \sum_{i=1}^{n} K_i x_i \qquad (15)$$

In which the K's are functions of solely the temperature and n is the number of components. For an ideal solution:

$$p_{tot} = \sum_{i=1}^{n} p_i^* x_i \qquad \text{...3.16} \quad (16)$$

And you might use Anionie's equation for p_i^*. Once the bubble point temperature is determined, the vapor composition can be calculated from

$$y_i = \frac{p_i^* x_i}{p_{tot}} \qquad \text{...3.17} \quad (17)$$

Dew Point Temperature

Dew Point: The temperature, at which the vapor just begins to condense at specified pressure, namely temperature values along the vapor pressure curve (See Figure 13.4).

♣ To calculate the dew point temperature (given the total pressure and vapor composition), you can write Eq.

(13.14) as $x_i = y_i / K_i$ and you know $\sum x_i = 1$ in the liquid phase. Consequently, you want to solve the equation

$$1 = \sum_{i=1}^{n} \frac{y_i}{K_i} \qquad (18) \; \dots 3.18$$

In which the K's are function of temperature as explained for the bubble point temperature calculation. For an ideal solution,

$$1 = p_{tot} \sum_{i=1}^{n} \frac{y_i}{p_i^*} \qquad (19)$$

Example 13

A gas containing nitrogen, benzene, and toluene is in equilibrium with 40 mole% benzene and 60 mole% toluene liquid mixtures at 100 ºC and 10 atm. Estimate the gas phase composition (mole fractions) using Raoult's law.

Antoine equation constants	A	B	C	Pressure (mm Hg) Temperature (K)
Benzene	15.9008	2788.51	- 52.36	
Toluene	16.0137	3096.52	- 53.67	

Solution

$$\ln p^* = A - \frac{B}{C+T} \Rightarrow p^*_B = \mathrm{Exp}\left(15.9008 - \frac{2788.51}{-52.36+373}\right) = 1344.9\,\mathrm{mmHg}$$

$$p^*_T = \mathrm{Exp}\left(16.0137 - \frac{3096.52}{-53.67+373}\right) = 553.8\,\mathrm{mmHg}$$

Raoult's law $p_i = p_i^* x_i$, and $p_i = y_i p_T$

$$y_B p_T = x_B p^*_B \Rightarrow y_B = \frac{0.4 \times 1344.9}{(10)(760)} = 0.071$$

$$y_T = \frac{0.6 \times 553.8}{(10)(760)} = 0.044, \qquad y_{N_2} = 1 - 0.071 - 0.044 = 0.885$$

Example 14

Air and liquid water are contained at equilibrium in a closed chamber at 75° C and 760 mm Hg. Calculate the molar composition of the gas phase. $p^*_{H_2O}$ (75° C) = 289 mm Hg

Solution

Since the gas and liquid are in equilibrium, the air must be saturated with water vapor (if it was not, more water would evaporate), so that Raoult's law may be applied:

$$y_{H_2O} = p^*_{H_2O}(75°C)/P$$

$$y_{H_2O} = \frac{289 \text{ mm Hg}}{760 \text{ mm Hg}} = \boxed{0.380 \frac{\text{mol } H_2O}{\text{mol}}}$$

$$y_{\text{dry air}} = 1 - y_{H_2O} = \boxed{0.620 \frac{\text{mol dry air}}{\text{mol}}}$$

Example 15

Use either Raoult's law or Henry's law to solve the following problems.

1. A gas containing 1.00 mole% ethane is in contact with water at 20.0° C and 20.0 atm. Estimate the mole fraction of dissolved ethane.
2. An equimolar liquid mixture of benzene (B) and toluene (T) is in equilibrium with its vapor at 30.0° C. What are the system pressure and the composition of the vapor?

(Henry's law constant for ethane in water at 20°C as 2.63 x 10^4 atm/mole fraction)

Solution

1. Hydrocarbons normally are relatively insoluble in water, so that the solution of ethane is probably extremely dilute. Let us therefore apply Henry's law.

$$x_{C_2H_6} = \frac{y_{C_2H_6}P}{H_{C_2H_6}} = \frac{(0.0100)(20.0 \text{ atm})}{2.63 \times 10^4 \text{ atm/mole fraction}} = \boxed{7.60 \times 10^{-6} \frac{\text{mol } C_2H_6}{\text{mol}}}$$

