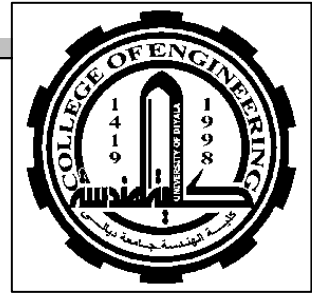


UNIVERSITY OF DAIYLA
COLLEGE OF ENGINEERING
CHEMICAL ENGINEERING DEPARTMENT



CHEMICAL ENGINEERING PRINCIPLES

For First Year Chemical Engineering Students

By

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Ph.D & Ms.C Chemical Engineering

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Reference books

1. David M. Himmelblau and James B. Riggs, "**Basic Principles and Calculations in Chemical Engineering**", Seventh Edition, (2004).
2. Richard M. Felder and Ronald W. Rousseau, "**Elementary Principles of Chemical Processes**", Third Edition, (1999).
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Chapter 1

Dimensions, Units, and Their Conversion

1.1 Units and Dimensions

Dimensions are our basic concepts of measurement such as length, time, mass, temperature, and so on; **units** are the means of expressing the dimensions, such as feet or centimeters for length, and hours or seconds for time.

In this lectures you will use the two most commonly used systems of units:

1. **SI**, formally called Le Systeme Internationale d'Unites, and informally called SI or more often (redundantly) the SI system of units.
2. **AE**, or American Engineering system of units.

Dimensions and their respective units are classified as fundamental or derived:

- **Fundamental** (or basic) dimensions/units are those that can be measured independently and are sufficient to describe essential physical quantities.
- **Derived** dimensions/units are those that can be developed in terms of the fundamental dimensions/units.

Tables 1.1 and 1.2 list both basic, derived, and alternative units in the SI and AE systems. Figure 1.1 illustrates the relation between the basic dimensions and some of the derived dimensions.

One of the best features of the SI system is that (except for time) units and their multiples and submultiples are related by standard factors designated by the **prefix** indicated in Table 1.3.

Table 1.1 SI Units

Physical Quantity	Name of Unit	Symbol for Unit*	Definition of Unit
<i>Basic SI Units</i>			
Length	metre, meter	m	
Mass	kilogramme, kilogram	kg	
Time	second	s	
Temperature	kelvin	K	
Molar amount	mole	mol	
<i>Derived SI Units</i>			
Energy	joule	J	$\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \rightarrow \text{Pa} \cdot \text{m}^3$
Force	newton	N	$\text{kg} \cdot \text{m} \cdot \text{s}^{-2} \rightarrow \text{J} \cdot \text{m}^{-1}$
Power	watt	W	$\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-3} \rightarrow \text{J} \cdot \text{s}^{-1}$
Density	kilogram per cubic meter		$\text{kg} \cdot \text{m}^{-3}$
Velocity	meter per second		$\text{m} \cdot \text{s}^{-1}$
Acceleration	meter per second squared		$\text{m} \cdot \text{s}^{-2}$
Pressure	newton per square meter, pascal		$\text{N} \cdot \text{m}^{-2}, \text{Pa}$
Heat capacity	joule per (kilogram · kelvin)		$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
<i>Alternative Units</i>			
Time	minute, hour, day, year	min, h, d, y	
Temperature	degree Celsius	°C	
Volume	litre, liter (dm^3)	L	
Mass	tonne, ton (Mg), gram	t, g	

Table 1.2 American Engineering (AE) System Units

Physical Quantity	Name of Unit	Symbol
<i>Some Basic Units</i>		
Length	foot	ft
Mass	pound (mass)	lb _m
Time	second, minute, hour, day	s, min, h (hr), day
Temperature	degree Rankine or degree Fahrenheit	°R or °F
Molar amount	pound mole	lb mol
<i>Derived Units</i>		
Force	pound (force)	lb _f
Energy	British thermal unit, foot pound (force)	Btu, (ft)(lb _f)
Power	horsepower	hp
Density	pound (mass) per cubic foot	lb _m /ft ³
Velocity	feet per second	ft/s
Acceleration	feet per second squared	ft/s ²
Pressure	pound (force) per square inch	lb _f /in. ² , psi
Heat capacity	Btu per pound (mass) per degree F	Btu/(lb _m)(°F)

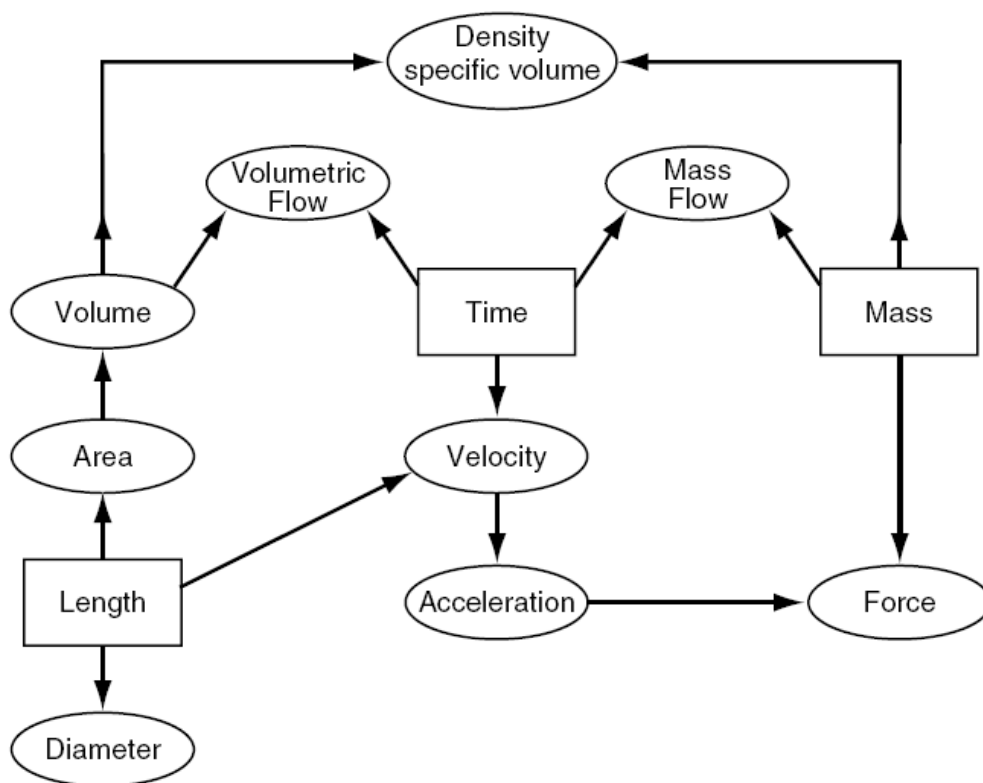


Figure 1.1 Relation between the basic dimensions (in boxes) and various derived dimensions (in ellipses).

Table 1.3 SI Prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^9	giga	G	10^{-1}	deci	d
10^6	mega	M	10^{-2}	centi	c
10^3	kilo	k	10^{-3}	milli	m
10^2	hecto	h	10^{-6}	micro	μ
10^1	deka	da	10^{-9}	nano	n

Operations with Units

The rules for handling units are essentially quite simple:

Addition, Subtraction, Equality

You can add, subtract, or equate numerical quantities only if the associated units of the quantities are the same. Thus, the operation

$$5 \text{ kilograms} + 3 \text{ joules}$$

Cannot be carried out because the units as well as the dimensions of the two terms are different. The numerical operation

$$10 \text{ pounds} + 5 \text{ grams}$$

can be performed (because the dimensions are the same, mass) only after the units are transformed to be the same, either pounds, grams, or ounces, or some other mass unit.

Multiplication and Division

You can multiply or divide unlike units at will such as

$$50(\text{kg})(\text{m})/(\text{s})$$

but you cannot cancel or merge units unless they are identical. Thus, $3 \text{ m}^2/60 \text{ cm}$ can be converted to $3 \text{ m}^2/0.6 \text{ m}$, and then to 5 m , but in m/s^2 , the units cannot be cancelled or combined.

Example 1

Add the following:

$$(a) 1 \text{ foot} + 3 \text{ seconds} \quad (b) 1 \text{ horsepower} + 300 \text{ watts}$$

Solution

The operation indicated by

$$1 \text{ ft} + 3 \text{ s}$$

has no meaning since the dimensions of the two terms are not the same. In the case of

$$1 \text{ hp} + 300 \text{ watts}$$

the dimensions are the same (energy per unit time), but the units are different. You must transform the two quantities into like units, such as horsepower or watts, before the addition can be carried out. Since $1 \text{ hp} = 746 \text{ watts}$,

$$746 \text{ watts} + 300 \text{ watts} = 1046 \text{ watts}$$

1.1.1 Conversion of Units and Conversion Factors

The procedure for converting one set of units to another is simply to multiply any number and its associated units by ratios termed **conversion factors** to arrive at the desired answer and its associated units.

If a plane travels at twice the speed of sound (assume that the speed of sound is 1100 ft/s), how fast is it going in miles per hour?

We formulate the conversion as follows

$$\frac{2 \times 1100 \text{ ft}}{\text{s}} \left| \frac{1 \text{ mi}}{5280 \text{ ft}} \right| \frac{60 \text{ s}}{1 \text{ min}} \left| \frac{60 \text{ min}}{1 \text{ hr}} \right|$$

$$\frac{\text{ft}}{\text{s}} \quad \frac{\text{mi}}{\text{s}} \quad \frac{\text{mi}}{\text{min}}$$

Example 2

(a) Convert 2 km to miles. (b) Convert 400 in.³/day to cm³/min.

Solution

(a) One way to carry out the conversion is to look up a direct conversion factor, namely 1.61 km = 1 mile:

$$\frac{2 \text{ km}}{1.61 \text{ km}} \left| \frac{1 \text{ mile}}{1.61 \text{ km}} \right| = 1.24 \text{ mile}$$

Another way is to use conversion factors you know

$$\frac{2 \text{ km}}{1 \text{ km}} \left| \frac{10^5 \text{ cm}}{1 \text{ m}} \right| \left| \frac{1 \text{ in.}}{2.54 \text{ cm}} \right| \left| \frac{1 \text{ ft}}{12 \text{ in.}} \right| \left| \frac{1 \text{ mile}}{5280 \text{ ft}} \right| = 1.24 \text{ mile}$$

$$(b) \frac{400 \text{ in.}^3}{\text{day}} \left| \left(\frac{2.54 \text{ cm}}{1 \text{ in.}} \right)^3 \right| \left| \frac{1 \text{ day}}{24 \text{ hr}} \right| \left| \frac{1 \text{ hr}}{60 \text{ min}} \right| = 4.55 \frac{\text{cm}^3}{\text{min}}$$

In part (b) note that not only are the numbers in the conversion of inches to centimeters raised to a power, but the units also are raised to the same power.

Example 3

An example of a semiconductor is ZnS with a particle diameter of 1.8 nanometers. Convert this value to (a) dm (decimeters) and (b) inches.

Solution

$$(a) \frac{1.8 \text{ nm}}{1 \text{ nm}} \left| \frac{10^{-9} \text{ m}}{1 \text{ nm}} \right| \left| \frac{10 \text{ dm}}{1 \text{ m}} \right| = 1.8 \times 10^{-8} \text{ dm}$$

$$(b) \frac{1.8 \text{ nm}}{1 \text{ nm}} \left| \frac{10^{-9} \text{ m}}{1 \text{ nm}} \right| \left| \frac{39.37 \text{ in.}}{1 \text{ m}} \right| = 7.09 \times 10^{-8} \text{ in.}$$

In the AE system the conversion of terms involving pound **mass** and pound **force** deserve special attention. Let us start the discussion with Newton's Law:

$$F = Cma \tag{1.1}$$

Where:

F = force

C = a constant whose numerical value and units depend on those selected for F, m, and a

m = mass

a = acceleration

In the SI system in which the unit of force is defined to be the Newton (N) when 1 kg is accelerated at 1 m/s², a conversion factor $C = 1 \text{ N}/(\text{Kg})(\text{m})/\text{s}^2$ must be introduced to have the force be 1 N:

$$F = \frac{1 \text{ N}}{\frac{(\text{kg})(\text{m})}{\text{s}^2}} \left| \frac{1 \text{ kg}}{\tilde{m}} \right| \left| \frac{1 \text{ m}}{\text{s}^2} \right|_{\tilde{a}} = 1 \text{ N} \quad (1.1)$$

Because the numerical value associated with the conversion factor is **1**, the conversion factor seems simple, even nonexistent, and the units are ordinarily ignored.

In the **AE** system an analogous conversion factor is required. If a mass of 1 lb_m is hypothetically accelerated at $g \text{ ft/s}^2$, where g is the acceleration that would be caused by gravity (about 32.2 ft/s² depending on the location of the mass), we can make the force be 1 lb_f by choosing the proper numerical value and units for the conversion factor C :

$$F = \left(\frac{1(\text{lb}_f)(\text{s}^2)}{32.174(\text{lb}_m)(\text{ft})} \right) \left(\frac{1 \text{ lb}_m}{\tilde{m}} \left| \frac{g \text{ ft}}{\text{s}^2} \right|_{\tilde{g}} \right) = 1 \text{ lb}_f \quad (1.2)$$

The inverse of the conversion factor with the numerical value **32.174** included is given the special symbol g_c

$$g_c = 32.174 \frac{(\text{ft})(\text{lb}_m)}{(\text{s}^2)(\text{lb}_f)}$$

But never forget that the pound (**mass**) and pound (**force**) are not the same units in the **AE** system.

Example 4

What is the potential energy in (ft)(lb_f) of a 100 lb drum hanging 10 ft above the surface of the earth with reference to the surface of the earth?

Solution

Potential energy = $P = m g h$

Assume that the 100 lb means 100 lb mass; $g =$ acceleration of gravity = 32.2 ft/s². Figure E1.4 is a sketch of the system.

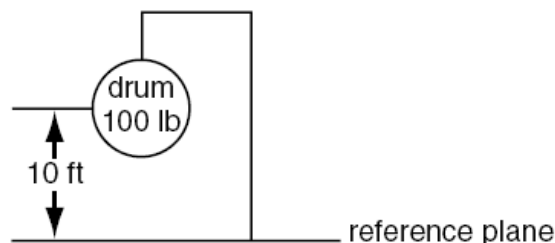


Figure E1.4

$$P = \frac{100 \text{ lb}_m}{\left| \frac{32.2 \text{ ft}}{\text{s}^2} \right|} \left| \frac{10 \text{ ft}}{32.174(\text{ft})(\text{lb}_m)} \right| \frac{(\text{s}^2)(\text{lb}_f)}{32.174(\text{ft})(\text{lb}_m)} = 1000 \text{ (ft)(lb}_f)$$

Notice that in the ratio of 32.2 ft/s^2 divided by $32.174[(\text{ft})(\text{lb}_m)]/[(\text{s}^2)(\text{lb}_f)]$, the numerical values are almost equal. Many engineers would solve the problem by saying that $100 \text{ lb} \times 10 \text{ ft} = 1000 (\text{ft})(\text{lb})$ without realizing that, in effect, they are canceling out the numbers in the g/g_c ratio, and that the lb in the solution means lb_f .

Example 5

In biological systems, production rate of glucose is $0.6 \mu\text{g mol}/(\text{mL})(\text{min})$. Determine the production rate of glucose for this system in the units of $\text{lb mol}/(\text{ft}^3)(\text{day})$.

Solution

Basis: 1 min

$$\begin{aligned} & \frac{0.6 \mu\text{g mol}}{(\text{mL})(\text{min})} \left| \frac{1 \text{ g mol}}{10^6 \mu\text{g mol}} \right| \left| \frac{1 \text{ lb mol}}{454 \text{ g mol}} \right| \left| \frac{1000 \text{ mL}}{1 \text{ L}} \right| \left| \frac{1 \text{ L}}{3.531 \times 10^{-2} \text{ ft}^3} \right| \left| \frac{60 \text{ min}}{\text{hr}} \right| \left| \frac{24 \text{ hr}}{\text{day}} \right| \\ & = 0.0539 \frac{\text{lb mol}}{(\text{ft}^3)(\text{day})} \end{aligned}$$

1.4 Dimensional Consistency (Homogeneity)

The concept of dimensional consistency can be illustrated by an equation that represents the pressure/volume/temperature behavior of a gas, and is known as van der Waals's equation.

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

Inspection of the equation shows that the constant **a** must have the units of $[(\text{pressure})(\text{volume})^2]$ for the expression in the first set of parentheses to be consistent throughout. If the units of pressure are **atm** and those of volume are cm^3 , **a** will have the units of $[(\text{atm})(\text{cm})^6]$. Similarly, **b** must have the same units as **V**, or in this particular case the units of cm^3 .

Example 6

Your handbook shows that microchip etching roughly follows the relation

$$d = 16.2 - 16.2e^{-0.021t} \quad t < 200$$

where **d** is the depth of the etch in microns (micrometers, μm) and **t** is the time of the etch in seconds. What are the units associated with the numbers 16.2 and 0.021? Convert the relation so that **d** becomes expressed in inches and **t** can be used in minutes.

Solution

Both values of **16.2** must have the associated units of microns (μm). The **exponential** must be **dimensionless** so that **0.021** must have the associated units of s^{-1} .

$$\begin{aligned} d_{\text{in}} &= \frac{16.2 \mu\text{m}}{10^6 \mu\text{m}} \left| \frac{1 \text{ m}}{39.37 \text{ in.}} \right| \left[1 - \exp \frac{-0.021}{\text{s}} \left| \frac{60 \text{ s}}{1 \text{ min}} \right| t_{\text{min}} \right] \\ &= 6.38 \times 10^{-4} (1 - e^{-1.26t_{\text{min}}}) \text{ inches} \end{aligned}$$

Non dimensional Groups:

As you proceed with the study of chemical engineering, you will find that groups of symbols may be put together, either by theory or based on experiment, that have no net units. Such collections of variables or parameters are called **dimensionless** or **nondimensional groups**. One example is the Reynolds number (group) arising in fluid mechanics.

$$\text{Reynolds number} = \frac{Dv\rho}{\mu} = N_{RE}$$

where D is the pipe diameter, say in cm; v is the fluid velocity, say in cm/s; ρ is the fluid density, say in g/cm³; and μ is the viscosity, say in centipoise, units that can be converted to g/(cm)(s). Introducing the consistent set of units for D , v , ρ , and μ into $Dv\rho/\mu$, you will find that all the units cancel out so that the numerical value of **1** is the result of the cancellation of the units.

$$\frac{\text{cm}}{\text{s}} \left| \frac{\text{cm}}{\text{s}} \right| \frac{\text{g}}{\text{cm}^3} \left| \frac{(\text{cm})(\text{s})}{\text{g}} \right|$$

Example 7

Explain without differentiating why the following differentiation cannot be correct:

$$\frac{d}{dx} \sqrt{1 + (x^2/a^2)} = \frac{2ax}{\sqrt{1 + (x^2/a^2)}}$$

where x is length and a is a constant.

Solution

- Observe that x and a must have the same units because the ratio x^2/a^2 must be dimensionless (because 1 is dimensionless).
- Thus, the left-hand side of the equation has units of $1/x$ (from d/dx). However, the right-hand side of the equation has units of x^2 (the product of ax).
- Consequently, something is wrong as the equation is not dimensionally consistent.

Questions

- Which of the following best represents the force needed to lift a heavy suitcase?
 - 25 N
 - 25 kN
 - 250 N
 - 250 kN
- Pick the correct answer(s); a watt is
 - one joule per second
 - equal to $1 \text{ (kg)(m}^2\text{)/s}^2$
 - the unit for all types of power
 - all of the above
 - none of the above
- Is kg/s a basic or derived unit in SI?
- Answer the following questions yes or no. Can you
 - divide ft by s?
 - divide m by cm?
 - multiply ft by s?
 - divide ft by cm?
 - divide m by (deg) K?
 - add ft and s?
 - subtract m and (deg) K
 - add cm and ft?
 - add cm and m²?
 - add 1 and 2 cm?
- Why is it not possible to add 1 ft and 1 ft²?
- What is g_c?
- Is the ratio of the numerator and denominator in a conversion factor equal to unity?
- What is the difference, if any, between pound force and pound mass in the AE system?

9. Could a unit of force in the SI system be kilogram force?
10. Contrast the procedure for converting units within the SI system with that for the AE system.
11. What is the weight of a one pound mass at sea level? Would the mass be the same at the center of Earth? Would the weight be the same at the center of Earth?
12. What is the mass of an object that weighs 9.80 kN at sea level?
13. Explain what dimensional consistency means in an equation.
14. Explain why the so-called dimensionless group has no net dimensions.
15. If you divide all of a series of terms in an equation by one of the terms, will the resulting series of terms be dimensionless?
16. How might you make the following variables dimensionless:
 - a. Length (of a pipe).
 - b. Time (to empty a tank full of water).

Answers:

1. (c)
2. (a)
3. Derived.
4. (a) - (e) yes; (f) and (g) no; (h) and (i) no; (j) no.
5. The dimensions are not the same.
6. A conversion factor in the American Engineering system of units.
7. Yes.
8. lb_f is force and lb_m is mass, and the dimensions are different.
9. The unit is not legal in SI.
10. In SI the magnitudes of many of the units are scaled on the basis of 10, in AE. Consequently, the units are often ignored in making conversion in SI.
11. (a) 1 lb_f in the AE system of units; (b) yes; (c) no.
12. 1000 kg.
13. All additive terms on the right-hand side of an equation must have the same dimensions as those on the left-hand side.
14. All of the units cancel out.
15. Yes.
16. (a) Divide by the radius or diameter; (b) divide by the total time to empty the tank, or by a fixed unit of time.

Problems

1. Classify the following units as correct or incorrect units in the SI system:
 - a. nm
 - b. K
 - c. sec
 - d. N/mm
 - e. kJ/(s)(m³)
2. Add 1 cm and 1 m.
3. Subtract 3 ft from 4 yards.
4. Divide $3\text{ m}^{1.5}$ by $2\text{ m}^{0.5}$.
5. Multiply 2 ft by 4 lb.
6. What are the value and units of g_c in the SI system?

7. Electronic communication via radio travels at approximately the speed of light (186,000 miles/second). The edge of the solar system is roughly at Pluto, which is 3.6×10^9 miles from Earth at its closest approach. How many hours does it take for a radio signal from Earth to reach Pluto?
8. Determine the kinetic energy of one pound of fluid moving in a pipe at the speed of 3 feet per second.
9. Convert the following from AE to SI units:
 - a. $4 \text{ lb}_m/\text{ft}$ to kg/m
 - b. $1.00 \text{ lb}_m/(\text{ft}^3)(\text{s})$ to $\text{kg}/(\text{m}^3)(\text{s})$
10. Convert the following $1.57 \times 10^{-2} \text{ g}/(\text{cm})(\text{s})$ to $\text{lb}_m/(\text{ft})(\text{s})$
11. Convert 1.1 gal to ft^3 .
12. Convert 1.1 gal to m^3 .
13. An orifice meter is used to measure the rate of flow of a fluid in pipes. The flow rate is related to the pressure drop by the following equation

$$u = c \sqrt{\frac{\Delta P}{\rho}}$$

Where u = fluid velocity

Δp = pressure drop 1force per unit area²

ρ = density of the flowing fluid

c = constant

What are the units of c in the SI system of units?

14. The thermal conductivity k of a liquid metal is predicted via the empirical equation

$$k = A \exp (B/T)$$

where k is in $\text{J}/(\text{s})(\text{m})(\text{K})$ and A and B are constants. What are the units of A and B ?

Answers:

1. (a), (d), (e) are correct.
2. Change units to get 101 cm.
3. Change units to get 9 ft.
4. 1.5 m.
5. 8 (ft)(lb).
6. 1, dimensionless.
7. 5.38 hr.
8. 0.14 (ft) (lb_f).
9. a. 5.96 kg/m; b. 16.0 kg/(m³)(s)
10. $1.06 * 10^{-3} \text{ lb}_m/(\text{ft})(\text{s})$
11. 0.15 ft^3
12. $4.16 * 10^{-3} \text{ m}^3$.
13. c is dimensionless
14. A has the same units as k ; B has the units of T .

1.2 Moles, Density and Concentration

1.2.1 Mole

In the SI system a mole is composed of 6.022×10^{23} (**Avogadro's number**) molecules. To convert the number of moles to mass and the mass to moles, we make use of the **molecular weight** – the mass per mole:

$$\text{Molecular Weight (MW)} = \frac{\text{Mass}}{\text{Mole}}$$

Thus, the calculations you carry out are

$$\text{the g mol} = \frac{\text{mass in g}}{\text{molecular weight}}$$

$$\text{the lb mol} = \frac{\text{mass in lb}}{\text{molecular weight}}$$

and

$$\text{Mass in g} = (\text{MW}) (\text{g mol})$$

$$\text{Mass in lb} = (\text{MW}) (\text{lb mol})$$

For example

$$\frac{100.0 \text{ g H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \left| \frac{1 \text{ g mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \right. = 5.56 \text{ g mol H}_2\text{O}$$

$$\frac{6.0 \text{ lb mol O}_2}{1 \text{ lb mol O}_2} \left| \frac{32.0 \text{ lb O}_2}{1 \text{ lb mol O}_2} \right. = 192 \text{ lb O}_2$$

- ❖ **The atomic weight** of an element is the mass of an atom based on the scale that assigns a mass of exactly 12 to the carbon isotope ^{12}C .
- ❖ A **compound** is composed of more than one atom, and the molecular weight of the compound is nothing more than the sum of the weights of atoms of which it is composed.

Example 8

What is the molecular weight of the following cell of a superconductor material? (The figure represents one cell of a larger structure.)

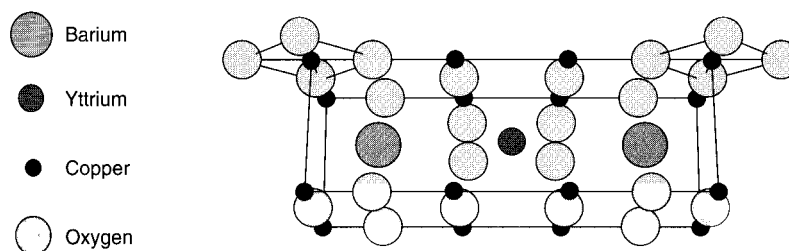


Figure E2.1

Solution

Element	Number of atoms	Atomic weights	Mass (g)
Ba	2	137.34	2(137.34)
Cu	16	63.546	16(63.546)
O	24	16.00	24(16.00)
Y	1	88.905	<u>1(88.905)</u>
		Total	1764.3

The molecular weight of the cell is 1764.3 g/g mol.

Example 9

If a bucket holds 2.00 lb of NaOH (MW=40), how many

- Pound moles of NaOH does it contain?
- Gram moles of NaOH does it contain?