2. Since benzene and toluene are structurally similar compounds, we may apply Raoult's law.

$$\ln p^* = A - \frac{B}{C+T}$$

$$= 6.906 - \frac{1211}{T + 220.8} \xrightarrow{T\ =\ 30°C} p^*_B = 119 \text{ mm Hg}$$

$$= 6.9533 - \frac{1343.9}{T + 219.38} \xrightarrow{T\ =\ 30°C} p^*_T = 36.7 \text{ mm Hg}$$

$$p_B = x_B p^*_B = (0.500)(119 \text{ mm Hg}) = 59.5 \text{ mm Hg}$$

$$p_T = x_T p^*_T = (0.500)(36.7 \text{ mm Hg}) = 18.35 \text{ mm Hg}$$

$$P = p_B + p_T = \boxed{77.9 \text{ mm Hg}}$$

$$y_B = p_B/P = \boxed{0.764 \text{ mole benzene/mole}}$$

$$y_T = p_T/P = \boxed{0.236 \text{ mole toluene/mole}}$$

Gibb's phase rule

The rule can be applied only to systems in equilibrium.

$$F = C - P + 2 \tag{20}$$

Where

F = number of degrees of freedom (i.e., the number of independent properties that have to be specified to determine all the intensive properties of each phase of the system of interest).

C = number of components in the system.

P = number of phases that can exist in the system; a phase is a homogeneous quantity of material such as a gas, a pure liquid, a solution, or a homogeneous solid.

Example 16

Calculate the number of degrees of freedom (how many additional intensive variables must be specified to fix the system) from the phase rule for the following materials at equilibrium:

(a) Pure liquid benzene.

(b) A mixture of ice and water only.

(c) A mixture of liquid benzene, benzene vapor, and helium gas.

(d) A mixture of salt and water designed to achieve a specific vapor pressure.

What variables might be specified in each case? Solution

$$F = C - P + 2$$

(a) C = 1, P = 1, hence F = 1 – 1 + 2 = 2. The temperature and pressure might be specified in the range in which benzene remains a liquid.

(b) C = 1, P = 2, hence F = 1 – 2 + 2 = 1. Once either the temperature or the pressure is specified, the other intensive variables are fixed.

(c) C = 2, P = 2, hence F = 2 – 2 + 2 = 2. A pair from temperature, pressure, or mole fraction can be specified.

(d) C = 2, P = 2, hence F = 2 – 2 + 2 = 2. Since a particular pressure is to be achieved, you would adjust the salt concentration and the temperature of the solution.

Note in (a) and (b) it would be unlikely that a vapor phase would not exist in practice, increasing P by 1 and reducing F by one.

Problems

1. Calculate the volume in ft^3 of 10 lb mol of an ideal gas at 68°F and 30 psia.

2. A steel cylinder of volume 2 m^3 contains methane gas (CH_4) at 50°C and 250 kPa absolute. How many kilograms of methane are in the cylinder?

3. What is the value of the ideal gas constant R to use if the pressure is to be expressed in atm, the temperature in Kelvin, the volume in cubic feet, and the quantity of material in pound moles?

4. Twenty-two kilograms per hour of CH_4 are flowing in a gas pipeline at 30°C and 920 mm Hg. What is the volumetric flow rate of the CH_4 in m^3 per hour?

5. What is the density of a gas that has a molecular weight of 0.123 kg/kg mol at 300 K and 1000 kPa?

6. What is the specific gravity of CH_4 at 70°F and 2 atm compared to air at S.C.?

7. A gas has the following composition at 120°F and 13.8 psia.

Component	Mol %
N_2	2
CH_4	79
C_2H_6	19

(a) What is the partial pressure of each component?

(b) What is the volume fraction of each component?

8. (a) If the C_2H_6 were removed from the gas in problem 7, what would be the subsequent pressure in the vessel?

   (b) What would be the subsequent partial pressure of the N_2?

9. What is the ideal critical volume? What is the advantage of using V_{ci}?

10. A carbon dioxide fire extinguisher has a volume of 40 L and is to be charged to a pressure of 20 atm at a storage temperature of 20°C. Determine the mass in kilograms of CO_2 at 1 atm.

11. Calculate the pressure of 4 g mol CO_2 contained in a 6.25 x 10^{-3} m^3 fire extinguisher at 25°C.

12. You measure that 0.00220 lb mol of a certain gas occupies a volume of 0.95 ft^3 at 1 atm and 32°F. If the equation of state for this gas is $pV = nRT(1 + bp)$, where b is a constant, find the volume at 2 atm and 71°F.