Solution

$$(a) \frac{2.00 \text{ lb NaOH}}{1} \left| \frac{1 \text{ lb mol NaOH}}{40.0 \text{ lb NaOH}} \right. = 0.050 \text{ lb mol NaOH}$$

$$(b_1) \frac{2.00 \text{ lb NaOH}}{1} \left| \frac{1 \text{ lb mol NaOH}}{40.0 \text{ lb NaOH}} \right| \frac{454 \text{ g mol}}{1 \text{ lb mol}} = 22.7 \text{ g mol}$$

$$(b_2) \frac{2.00 \text{ lb NaOH}}{1 \text{ lb}} \left| \frac{454 \text{ g}}{1 \text{ lb}} \right| \frac{1 \text{ g mol NaOH}}{40.0 \text{ g NaOH}} = 22.7 \text{ g mol}$$

Example 10

How many pounds of NaOH (MW=40) are in 7.50 g mol of NaOH?

Solution

$$\frac{7.50 \text{ g mol NaOH}}{1} \left| \frac{1 \text{ lb mol}}{454 \text{ g mol}} \right| \frac{40.0 \text{ lb NaOH}}{1 \text{ lb mol NaOH}} = 0.661 \text{ lb NaOH}$$

1.2.2 Density

Density is the ratio of mass per unit volume, as for example, kg/m³ or lb/ft³. Density has both a numerical value and units. **Specific volume** is the inverse of density, such as cm³/g or ft³/lb.

$$\rho = \text{density} = \frac{\text{mass}}{\text{volume}} = \frac{m}{V}$$

$$\hat{V} = \text{specific volume} = \frac{\text{volume}}{\text{mass}} = \frac{V}{m}$$

For example, given that the density of n-propyl alcohol is 0.804 g/cm³, what would be the volume of 90.0 g of the alcohol? The calculation is

$$\frac{90.0 \text{ g}}{1} \left| \frac{1 \text{ cm}^3}{0.804 \text{ g}} \right. = 112 \text{ cm}^3$$

- ❖ In a packed bed of solid particles containing void spaces, the bulk density is

$$\rho_B = \text{bulk density} = \frac{\text{total mass of solids}}{\text{total empty bed volume}}$$

❖ A homogeneous mixture of two or more components, whether solid, liquid, or gaseous, is called a **solution**.

For some solutions, the density of the solution is

$$V = \sum_{i=1}^n V_i \quad \text{where } n = \text{number of components}$$

$$m = \sum_{i=1}^n m_i$$

$$\rho_{\text{solution}} = \frac{m}{V}$$

For others you cannot.

Specific Gravity

Specific gravity is commonly thought of as a dimensionless ratio.

$$\text{sp.gr. of } A = \text{specific gravity of } A = \frac{(\text{g/cm}^3)_A}{(\text{g/cm}^3)_{\text{ref}}} = \frac{(\text{kg/m}^3)_A}{(\text{kg/m}^3)_{\text{ref}}} = \frac{(\text{lb/ft}^3)_A}{(\text{lb/ft}^3)_{\text{ref}}}$$

- ◆ The reference substance for **liquids** and **solids** normally is **water**.
- ◆ The density of water is **1.000 g/cm³, 1000 kg/m³, or 62.43 lb/ft³ at 4°C**.
- ◆ The specific gravity of **gases** frequently is referred to **air**, but may be referred to other gases.

For Example If dibromopentane (DBP) has a specific gravity of 1.57, what is the density in (a) g/cm³? (b) lb_m/ft³? and (c) kg/m³?

$$(a) \quad \frac{1.57 \frac{\text{g DBP}}{\text{cm}^3}}{1.00 \frac{\text{g H}_2\text{O}}{\text{cm}^3}} \left| \frac{1.00 \frac{\text{g H}_2\text{O}}{\text{cm}^3}}{1.00 \frac{\text{g H}_2\text{O}}{\text{cm}^3}} \right| = 1.57 \frac{\text{g DBP}}{\text{cm}^3}$$

$$(b) \quad \frac{1.57 \frac{\text{lb DBP}}{\text{ft}^3}}{1.00 \frac{\text{lb H}_2\text{O}}{\text{ft}^3}} \left| \frac{62.4 \frac{\text{lb H}_2\text{O}}{\text{ft}^3}}{62.4 \frac{\text{lb H}_2\text{O}}{\text{ft}^3}} \right| = 97.97 \frac{\text{lb DBP}}{\text{ft}^3}$$

$$(c) \quad \frac{1.57 \text{g DBP}}{\text{cm}^3} \left| \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 \right| \frac{1 \text{ kg}}{1000 \text{ g}} = 1.57 \times 10^3 \frac{\text{kg DBP}}{\text{m}^3}$$

or

$$\frac{1.57 \frac{\text{kg DBP}}{\text{m}^3}}{1.00 \frac{\text{kg H}_2\text{O}}{\text{m}^3}} \left| \frac{1.00 \times 10^3 \text{kg H}_2\text{O}}{1.00 \times 10^3 \text{kg H}_2\text{O}} \right| = 1.57 \times 10^3 \frac{\text{kg DBP}}{\text{m}^3}$$

Example 11

If a 70% (by weight) solution of glycerol has a specific gravity of 1.184 at 15°C, what is the density of the solution in (a) g/cm³? (b) lbm/ft³? and (c) kg/m³?

Solution

$$(a) (1.184 \text{ g glycerol/cm}^3) / (1 \text{ g water/cm}^3) * (1 \text{ g water/cm}^3) = 1.184 \text{ g solution/cm}^3.$$

$$(b) (1.184 \text{ lb glycerol/ft}^3) / (1 \text{ lb water/ft}^3) * (62.4 \text{ lb water/ft}^3) = 73.9 \text{ lb solution/ft}^3.$$

$$(c) (1.184 \text{ kg glycerol/m}^3) / (1 \text{ kg water/m}^3) * (1000 \text{ kg water/m}^3) = 1.184 * 10^3 \text{ kg solution/m}^3.$$

The specific gravity of petroleum products is often reported in terms of a hydrometer scale called °API. The equation for the API scale is

$$^{\circ}\text{API} = \frac{141.5}{\text{sp.gr.} \frac{60^{\circ}\text{F}}{60^{\circ}\text{F}}} - 131.5 \quad (\text{API gravity}) \quad (2.1)$$

or

$$\text{sp.gr.} \frac{60^{\circ}}{60^{\circ}} = \frac{141.5}{^{\circ}\text{API} + 131.5} \quad (2.2)$$

The **volume** and therefore the **density** of petroleum products vary with **temperature**, and the petroleum industry has established 60 °F as the standard temperature for volume and API gravity.

Example 12

In the production of a drug having a molecular weight of 192, the exit stream from the reactor flows at a rate of 10.5 L/min. The drug concentration is 41.2% (in water), and the specific gravity of the solution is 1.024. Calculate the concentration of the drug (in kg/L) in the exit stream, and the flow rate of the drug in kg mol/min.

Solution

Take 1 kg of the exit solution as a basis for convenience.

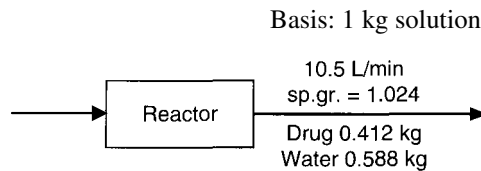


Figure E2.5

$$\text{density of solution} = \frac{1.024 \frac{\text{g soln}}{\text{cm}^3}}{1.000 \frac{\text{g H}_2\text{O}}{\text{cm}^3}} \left| \frac{1.000 \frac{\text{g H}_2\text{O}}{\text{cm}^3}}{1.000 \frac{\text{g H}_2\text{O}}{\text{cm}^3}} \right| = 1.024 \frac{\text{g soln}}{\text{cm}^3}$$

$$\frac{0.412 \text{ kg drug}}{1.000 \text{ kg soln}} \left| \frac{1.024 \text{ g soln}}{1 \text{ cm}^3} \right| \left| \frac{1 \text{ kg}}{10^3 \text{ g}} \right| \left| \frac{10^3 \text{ cm}^3}{1 \text{ L}} \right| = 0.422 \text{ kg drug/L soln}$$

To get the flow rate, take a different basis, namely 1 minute.

Basis: 1 min = 10.5 L solution

$$\frac{10.5 \text{ L soln}}{1 \text{ min}} \left| \frac{0.422 \text{ kg drug}}{1 \text{ L soln}} \right| \left| \frac{1 \text{ kg mol drug}}{192 \text{ kg drug}} \right| = 0.023 \text{ kg mol/min}$$

Flow Rate

For continuous processes the **flow rate** of a process stream is the rate at which material is transported through a pipe. The **mass flow rate** (\dot{m}) of a process stream is the **mass** (m) transported through a line per unit **time** (t).

$$\dot{m} = \frac{m}{t}$$

The **volumetric flow rate** (F) of a process stream is the **volume** (V) transported through a line per unit **time**.

$$F = \frac{V}{t}$$

The **molar flow rate** (\dot{n}) of a process stream is the number of **moles** (n) of a substance transported through a line per unit **time**.

$$\dot{n} = \frac{n}{t}$$

Mole Fraction and Mass (Weight) Fraction

- ☒ **Mole fraction** is simply the number of moles of a particular compound in a mixture or solution divided by the total number of moles in the mixture or solution.
- ☒ This definition holds for **gases, liquids, and solids**.
- ☒ Similarly, the **mass (weight) fraction** is nothing more than the **mass (weight)** of the compound divided by the total mass (weight) of all of the compounds in the mixture or solution.

Mathematically, these ideas can be expressed as

$$\text{mole fraction of } A = \frac{\text{moles of } A}{\text{total moles}}$$

$$\text{mass (weight) fraction of } A = \frac{\text{mass of } A}{\text{total mass}}$$

Mole percent and **mass (weight) percent** are the respective fractions times **100**.

Example 13

An industrial-strength drain cleaner contains 5 kg of water and 5 kg of NaOH. What are the mass (weight) fractions and mole fractions of each component in the drain cleaner container?

Solution

Basis: 10 kg of total solution

Component	kg	Weight fraction	Mol. Wt.	kg mol	Mole fraction
H ₂ O	5.00	$\frac{5.00}{10.0} = 0.500$	18.0	0.278	$\frac{0.278}{0.403} = 0.69$
NaOH	5.00	$\frac{5.00}{10.00} = 0.500$	40.0	0.125	$\frac{0.125}{0.403} = 0.31$
Total	10.00	1.000		0.403	1.00

The kilogram moles are calculated as follows:

$$\frac{5.00 \text{ kg H}_2\text{O}}{18.0 \text{ kg H}_2\text{O}} \left| \frac{1 \text{ kg mol H}_2\text{O}}{18.0 \text{ kg H}_2\text{O}} \right. = 0.278 \text{ kg mol H}_2\text{O}$$

$$\frac{5.00 \text{ kg NaOH}}{40.0 \text{ kg NaOH}} \left| \frac{1 \text{ kg mol NaOH}}{40.0 \text{ kg NaOH}} \right. = 0.125 \text{ kg mol NaOH}$$

Adding these quantities together gives the total kilogram moles.

Example 14

In normal living cells, the nitrogen requirement for the cells is provided from protein metabolism (i.e., consumption of the protein in the cells). When individual cells are commercially grown, $(\text{NH}_4)_2\text{SO}_4$ is usually used as the source of nitrogen. Determine the amount of $(\text{NH}_4)_2\text{SO}_4$ consumed in a fermentation medium in which the final cell concentration is 35 g/L in a 500 L volume of the fermentation medium. Assume that the cells contain 9 wt. % N, and that $(\text{NH}_4)_2\text{SO}_4$ is the only nitrogen source.

Solution

Basis: 500 L solution containing 35 g/L

$$\frac{500 \text{ L}}{1} \left| \frac{35 \text{ g cell}}{\text{L}} \right| \left| \frac{0.09 \text{ g N}}{1 \text{ g cell}} \right| \left| \frac{1 \text{ g mol N}}{14 \text{ g N}} \right| \times \frac{1 \text{ g mol } (\text{NH}_4)_2\text{SO}_4}{1 \text{ g mol N}} \left| \frac{132 \text{ g } (\text{NH}_4)_2\text{SO}_4}{1 \text{ g mol } (\text{NH}_4)_2\text{SO}_4} \right| = 14,850 \text{ g } (\text{NH}_4)_2\text{SO}_4$$

Analyses of Multi Components Solutions and Mixtures

The **composition of gases** will always be presumed to be given in **mole percent** or **fraction** unless specifically stated otherwise.

The **composition of liquids and solids** will be given by **mass (weight) percent** or **fraction** unless otherwise specifically stated.

For Example Table below lists the detailed composition of dry air (composition of air 21% O_2 and 79% N_2).

Basis 100 mol of air

Component	Moles = percent	Mol. wt.	Lb or kg	Weight %
O_2	21.0	32	672	23.17
N_2	79.0	28.2	2228	76.83
Total	100		2900	100.00

The average molecular weight is 2900 lb/100 lb mol = 29.0, or 2900 kg/100 kg mol = 29

1.2.3 Concentration

Concentration generally refers to the quantity of some substance per unit volume.

- Mass per unit volume (lb of solute/ft³ of solution, g of solute/L, lb of solute/barrel, kg of solute/m³).
- Moles per unit volume (lb mol of solute/ft³ of solution, g mol of solute/L, g mol of solute/cm³).
- Parts per million (**ppm**); parts per billion (**ppb**), a method of expressing the concentration of extremely dilute solutions; **ppm is equivalent to a mass (weight) fraction for solids and liquids** because the total amount of material is of a much higher order of magnitude than the amount of solute; it is a **mole fraction for gases**.
- Parts per million by volume (ppmv) and parts per billion by volume (ppbv)
- Other methods of expressing concentration with which you may be familiar are molarity (g mol/L), molality (mole solute/kg solvent), and normality (equivalents/L).