13. Calculate the temperature of 2 g mol of a gas using van der Waals' equation with $a = 1.35 * l0^{-6}\ m^6(atm)(g\ mol^{-2})$, $b = 0.0322 * l0^{-3}\ (m^3)(g\ mol^{-1})$ if the pressure is 100 kPa and the volume is 0.0515 m^3.

14. Calculate the pressure of 10 kg mol of ethane in a 4.86 m^3 vessel at 300 K using two equations of state: (a) ideal gas and (b) Soave-Redlich-Kwong. Compare with your answer the observed value of 34.0 atm.

15. One pound mole of a mixture containing 0.400 lb mol of N_2 and 0.600 lb mol C_2H_4 at 50°C occupies a volume of 1.44 ft^3. What is the pressure in the vessel? Compute your answer by Kay's method.
16. Use the Antoine equation to calculate the vapor pressure of ethanol at 50°C, and compare with the experimental value (Experimental $p^* = 219.9$ mm Hg)
17. What does the term "saturated gas" mean?
18. If a container with a volumetric ratio of air to liquid water of 5 is heated to 60°C and equilibrium is reached, will there still be liquid water present? at 125°C?
19. A mixture of air and benzene contains 10 mole% benzene at 43°C and 105 kPa pressure. At what temperature does the first liquid form? What is the liquid?
20. The dew point of water in atmospheric air is 82°F. What is the mole fraction of water vapor in the air if the barometric pressure is 750 mm Hg?
21. Ten pounds of $KClO_3$ is completely decomposed and the oxygen evolved collected over water at 80°F. The barometer reads 29.7 in. Hg. What weight of saturated oxygen is obtained?
22. If a gas is saturated with water vapor, describe the state of the water vapor and the air if it is:
    (a) Heated at constant pressure.
    (b) Cooled at constant pressure.
    (c) Expanded at constant temperature.
    (d) Compressed at constant temperature.

23. Calculate (a) the pressure at the dew point for the following mixture at 100 °F and (b) the liquid composition.

Component	Mole fraction	K values at psia of		
		190	200	210
C_2H_6	0.218	3.22	3.07	2.92
C_3H_8	0.665	1.005	0.973	0.92
i-C_4H_{10}	0.1073	0.45	0.43	0.41

n- C_4H_{10}	0.0097	0.315	0.305	0.295
Total	1			

24. Is the critical point a single phase? If not, what phases are present? Repeat for the triple point (for water).

25. A vessel contains air: N_2 (g), O_2 (g), and Ar (g).

(a) How many phases, components, and degrees of freedom are there according to the phase rule?

(b) Repeat for a vessel one-third filled with liquid ethanol and two-thirds filled with N_2 plus ethanol vapor.

Answers:

1. 1883 ft^3

2. 2.98 kg

3. 1.32

4. 28.3 m^3/hr

5. 0.0493 kg/m^3

6. 1.02 (lb CH_4/ft^3 at 70 °F and 2 atm)/ (lb air/ ft^3 at S.C.)

7. N_2, 0.28 psia; CH_4, 10.9 psia; C_2H_6, 2.62 psia

8. (a) 11.12 psia at 2 ft^3 and 120°F; (b) 0.28 psia at 2 ft^3 and 120°F

9. $V_{ci} = R\,T_c/P_c$. It can be used to calculate V_{ri}, which is a parameter on the Nelson and Obert charts.

10. 1.65 kg

11. 14.9 atm

12. V = 0.60 ft^3

13. 314 K

14. (a) 50.7 atm; (b) 34.0 atm

15. 262 atm

16. predicted 220.9 mm Hg

17. The partial pressure of the vapor equals the vapor pressure of the gas. Liquid and vapor are in equilibrium.

18. Yes; yes

19. 21°C; benzene

20. 0.0373

21. 4.00 lb

22. (a) Both gas; (b) some liquid water, residual is gas; (c) both gas; (d) some liquid water, residual is gas.

23. 190 psia; C_2H_6 = 0.0677, C_3H_8 = 0.66, i-C_4H_{10} = 0.2415, n- C_4H_{10} = 0.0308.

24. No, gas and liquid in equilibrium. The triple point in the p – T projection in actually a line on the p – V – T surface. The pressure and temperature are fixed but the volume is not fixed. 25. (a) C = 3, P = 1, F = 4; (b) C = 2, P = 2, F = 2