Example 14

The current OSHA 8-hour limit for HCN (MW = 27.03) in air is 10.0 ppm. A lethal dose of HCN in air is (from the Merck Index) 300 mg/kg of air at room temperature. How many mg HCN/kg air is 10.0 ppm? What fraction of the lethal dose is 10.0 ppm?

Solution

Basis: 1 kg mol of the air/HCN mixture

$$\text{The 10.0 ppm is } \frac{10.0 \text{ g mol HCN}}{10^6(\text{air} + \text{HCN})\text{g mol}} = \frac{10.0 \text{ g mol HCN}}{10^6 \text{ g mol air}}$$

$$\text{a. } \frac{10.0 \text{ g mol HCN}}{10^6 \text{ g mol air}} \left| \frac{27.03 \text{ g HCN}}{1 \text{ g mol HCN}} \right| \frac{1 \text{ g mol air}}{29 \text{ g air}} \left| \frac{1000 \text{ mg HCN}}{1 \text{ g HCN}} \right| \times \frac{1000 \text{ g air}}{1 \text{ kg air}} = 9.32 \text{ mg HCN/kg air}$$

$$\text{b. } \frac{9.32}{300} = 0.031$$

Example 15

A solution of HNO_3 in water has a specific gravity of 1.10 at 25°C . The concentration of the HNO_3 is 15 g/L of solution. What is the

- Mole fraction of HNO_3 in the solution?
- ppm of HNO_3 in the solution?

Solution

Basis: 1 L of solution

$$\frac{15 \text{ g HNO}_3}{1 \text{ L soln}} \left| \frac{1 \text{ L}}{1000 \text{ cm}^3} \right| \frac{1 \text{ cm}^3}{1.10 \text{ g soln}} = 0.01364 \frac{\text{g HNO}_3}{\text{g soln}}$$

Basis: 100 g solution

The mass of water in the solution is: $100 - 0.0134 = 99.986 \text{ g H}_2\text{O}$.

	g	MW	g mol	mol fraction
a. HNO_3	0.01364	63.02	2.164×10^{-4}	3.90×10^{-5}
H_2O	99.986	18.016	<u>5.550</u>	<u>1.00</u>
Total			5.550	1.00
b.	$\frac{0.01364}{1}$	$\frac{13,640}{10^6}$	or 13,640 ppm	

Example 16

To avoid the possibility of explosion in a vessel containing gas having the composition of 40% N_2 , 45% O_2 , and 15% CH_4 , the recommendation is to dilute the gas mixture by adding an equal amount of pure N_2 . What is the final mole fraction of each gas?

Solution

The basis is 100 moles of initial gas

Composition	Original Mixture mol%	After Addition	Final Mixture Mole Fraction
N_2	40 \longrightarrow 100	140	$140/200 = 0.70$
O_2	45	45	$45/200 = 0.23$
CH_4	15	15	$15/200 = 0.07$
Total	100	200	1.00

Questions

- Answer the following questions true or false:
 - The pound mole is comprised of 2.73×10^{26} molecules
 - The kilogram mole is comprised of 6.022×10^{26} molecules.
 - Molecular weight is the mass of a compound or element per mole.
- What is the molecular weight of acetic acid (CH₃COOH)?
- For numbers such as 2 mL of water + 2 mL of ethanol, does the sum equal to 4 mL of the solution?
- Answer the following questions true or false:
 - The inverse of the density is the specific volume.
 - Density of a substance is the mass per unit volume.
 - The density of water is less than the density of mercury.
- A cubic centimeter of mercury has a mass of 13.6 g at Earth's surface. What is the density of mercury?
- What is the approximate density of water at room temperature in kg/m³?
- For liquid HCN, a handbook gives: sp. gr. $10^{\circ}\text{C}/4^{\circ}\text{C} = 1.2675$. What does this statement mean?
- Answer the following questions true or false:
 - The density and specific gravity of mercury are the same.
 - Specific gravity is the ratio of two densities.
 - If you are given the value of a reference density, you can determine the density of a substance of interest by multiplying by the specific gravity.
 - The specific gravity is a dimensionless quantity.
- A mixture is reported as 15% water and 85% ethanol. Should the percentages be deemed to be by mass, mole, or volume?
- Answer the following questions true or false:
 - In engineering practice the compositions of liquids and solids are usually denoted in weight (mass) fraction or percent.
 - In engineering practice the composition of gases is usually denoted in mole fraction or percent.
 - e. A pseudo-average molecular weight can be calculated for a mixture of pure components whether solid, liquid, or gases.
- Do parts per million denote a concentration that is a mole ratio?
- Does the concentration of a component in a mixture depend on the amount of the mixture?
- Pick the correct answer. How many ppm are there in 1 ppb? (a) 1000, (b) 100, (c) 1, (d) 0.1, (e) 0.01, (f) 0.001?
- How many ppb are there in 1 ppm?
- Does 50 ppm represent an increase of five times a value of 10 ppm?

Answers:

- (a) T; (b) T; (c) T
- 60.05
- No
- (a) T; (b) T; (c) T
- 13.6 g/cm³
- 1000 kg/m³

7. The statement means that the density at 10°C of liquid HCN is 1.2675 times the density of water at 4°C .
8. (a) F – the units differ; (b) T; (c) T; (d) F.
9. Mass
10. (a) T; (b) T; (c) T
11. For gases but not for liquids or solids.
12. No
13. 0.001
14. 1000
15. No (4 times)

Problems

1. Convert the following:
 - a) 120 g mol of NaCl to g.
 - b) 120 g of NaCl to g mol.
 - c) 120 lb mol of NaCl to lb.
 - d) 120 lb of NaCl to lb mol.
2. Convert 39.8 kg of NaCl per 100 kg of water to kg mol of NaCl per kg mol of water.
3. How many lb mol of NaNO_3 are there in 100 lb?
4. The density of a material is 2 kg/m^3 . What is its specific volume?
5. An empty 10 gal tank weighs 4.5 lb. What is the total weight of the tank plus the water when it is filled with 5 gal of water?
6. If you add 50 g of sugar to 500 mL of water, how do you calculate the density of the sugar solution?
7. For ethanol, a handbook gives: sp. gr. $60^{\circ}\text{F} = 0.79389$. What is the density of ethanol at 60°F ?
8. The specific gravity of steel is 7.9. What is the volume in cubic feet of a steel ingot weighing 4000 lb?
9. The specific gravity of a solution is 0.80 at 70°F . How many cubic feet will be occupied by 100 lb of the solution at 70°F ?
10. A solution in water contains 1.704 kg of $\text{HNO}_3/\text{kg H}_2\text{O}$, and the solution has a specific gravity of 1.382 at 20°C . What is the mass of HNO_3 in kg per cubic meter of solution at 20°C ?
11. Forty gal/min of a hydrocarbon fuel having a specific gravity of 0.91 flows into a tank truck with a load limit of 40,000 lb of fuel. How long will it take to fill the tank in the truck?
12. Pure chlorine enters a process. By measurement it is found that 2.4 kg of chlorine pass into the process every 3.1 minutes. Calculate the molar flow rate of the chlorine in kg mol/hr.
13. Commercial sulfuric acid is 98% H_2SO_4 and 2% H_2O . What is the mole ratio of H_2SO_4 to H_2O ?
14. A compound contains 50% sulfur and 50% oxygen by mass. Is the empirical formula of the compound (1) SO, (2) SO_2 , (3) SO_3 , or (4) SO_4 ?
15. How many kg of activated carbon (a substance used in removing trace impurities) must be mixed with 38 kg of sand so that the final mixture is 28% activated carbon?
16. A gas mixture contains 40 lb of O_2 , 25 lb of SO_2 , and 30 lb of SO_3 . What is the composition of the mixture in mole fractions?
17. Saccharin, an artificial sweetener that is 3000 times sweeter than sucrose, is composed of 45.90% carbon, 2.73% hydrogen, 26.23% oxygen, 7.65% nitrogen, and 17.49% sulfur. Is the molecular formula of saccharin (a) $\text{C}_{14}\text{H}_{10}\text{O}_6\text{N}_2\text{S}_2$, (b) $\text{C}_5\text{H}_7\text{O}_3\text{NS}$, (c) $\text{C}_8\text{H}_9\text{O}_2\text{NS}$, and (d) $\text{C}_7\text{H}_5\text{O}_3\text{NS}$?

18. A mixture of gases is analyzed and found to have the following composition: CO₂ 12.0%, CO 6.0%, CH₄ 27.3%, H₂ 9.9% and N₂ 44.8%. How much will 3 lb mol of this gas weigh?
19. A liquefied mixture of n-butane, n-pentane, and n-hexane has the following composition: n-C₄H₁₀ 50%, n-C₅H₁₂ 30%, and n-C₆H₁₄ 20%. For this mixture, calculate:
- The weight fraction of each component.
 - The mole fraction of each component.
 - The mole percent of each component.
 - The average molecular weight of the mixture.
20. How many mg/L is equivalent to a 1.2% solution of a substance in water?

Answers:

- (a) 7010 g; (b) 2.05 g mol; (c) 7010 lb; (d) 2.05 lb mol
- 0.123 kg mol NaCl/kg mol H₂O
- 1.177 lb mol
- 0.5 m³/kg
- 46.2 lb
- Measure the mass of water (should be about 500g) and add it to 50 g. Measure the volume of the solution (will not be 450 mL). Divide the mass by the volume.
- 0.79389 g/cm³ (assuming the density of water is also at 60°F)
- 8.11 ft³
- 2 ft³
- 870 kg HNO₃/m³ solution.
- 132 min
- 0.654 kg mol/hr
- 9
- SO₂
- 14.8 kg
- O₂ 0.62; SO₂ 0.19; SO₃ 0.19
- (d)
- 72.17 lb
- (a) C₄: 0.50, C₅: 0.30, C₆: 0.20; (b) C₄: 0.57, C₅: 0.28, C₆: 0.15; (c) C₄: 57, C₅: 28, C₆: 15; (d) 66.4 kg/kg mol
- 12000 mg/L .

1.3 Choosing a Basis

- ❖ A **basis** is a reference chosen by you for the calculations you plan to make in any particular problem, and a proper choice of basis frequently makes the problem much easier to solve.
- ❖ The **basis** may be a **period of time** such as **hours**, or a given **mass of material**, such as **5 kg** of CO₂, or some other convenient quantity.
- ❖ For **liquids** and **solids** in which a **mass (weight)** analysis applies, a convenient basis is often **1 or 100 lb or kg**; similarly, **1 or 100 moles** is often a good choice for a **gas**.

Example 17

Gas mixture 10.0% H₂, 40.0% CH₄, 30.0% CO, and 20.0% CO₂, what is the average molecular weight of the gas?

Solution

Basis: 100 kg mol or lb mol of gas

Component	Percent = kg mol or lb mol	Mol wt.	Kg or lb
CO ₂	20.0	44.0	880
CO	30.0	28.0	840
CH ₄	40.0	16.04	642
H ₂	10.0	2.02	20
Total	100.0		2382

$$\text{Average molecular weight} = \frac{2382 \text{ kg}}{100 \text{ kg mol}} = 23.8 \text{ kg/kg mol}$$

Other Method for Solution:

$$\text{Average molecular weight} = 0.2 * 44 + 0.3 * 28 + 0.4 * 16.04 + 0.1 * 2.02 = 23.8 \text{ kg/kg mol}$$

Example 18

A liquefied mixture has the following composition: n-C₄H₁₀ 50% (MW=58), n-C₅H₁₂ 30% (MW=72), and n-C₆H₁₄ 20% (MW=86). For this mixture, calculate: (a) mole fraction of each component. (b) Average molecular weight of the mixture.

Solution

Basis: 100 kg

	% = kg	wt fr	MW	kg mol	mol fr
n - C ₄ H ₁₀	50	0.50	58	0.86	0.57
n - C ₅ H ₁₂	30	0.30	72	0.42	0.28
n - C ₆ H ₁₄	20	0.20	86	0.23	0.15
	100	1.00		1.51	1.00

$$\text{Average molecular weight} = \frac{\text{total mass}}{\text{total mol}} = \frac{100 \text{ kg}}{1.51 \text{ kg mol}} = 66$$

Example 19

In a ternary alloy such as Nd_{4.5}Fe₇₇B_{18.5} the average grain size is about 30 nm. By replacing 0.2 atoms of Fe with atoms of Cu, the grain size can be reduced (improved) to 17 nm.

- What is the molecular formula of the alloy after adding the Cu to replace the Fe?
- What is the mass fraction of each atomic species in the improved alloy?

Solution

Basis: 100 g mol (or atoms) of Nd_{4.5}Fe₇₇B_{18.5}

- The final alloy is Nd_{4.5}Fe_{76.8}B_{18.5}Cu_{0.2}.
- Use a table to calculate the respective mass fractions.

Component	Original g mol	Final g mol	MW	g	Mass fraction
Nd	4.5	4.5	144.24	649.08	0.126
Fe	77	76.8	55.85	4289.28	0.833
B	<u>18.5</u>	18.5	10.81	199.99	0.039
Cu		<u>0.2</u>	63.55	<u>12.71</u>	<u>0.002</u>
Total	100.0	100.0		5151.06	1.000

Example 20

A medium-grade bituminous coal analyzes as follows:

Component	Percent
S	2
N	1
O	6
Ash	11
Water	3
Residuum	77

The residuum is C and H, and the mole ratio in the residuum is $H/C = 9$. Calculate the weight (mass) fraction composition of the coal with the ash and the moisture omitted (ash – and moisture – free).

Solution

Take as a basis 100 kg of coal because then percent = kilograms.

Basis: 100 kg of coal

The sum of the S + N + O + ash + water is $2 + 1 + 6 + 11 + 3 = 23$ kg

We need to determine the individual kg of **C** and of **H** in the **77 kg** total residuum.

To determine the kilograms of C and H, you have to select a new basis.

Basis: 100 kg mol (Because the H/C ratio is given in terms of moles, not weight)

Component	Mole fraction	kg mol	Mol. wt.	kg	Mass fraction
H	$\frac{9}{1+9} = 0.90$	90	1.008	90.7	0.43
C	$\frac{1}{1+9} = 0.10$ $\frac{1}{10} = 1.00$	$\frac{10}{100}$	12	$\frac{120}{210.7}$	$\frac{0.57}{1.00}$

H: (77kg) (0.43) = 33.15 kg

C: (77kg) (0.57) = 43.85 kg

Finally, we can prepare a table summarizing the results on the basis of **1 kg of the coal ash-free and water-free**.

Component	kg	Wt. fraction
C	43.85	0.51
H	33.15	0.39
S	2	0.02
N	1	0.01
O	<u>6</u>	<u>0.07</u>
Total	86.0	1.00

1.4 Temperature

- ★ **Temperature** is a measure of the energy (mostly kinetic) of the molecules in a system. This definition tells us about the amount of energy.
- ★ Other scientists prefer to say that **temperature** is a property of the state of thermal equilibrium of the system with respect to other systems because temperature tells us about the capability of a system to transfer energy (as heat).

Four types of temperature:

Two based on a **relative scale**, **degrees Fahrenheit (°F)** and **Celsius (°C)**, and two based on an **absolute scale**, **degree Rankine (°R)** and **Kelvin (K)**.

Temperature Conversion

$$\Delta^{\circ}\text{F} = \Delta^{\circ}\text{R}$$

$$\Delta^{\circ}\text{C} = \Delta\text{K}$$

Also, the $\Delta^{\circ}\text{C}$ is larger than the $\Delta^{\circ}\text{F}$

$$\frac{\Delta^{\circ}\text{C}}{\Delta^{\circ}\text{F}} = 1.8 \quad \text{or} \quad \Delta^{\circ}\text{C} = 1.8 \Delta^{\circ}\text{F}$$

$$\frac{\Delta\text{K}}{\Delta^{\circ}\text{R}} = 1.8 \quad \text{or} \quad \Delta\text{K} = 1.8 \Delta^{\circ}\text{R}$$

The proper meaning of the symbols $^{\circ}\text{C}$, $^{\circ}\text{F}$, **K**, and $^{\circ}\text{R}$, as either the temperature or the unit temperature difference, must be interpreted from the context of the equation or sentence being examined.

Suppose you have the relation:

$$T_{^{\circ}\text{F}} = a + bT_{^{\circ}\text{C}}$$

What are the units of **a** and **b**? The units of **a** must be $^{\circ}\text{F}$ for consistency. The correct units for **b** must involve the conversion factor ($1.8 \Delta^{\circ}\text{F}/\Delta^{\circ}\text{C}$), the factor that converts the size of a interval on one temperature scale

$$T_{^{\circ}\text{F}} = a_{^{\circ}\text{F}} + \left(\frac{1.8 \Delta^{\circ}\text{F}}{\Delta^{\circ}\text{C}} \right) T_{^{\circ}\text{C}}$$

Unfortunately, the units for **b** are usually ignored; just the value of **b** (1.8) is employed.

- ★ The relations between $^{\circ}\text{C}$, $^{\circ}\text{F}$, **K**, and $^{\circ}\text{R}$ are:

$$T_{^{\circ}\text{R}} = T_{^{\circ}\text{F}} \left(\frac{1 \Delta^{\circ}\text{R}}{1 \Delta^{\circ}\text{F}} \right) + 460^{\circ}\text{R} \quad \text{Or} \quad T_{^{\circ}\text{R}} = T_{^{\circ}\text{F}} + 460$$

$$T_{\text{K}} = T_{^{\circ}\text{C}} \left(\frac{1 \Delta\text{K}}{1 \Delta^{\circ}\text{C}} \right) + 273 \text{ K} \quad \text{Or} \quad T_{\text{K}} = T_{^{\circ}\text{C}} + 273$$

$$T_{^{\circ}\text{F}} - 32^{\circ}\text{F} = T_{^{\circ}\text{C}} \left(\frac{1.8 \Delta^{\circ}\text{F}}{1 \Delta^{\circ}\text{C}} \right)$$

$$T_{^{\circ}\text{C}} = (T_{^{\circ}\text{F}} - 32^{\circ}\text{F}) \left(\frac{1 \Delta^{\circ}\text{C}}{1.8 \Delta^{\circ}\text{F}} \right) \quad \text{Or} \quad T_{^{\circ}\text{F}} = 1.8 T_{^{\circ}\text{C}} + 32$$

Example 21

Convert 100 °C to (a) K, (b) °F, and (c) °R.

Solution

$$(a) (100 + 273)^\circ\text{C} \frac{1 \Delta\text{K}}{1 \Delta^\circ\text{C}} = 373 \text{ K}$$

or with suppression of the Δ symbol,

$$(100 + 273)^\circ\text{C} \frac{1 \text{ K}}{1^\circ\text{C}} = 373 \text{ K}$$

$$(b) (100^\circ\text{C}) \frac{1.8 \Delta^\circ\text{F}}{1 \Delta^\circ\text{C}} + 32^\circ\text{F} = 212^\circ\text{F}$$

$$(c) (212 + 460)^\circ\text{F} \frac{1 \Delta^\circ\text{R}}{1 \Delta^\circ\text{F}} = 672^\circ\text{R}$$

or

$$(373 \text{ K}) \frac{1.8 \Delta^\circ\text{R}}{1 \Delta\text{K}} = 672^\circ\text{R}$$

Example 22

The heat capacity of sulfuric acid has the units $\text{J}/(\text{g mol})(^\circ\text{C})$, and is given by the relation

$$\text{Heat capacity} = 139.1 + 1.56 * 10^{-1} T$$

where T is expressed in °C. Modify the formula so that the resulting expression has the associated units of $\text{Btu}/(\text{lb mol})$ (°R) and T is in °R.

Solution

$$T_{\circ\text{F}} = 1.8 T_{\circ\text{C}} + 32 \longrightarrow T_{\circ\text{C}} = (T_{\circ\text{F}} - 32)/1.8$$

$$T_{\circ\text{R}} = T_{\circ\text{F}} + 460 \longrightarrow T_{\circ\text{F}} = T_{\circ\text{R}} - 460$$

$$\therefore T_{\circ\text{C}} = [T_{\circ\text{R}} - 460 - 32]/1.8$$

$$\text{heat capacity} = \left\{ 139.1 + 1.56 \times 10^{-1} \overbrace{\left[(T_{\circ\text{R}} - 460 - 32) \frac{1}{1.8} \right]}^{T_{\circ\text{C}}} \right\} \times \underbrace{\frac{1 \text{ J}}{(\text{g mol})(^\circ\text{C})} \left| \frac{1 \text{ Btu}}{1055 \text{ J}} \right| \frac{454 \text{ g mol}}{1 \text{ lb mol}} \left| \frac{1^\circ\text{C}}{1.8^\circ\text{R}} \right|}_{\text{conversion factors}} =$$

$$= 23.06 + 2.07 \times 10^{-2} T_{\circ\text{R}}$$

Note the suppression of the Δ symbol in the conversion between °C and °R.

Problems

- Complete the following table with the proper equivalent temperatures:

°C	°F	K	°R
-40	_____	_____	_____
_____	77.0	_____	_____
_____	_____	698	_____
_____	_____	_____	69.8

- The heat capacity of sulfur is $C_p = 15.2 + 2.68T$, where C_p is in $\text{J}/(\text{g mol})(\text{K})$ and T is in K. Convert this expression so that C_p is in $\text{cal}/(\text{g mol})(^\circ\text{F})$ with T in °F.

Answers:

1.

°C	°F	K	°R
-40.0	-40.0	233	420
25.0	77.0	298	537
425	796	698	1256
-234	-390	38.8	69.8

2. $C_p = 93.2 + 0.186 T_{\text{°F}}$

1.5 Pressure**Pressure and Its Units**

Pressure is defined as “the normal (perpendicular) **force** per unit **area** (Figure 5.1). The pressure at the bottom of the static (nonmoving) column of mercury exerted on the sealing plate is

$$p = \frac{F}{A} = \rho gh + p_0 \quad (5.1)$$

Where p = pressure at the bottom of the column of the fluid, F = force, A = area, ρ = density of fluid
 g = acceleration of gravity, h = height of the fluid column, and p_0 = pressure at the top of the column of fluid

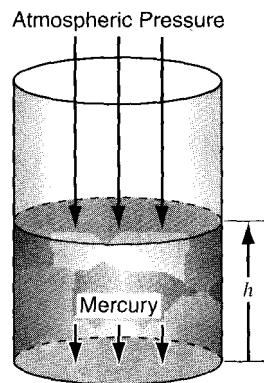


Figure 5.1 Pressure is the normal force per unit area. Arrows show the force exerted on the respective areas

For Example, suppose that the cylinder of fluid in Figure 5.1 is a column of mercury that has an area of 1 cm^2 and is 50 cm high. The density of the Hg is 13.55 g/cm^3 . Thus, the force exerted by the mercury alone on the 1 cm^2 section of the bottom plate by the column of mercury is

$$F = \frac{13.55 \text{ g}}{\text{cm}^3} \left| \frac{980 \text{ cm}}{\text{s}^2} \right| \left| \frac{50 \text{ cm}}{\text{cm}} \right| \left| \frac{1 \text{ cm}^2}{\text{cm}^2} \right| \left| \frac{1 \text{ kg}}{1000 \text{ g}} \right| \left| \frac{1 \text{ m}}{100 \text{ cm}} \right| \left| \frac{1(\text{N})(\text{s}^2)}{1(\text{kg})(\text{m})} \right|$$

$$= 6.64 \text{ N}$$

The pressure on the section of the plate covered by the mercury is the force per unit area of the mercury plus the pressure of the atmosphere

$$p = \frac{6.64 \text{ N}}{1 \text{ cm}^2} \left| \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^2 \right| \left| \frac{(1 \text{ m}^2)(1 \text{ Pa})}{(1 \text{ N})} \right| \left| \frac{1 \text{ kPa}}{1000 \text{ Pa}} \right| + p_0 = 66.4 \text{ kPa} + p_0$$

If we had started with units in the AE system, the pressure would be computed as [the density of mercury is $845.5 \text{ lb}_m/\text{ft}^3$]

$$p = \frac{845.5 \text{ lb}_m}{1 \text{ ft}^3} \left| \frac{32.2 \text{ ft}}{\text{s}^2} \right| \left| \frac{50 \text{ cm}}{2.54 \text{ cm}} \right| \left| \frac{1 \text{ in.}}{12 \text{ in.}} \right| \left| \frac{1 \text{ ft}}{32.174(\text{ft})(\text{lb}_m)} \right| \frac{(\text{s})^2(\text{lb}_f)}{+ p_0}$$

$$= 1388 \frac{\text{lb}_f}{\text{ft}^2} + p_0$$

Measurement of Pressure

Pressure, like temperature, can be expressed using either an **absolute** or a **relative scale**.

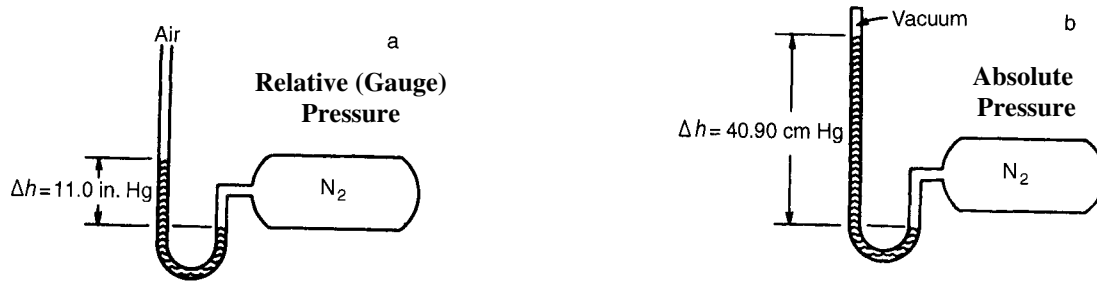


Figure 5.2 (a) **Open-end manometer** showing a pressure above atmospheric pressure. (b) **Manometer** measuring an **absolute pressure**.

The relationship between **relative** and **absolute pressure** is given by the following expression:

$$\text{Gauge Pressure} + \text{Barometer Pressure} = \text{Absolute Pressure} \quad \dots 5.2$$

- ☒ The **standard atmosphere** is defined as the pressure (in a standard gravitational field) equivalent to 1 atm or 760 mm Hg at 0°C or other equivalent.

The **standard atmosphere** is equal to

- ◆ 1.00 atmospheres (atm)
- ◆ 33.91 feet of water (ft H₂O)
- ◆ 14.7 pounds (force) per square inch absolute (psia)
- ◆ 29.92 inches of mercury (in. Hg)
- ◆ 760.0 millimeters of mercury (mm Hg)
- ◆ 1.013 * 10⁵ pascal (Pa) or newtons per square meter (N/m²); or 101.3 kPa

For Example, convert 35 psia to inches of mercury and kPa.

$$\frac{35 \text{ psia}}{14.7 \text{ psia}} \left| \frac{29.92 \text{ in. Hg}}{14.7 \text{ psia}} \right| = 71.24 \text{ in Hg}$$

$$\frac{35 \text{ psia}}{14.7 \text{ psia}} \left| \frac{101.3 \text{ kPa}}{14.7 \text{ psia}} \right| = 241 \text{ kPa}$$

For Example, What is the equivalent **pressure** to **1 kg/cm²** (i.e., **kg_f/cm²**) in pascal (g = 9.8 m/s²)
 [1 kg/cm²] * [9.8 m/s²] * [(100 cm/1 m)²] = 9.8 * 10⁴ N/m² (or Pa)

Example 23

What is the equivalent pressure to 60 Gpa (gigapascal) in

- (a) atmospheres
- (b) psia
- (c) inches of Hg
- (d) mm of Hg

Solution

Basis: 60 GPa

$$(a) \frac{60 \text{ GPa}}{1 \text{ GPa}} \left| \frac{10^6 \text{ kPa}}{1 \text{ GPa}} \right| \frac{1 \text{ atm}}{101.3 \text{ kPa}} = 0.59 \times 10^6 \text{ atm}$$

$$(b) \frac{60 \text{ GPa}}{1 \text{ GPa}} \left| \frac{10^6 \text{ kPa}}{1 \text{ GPa}} \right| \frac{14.696 \text{ psia}}{101.3 \text{ kPa}} = 8.70 \times 10^6 \text{ psia}$$

$$(c) \frac{60 \text{ GPa}}{1 \text{ GPa}} \left| \frac{10^6 \text{ kPa}}{1 \text{ GPa}} \right| \frac{29.92 \text{ in. Hg}}{101.3 \text{ kPa}} = 1.77 \times 10^7 \text{ in. Hg}$$

$$(d) \frac{60 \text{ GPa}}{1 \text{ GPa}} \left| \frac{10^6 \text{ kPa}}{1 \text{ GPa}} \right| \frac{760 \text{ mm Hg}}{101.3 \text{ kPa}} = 4.50 \times 10^8 \text{ mm Hg}$$

Example 24

The pressure gauge on a tank of CO₂ used to fill soda-water bottles reads 51.0 psi. At the same time the barometer reads 28.0 in. Hg. What is the absolute pressure in the tank in psia? See Figure E5.2.

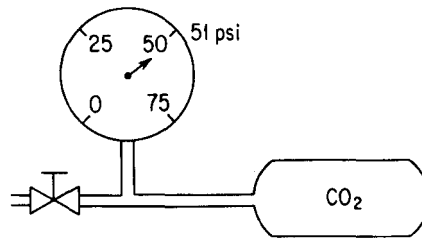


Figure E5.2

Solution

$$\text{Atmospheric pressure} = \frac{28.0 \text{ in. Hg}}{29.92 \text{ in Hg}} \left| \frac{14.7 \text{ psia}}{14.7 \text{ psia}} \right| = 13.76 \text{ psia}$$

The absolute pressure in the tank is

$$51.0 \text{ psia} + 13.76 \text{ psia} = 64.8 \text{ psia}$$

Example 25

Small animals such as mice can live (although not comfortably) at reduced air pressures down to 20 kPa absolute. In a test, a mercury manometer attached to a tank, as shown in Figure E5.3, reads 64.5 cm Hg and the barometer reads 100 kPa. Will the mice survive?

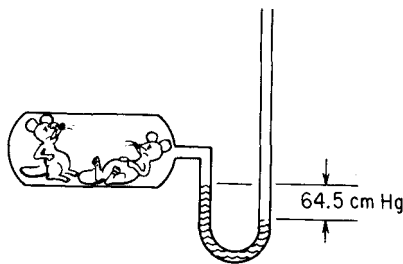


Figure E5.3

Solution

You are expected to realize from the figure that the tank is **below atmospheric pressure** because the **left leg** of the **manometer is higher** than the **right leg**, which is open to the atmosphere. Consequently, to get the **absolute pressure** you **subtract** the **64.5 cm Hg** from the **barometer reading**.

The **absolute pressure** in the tank is

$$100 \text{ kPa} - \frac{64.5 \text{ cm Hg}}{76.0 \text{ cm Hg}} \left| \frac{101.3 \text{ kPa}}{76.0 \text{ cm Hg}} \right. = 100 - 86 = 14 \text{ kPa absolute}$$

The mice probably will **not survive**.

Differential Pressure Measurements

When the columns of fluids are at equilibrium (see Figure 5.3), the relationship among ρ_1 , ρ_2 , ρ_3 , and the heights of the various columns of fluid is as follows:

$$P_1 + \rho_1 d_1 g = P_2 + \rho_2 d_2 g + \rho_3 d_3 g \quad \dots 5.3$$

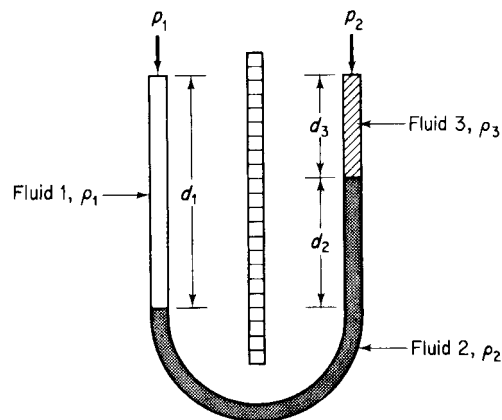


Figure 5.3 Manometer with three fluids.

Note

If fluids 1 and 3 are **gases**, and fluid 2 is **mercury**, the density of the **gas** is **so much less** than that of **mercury** that you can **ignore** the term involving the gas in Equation (5.3) for practical applications.

- * Can you show for the case in which $\rho_1 = \rho_3 = \rho$ that the manometer expression reduces to the differential manometer equation:

$$P_1 - P_2 = (\rho_2 - \rho) g d_2 \quad \dots 5.4$$

Example 26

In measuring the flow of fluid in a pipeline as shown in Figure E5.4, a differential manometer was used to determine the pressure difference across the orifice plate. The flow rate was to be calibrated with the observed pressure drop (difference). Calculate the **pressure drop** $p_1 - p_2$ in pascals for the manometer reading in Figure E5.4.

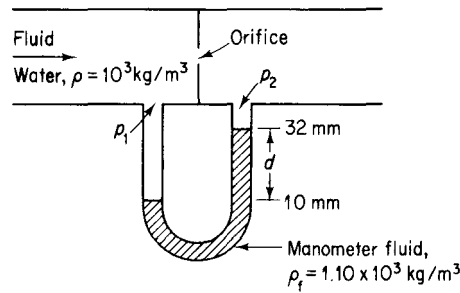


Figure E5.4

Solution

In this problem you **cannot ignore the water density** above the manometer fluid.

$$p_1 - p_2 = (\rho_f - \rho)gd$$

$$= \frac{(1.10 - 1.00)10^3 \text{ kg}}{\text{m}^3} \left| \frac{9.807 \text{ m}}{\text{s}^2} \right| \left| \frac{(22)(10^{-3})\text{m}}{(\text{kg})(\text{m})} \right| \left| \frac{1(\text{N})(\text{s}^2)}{1(\text{Pa})(\text{m}^2)} \right|$$

$$= 21.6 \text{ Pa}$$

Example 5.5

Air is flowing through a duct **under** a draft of 4.0 cm H₂O. The barometer indicates that the atmospheric pressure is 730 mm Hg. What is the absolute pressure of the air in inches of mercury? See Figure E5.5

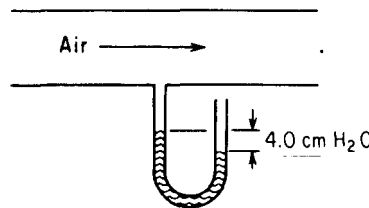


Figure E5.5

Solution

In this problem you **can ignore the gas density** above the manometer fluid and the air above the open end of the manometer.

$$\text{Atmospheric pressure} = \frac{730 \text{ mm Hg}}{760 \text{ mm Hg}} \left| \frac{29.92 \text{ in. Hg}}{1} \right| = 28.7 \text{ in. Hg}$$

Next, convert 4.0 cm H₂O to in. Hg:

$$\frac{4.0 \text{ cm H}_2\text{O}}{2.54 \text{ cm}} \left| \frac{1 \text{ in.}}{12 \text{ in.}} \right| \left| \frac{1 \text{ ft}}{33.91 \text{ ft H}_2\text{O}} \right| \left| \frac{29.92 \text{ in. Hg}}{1} \right| = 0.12 \text{ in. Hg}$$

Since the reading is 4.0 cm H₂O draft (**under atmospheric**), the absolute reading in uniform units is

$$28.7 \text{ in. Hg} - 0.12 \text{ in. Hg} = 28.6 \text{ in. Hg absolute}$$

Questions

- Figure SAT5.1Q2 shows four closed containers completely filled with water. Order the containers from the one exerting the highest pressure to the lowest on their respective base.

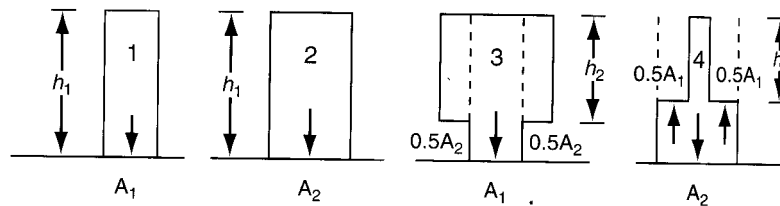


Figure SAT5.1Q2

2. Answer the following questions true or false:
 - a. Atmospheric pressure is the pressure of the air surrounding us and changes from day to day
 - b. The standard atmosphere is a constant reference atmosphere equal to 1.000 atm or the equivalent pressure in other units.
 - c. Absolute pressure is measured relative to a vacuum.
 - d. Gauge pressure is measured upward relative to atmospheric pressure.
 - e. Vacuum and draft pressures are measured downward from atmospheric pressure.
 - f. You can convert from one type of pressure measurement to another using the standard atmosphere.
 - g. A manometer measures the pressure difference in terms of the height of fluid (s) in the manometer tube.
3. What is the equation to convert gauge pressure to absolute pressure?
4. What are the values and units of the standard atmosphere for six different methods of expressing pressure?
5. What is the equation to convert vacuum pressure to absolute pressure?

Answers:

1. 3 is the highest pressure; next are 1 and 2, which are the same; and 4 is last. The decisions are made by dividing the weight of water by the base area.
2. All are true
3. Gauge pressure + barometric pressure = absolute pressure
4. See lectures
5. Barometric pressure - vacuum pressure = absolute pressure

Problems

1. Convert a pressure of 800 mm Hg to the following units:
 - a. psia b. kPa c. atm d. ft H₂O
2. Your textbook lists five types of pressures: atmospheric pressure, barometric pressure, gauge pressure, absolute pressure, and vacuum pressure.
 - a. What kind of pressure is measured by the device in Figure SAT5.2P2A?

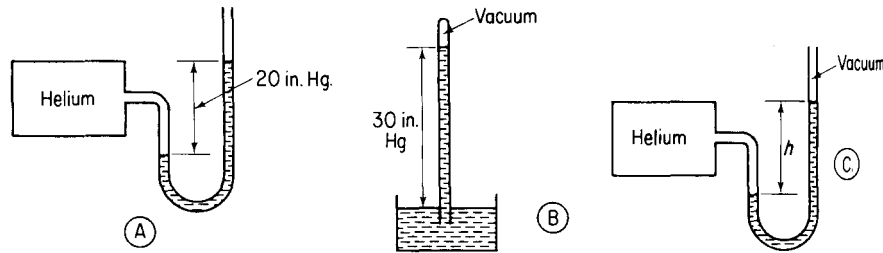


Figure SAT5.2P2A

- b. What kind of pressure is measured by the device in Figure SAT5.2P2B?
- c. What would be the reading in Figure SAT5.2P2C assuming that the pressure and temperature inside and outside the helium tank are the same as in parts (a) and (b)?
3. An evaporator shows a reading of 40 kPa vacuum. What is the absolute pressure in the evaporator in kPa?
4. A U-tube manometer filled with mercury is connected between two points in a pipeline. If the manometer reading is 26 mm of Hg, calculate the pressure difference in kPa between the points when (a) water is flowing through the pipeline, and (b) also when air at atmospheric pressure and 20°C with a density of 1.20 kg/m³ is flowing in the pipeline.
5. A Bourdon gauge and a mercury manometer are connected to a tank of gas, as shown in Figure SAT5.3P2. If the reading on the pressure gauge is 85 kPa, what is h in centimeters of Hg?

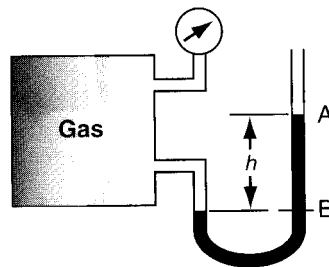


Figure SAT5.3P2

Answers:

1. (a) 15.5; (b) 106.6; (c) 1.052; (d) 35.6
2. (A) Gauge pressure; (B) barometric pressure, absolute pressure; (C) 50 in. Hg
3. In the absence of a barometric pressure value, assume 101.3 kPa. The absolute pressure is 61.3 kPa.
4. The Hg is static. (a) 3.21 kPa; (b) 3.47 kPa
5. 63.8 cm Hg.

Chapter Two

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**”

Open and Closed Systems

a. System

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 H₂O**. 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**.

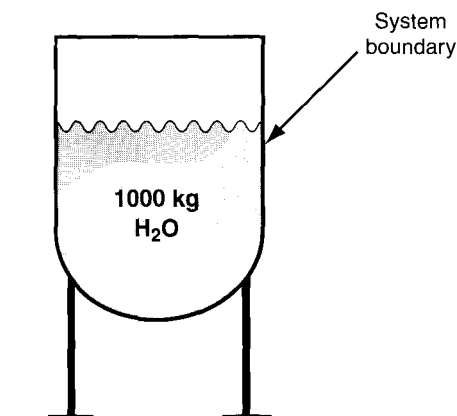


Figure 1 Closed system.

c. Open System

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

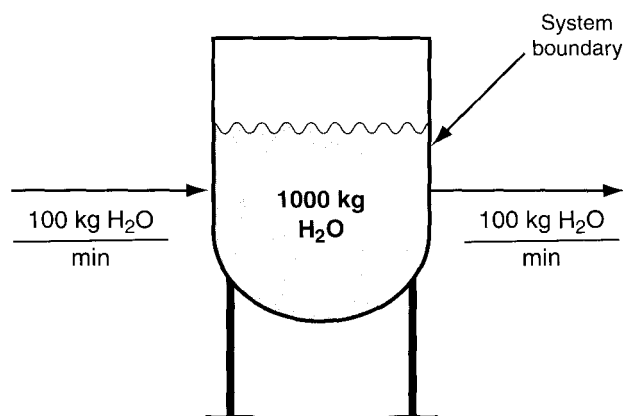


Figure 2 Open steady – state system.

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 **conditions** inside the process (specifically the amount of water in the vessel in Figure 2) **remain unchanged with time**, and
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.

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**.

★ 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**.

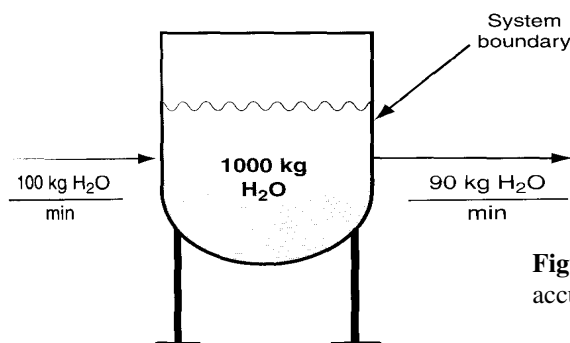


Figure 3 Initial conditions for an open unsteady – state system with accumulation.

★ 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).

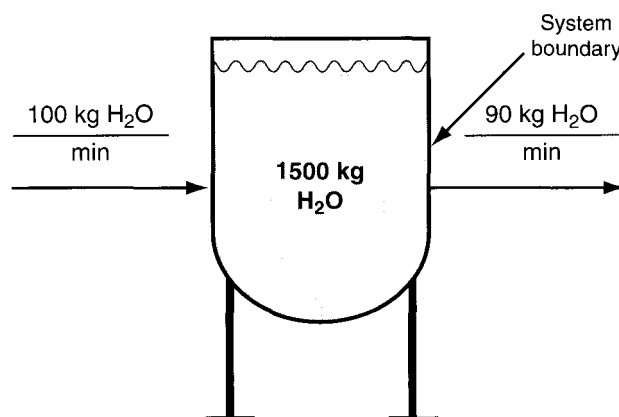


Figure 4 The condition of the open unsteady – state system with accumulation after 50 minutes.

- ★ **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.

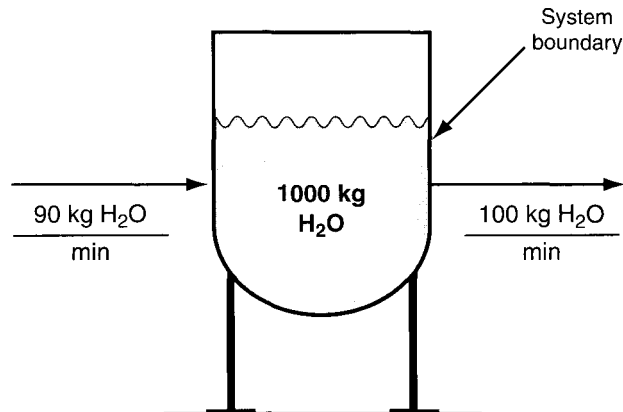


Figure 5 Initial conditions for an unsteady – state process with negative accumulation.

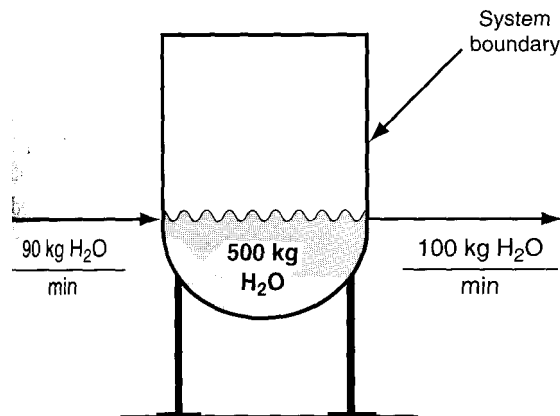


Figure 6 Condition of the open unsteady – state system with negative accumulation after 50 minutes.

- ★ **The material balance for a single component process is**

$$\left\{ \begin{array}{l} \text{Accumulation of material} \\ \text{within the system} \end{array} \right\} = \left\{ \begin{array}{l} \text{Total flow into} \\ \text{the system} \end{array} \right\} - \left\{ \begin{array}{l} \text{Total flow out} \\ \text{of the system} \end{array} \right\} \dots 6.1$$

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.

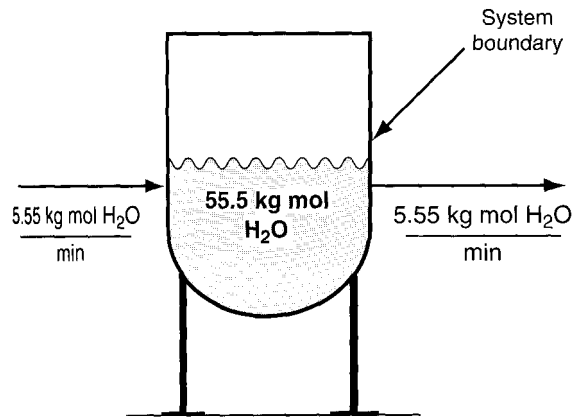


Figure 7 The system in Figure 2 with the flow rates shown in kg mol.

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

$$\text{What goes in must come out} \quad (\text{In} = \text{Out}) \quad \dots 6.2$$

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

$$\{\text{Accumulation}\} = \left\{ \begin{array}{l} \text{Final material} \\ \text{in the system} \end{array} \right\} - \left\{ \begin{array}{l} \text{Initial material} \\ \text{in the system} \end{array} \right\} \quad (6.3)$$

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**

$$\left\{ \begin{array}{l} \text{Final material} \\ \text{in the system} \\ \text{at } t_2 \end{array} \right\} - \left\{ \begin{array}{l} \text{Initial material} \\ \text{in the system} \\ \text{at } t_1 \end{array} \right\} = \left\{ \begin{array}{l} \text{Flow into} \\ \text{the system} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\} - \left\{ \begin{array}{l} \text{Flow out of} \\ \text{the system} \\ \text{from } t_1 \text{ to } t_2 \end{array} \right\} \dots 6.4$$

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 \$1.349 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,

$$\therefore y = 1 - x$$

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

$$\begin{array}{c} \text{Accumulation} \\ \left| \frac{89 \text{ octane}}{1 \text{ gal}} \right| \frac{1 \text{ gal}}{1} - 0 = \left| \frac{87 \text{ octane}}{1 \text{ gal}} \right| \frac{x \text{ gal}}{1} + \left| \frac{93 \text{ octane}}{1 \text{ gal}} \right| \frac{(1 - x) \text{ gal}}{1} \end{array}$$

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

The cost of the blended gasoline is $(2/3) (\$1.149) + (1/3) (\$1.349) = \$ 1.216$

A value less than the cost of the 89 octane gasoline (\$1.269).

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**.

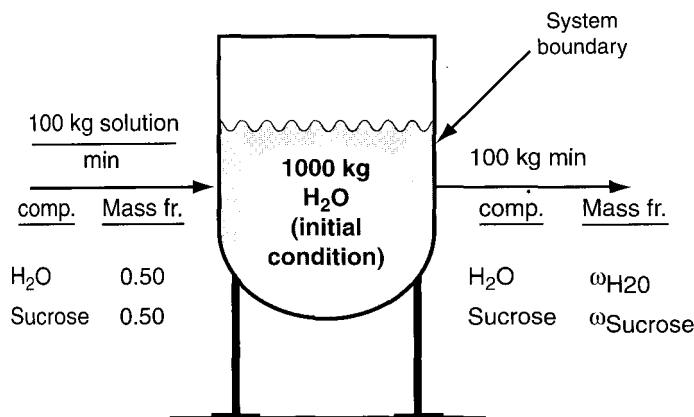


Figure 8 An open system involving two components.

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 **$F_1 = 9000 \text{ kg/hr}$ as the basis, or $F_2 = 1000 \text{ kg/hr}$ 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**:

Balances	Flow in		Flow out	Accum.
	F_1	F_2		
NaOH	450	500	950	= 0
H ₂ O	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 H₂O = 18).

$$\begin{aligned} \text{NaOH: } & \frac{450}{40} = 11.25 & \frac{500}{40} = 12.50 & \frac{950}{40} = 23.75 \\ \text{H}_2\text{O: } & \frac{8550}{18} = 475 & \frac{500}{18} = 27.78 & \frac{9050}{18} = 502.78 \end{aligned}$$

Then the component and total balances in **kg mol** are:

Balances	Flow in		Flow out	Accum.
	F_1	F_2		
NaOH	11.25	12.50	23.75	= 0
H ₂ O	475	27.78	502.78	= 0
Total	486.25	40.28	536.53	= 0

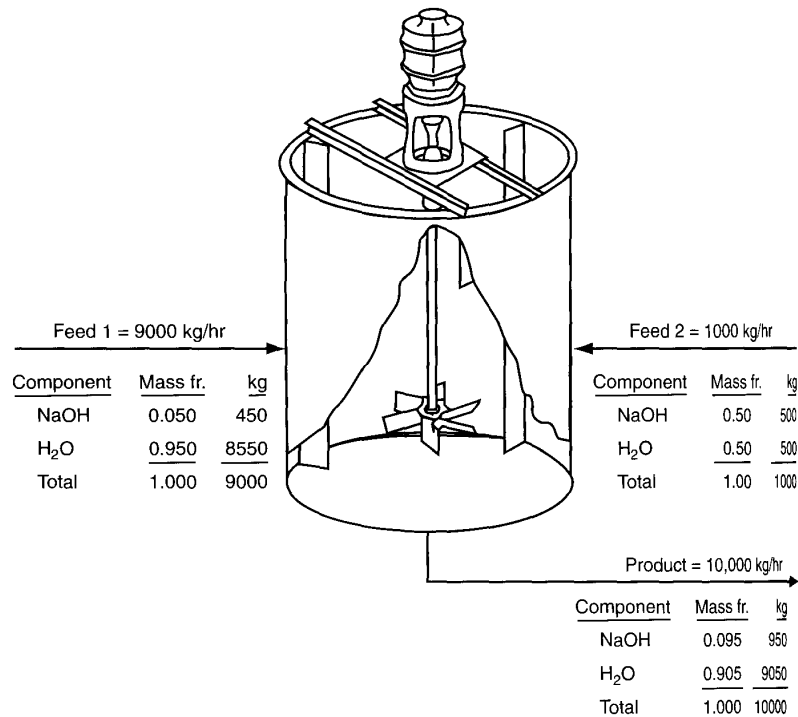


Figure 9 Mixing of a dilute stream of NaOH with a concentrated stream of NaOH. Values below the stream arrows are based on 1 hour of operation.

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/cm³.

Solution

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

Basis = 1 hour

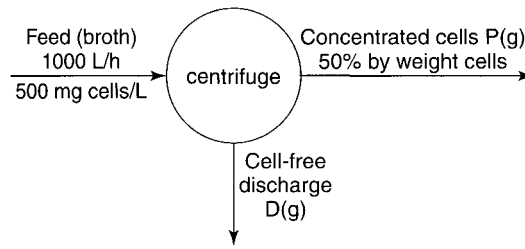


Figure E6.2

M.B. on cells

In (mass) = Out (mass)

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

P = 1000 g

M.B. on fluid

In (mass) = Out (mass)

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

D = (10⁶ - 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 **HCl** reacts with **NaOH** by the following reaction:

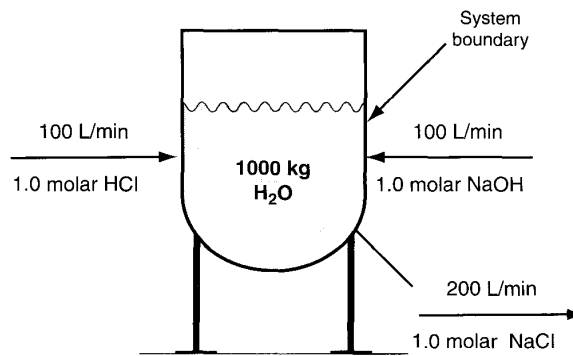
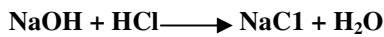


Figure 10 Reactor for neutralizing HCl with NaOH.

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

$$\left\{ \begin{array}{c} \text{Accumulation} \\ \text{within the} \\ \text{system} \end{array} \right\} = \left\{ \begin{array}{c} \text{Input} \\ \text{through} \\ \text{the system} \\ \text{boundaries} \end{array} \right\} - \left\{ \begin{array}{c} \text{Output} \\ \text{through} \\ \text{the system} \\ \text{boundaries} \end{array} \right\} + \left\{ \begin{array}{c} \text{Generation} \\ \text{within the} \\ \text{system} \end{array} \right\} - \left\{ \begin{array}{c} \text{Consumption} \\ \text{within the} \\ \text{system} \end{array} \right\} \quad \dots 6.5$$

Material Balances for Batch and Semi-Batch Processes

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

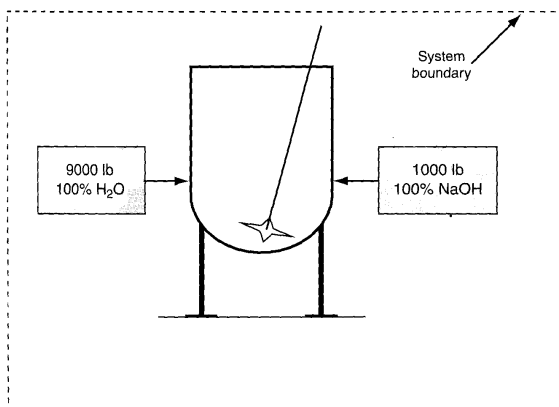


Figure 11a The initial state of a batch mixing process.

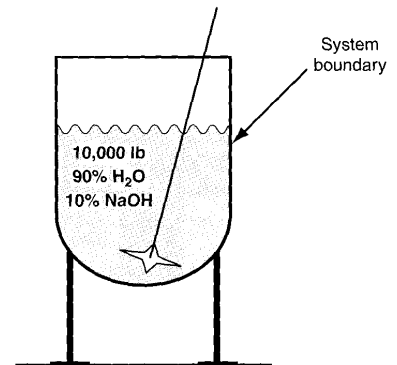


Figure 11b The final state of a batch mixing process.

- ◆ 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

H₂O = 9,000 lb

Total = 10,000 lb

Initial conditions: All value = 0

Flows in:

NaOH = 1,000 lb

H₂O = 9,000 lb

Total 10,000 lb

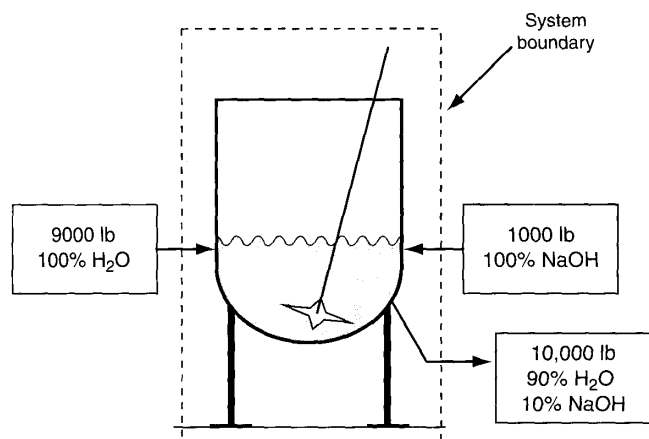


Figure 12 The batch process in Figure 11 represented as an open system.

- ☒ 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.
- ☒ 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:

$$\text{NaOH} = 1,000 \text{ lb}$$

$$\underline{\text{H}_2\text{O}} = 9,000 \text{ lb}$$

$$\text{Total} = 10,000 \text{ lb}$$

Flows out: All values = 0

Flows in:

$$\text{NaOH} = 1,000 \text{ lb}$$

$$\underline{\text{H}_2\text{O}} = 9,000 \text{ lb}$$

$$\text{Total} = 10,000 \text{ lb}$$

Initial conditions: All values = 0

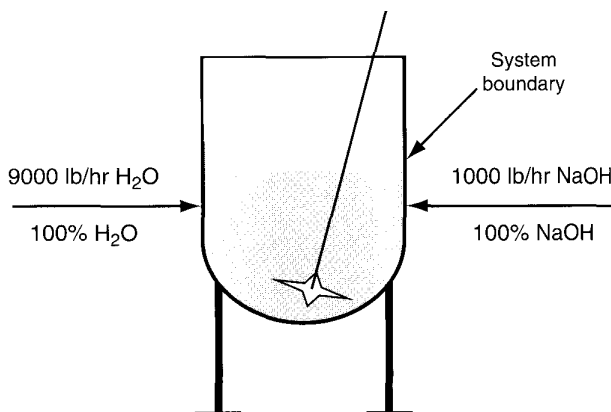


Figure 6.13 Initial condition for the semi-batch mixing process. Vessel is empty.

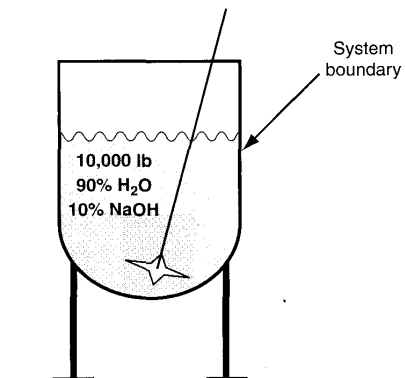


Figure 13b Condition of a semi-batch mixing process after 1 hour of operation.

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/cm³).

Solution

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

The initial mass of the motor oil in the tank was

$$(10000 \text{ gal})(3.785 \text{ lit/1 gal})(1000 \text{ cm}^3/1 \text{ lit})(0.8 \text{ g/cm}^3)(1 \text{ lb}/454 \text{ g}) = 66700 \text{ lb}$$

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

<u>Initial</u>	=	<u>unloaded</u>	+	<u>residual discharged on cleaning</u>
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?
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
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:	<u>Pounds per hour</u>
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, (polychlorinated 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?

Answers:

1. 7,740 lb/hr
2. 1.49×10^{-3} mg/L.

2.2 General Strategy for Solving Material Balance Problems**Problem Solving**

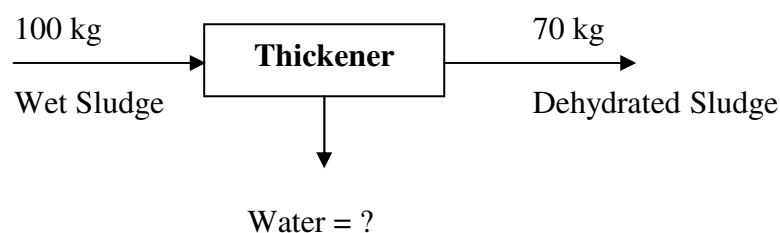
An orderly method of analyzing problems and presenting their solutions represents training in logical thinking that is of considerably greater value than mere knowledge of how to solve a particular type of problem.

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.

Example 4

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

$$\underline{\text{In}} = \underline{\text{Out}}$$

$$100 \text{ kg} = 70 \text{ kg} + \text{kg of water}$$

Consequently, the water amounts to 30 kg.

Example 5

A continuous mixer mixes NaOH with H₂O 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 H₂O 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.

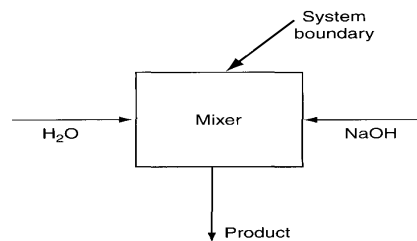
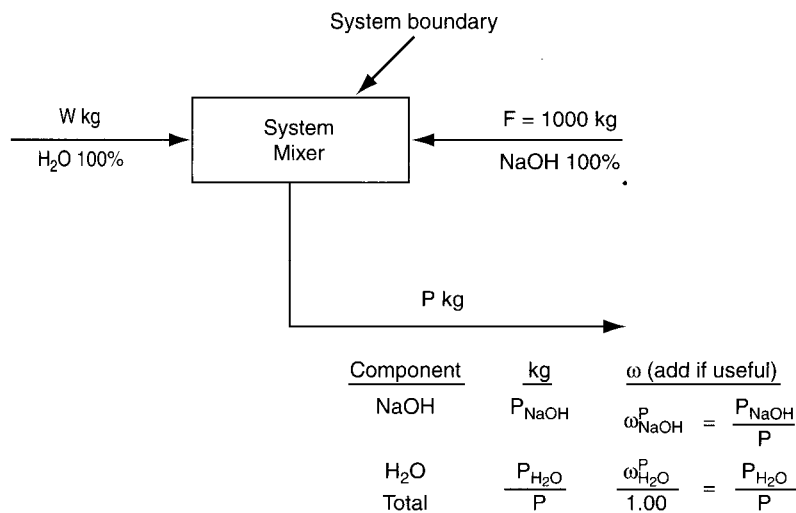


Figure E7.2

2. Because no contrary information is provided about the composition of the H₂O and NaOH streams, we will assume that they are 100% H₂O and NaOH, respectively.



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 $P_{\text{H}_2\text{O}}$.
5. You can write three material balances:
 - one for the NaOH
 - one for the H₂O
 - 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

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

$$\text{H}_2\text{O balance: } W = P_{\text{H}_2\text{O}} \quad \text{or} \quad W - P_{\text{H}_2\text{O}} = 0 \quad (2)$$

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

$$\text{Sum of components in } P: P_{\text{NaOH}} + P_{\text{H}_2\text{O}} = P \quad \text{or} \quad P_{\text{NaOH}} + P_{\text{H}_2\text{O}} - P = 0 \quad (4)$$

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:

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

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

7. Solve equations:

$$W = 0.9P \text{ substitute in total balance } 1000 + 0.9P = P$$

$$\therefore P = 10000 \text{ kg \& } W = 0.9 * 10000 = 9000 \text{ kg} \quad (\text{The basis is still 1 hr } (F_{\text{NaOH}} = 1000 \text{ kg}))$$

From these two values you can calculate the amount of H₂O and NaOH in the product

$$\text{From the } \begin{cases} \text{NaOH balance:} \\ \text{H}_2\text{O balance:} \end{cases} \text{ you get } \begin{cases} P_{\text{NaOH}} = 1000 \text{ kg} \\ P_{\text{H}_2\text{O}} = 9000 \text{ kg} \end{cases}$$

Then

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

$$\omega_{\text{H}_2\text{O}}^P = \frac{9,000 \text{ kg H}_2\text{O}}{10,000 \text{ kg Total}} = 0.9$$

Note

$$\omega_{\text{NaOH}}^P + \omega_{\text{H}_2\text{O}}^P = 1$$

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

$$P_{\text{NaOH}} + P_{\text{H}_2\text{O}} = \dot{P}$$

$$1,000 + 9,000 = 10,000$$

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 (1) 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.

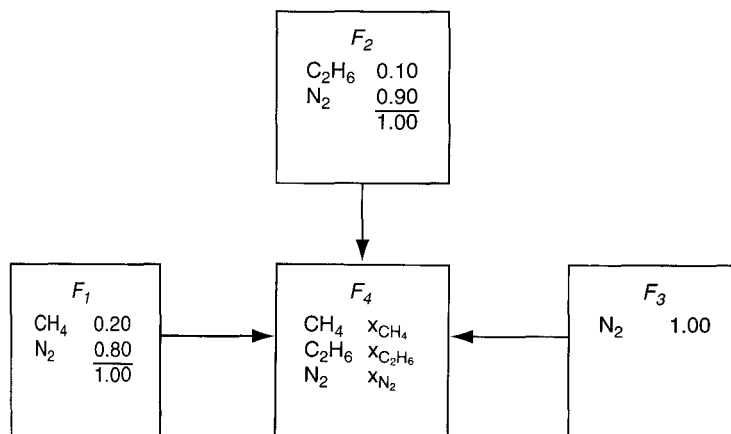


Figure 11

Do you count **seven unknowns** — **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 $(X_{\text{CH}_4}/X_{\text{C}_2\text{H}_6}) = 1.5$
- ◆ One summation of mole fractions: $\sum x_i^{F_4} = 1$

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 .

Example 8

In the growth of biomass $\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.16}\text{S}_{0.0045}\text{P}_{0.0055}$, with the system comprised of the biomass and the substrate, the substrate contains the carbon source for growth, $\text{C}_\alpha\text{H}_\beta\text{O}_\gamma$, 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:

	$\text{CH}_{1.8}\text{O}_{0.5}\text{N}_{0.16}\text{S}_{0.0045}\text{P}_{0.0055}$	$\text{C}_\alpha\text{H}_\beta\text{O}_\gamma$	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

- What does the concept “solution of a material balance problem” mean?
- (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?
- 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?
- What is the major category of implicit constraints (equations) you encounter in material balance problems?
- 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:

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

Problems

- 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,
 - Determine how many independent balances can be written.
 - List the names of the balances.
 - Determine how many unknown variables can be solved for.
 - List their names and symbols.
 - Determine the composition of P.
- Can you solve these three material balances for F, D, and P? Explain why not.

$$0.1F + 0.3D = 0.2P$$

$$0.9F + 0.7D = 0.8P$$

$$F + D = P$$

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.

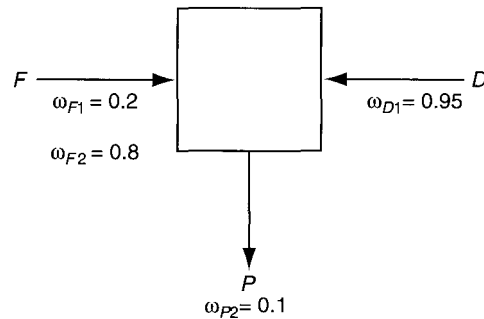


Figure SAT7.2P3

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

Answers:

- (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
- Not for a unique solution because only two of the equations are independent.
- F, D, P, ω_{D2} , ω_{P1}
- 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.

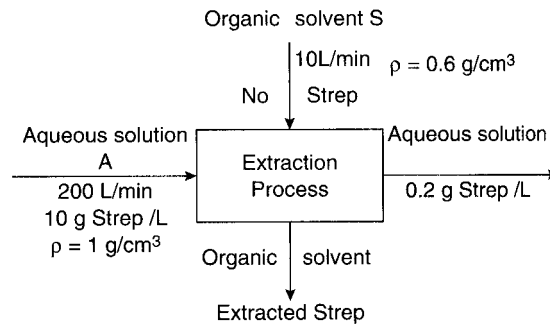


Figure E8.1

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:

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

$$x = 196 \text{ g Strep/L of solvent}$$

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?

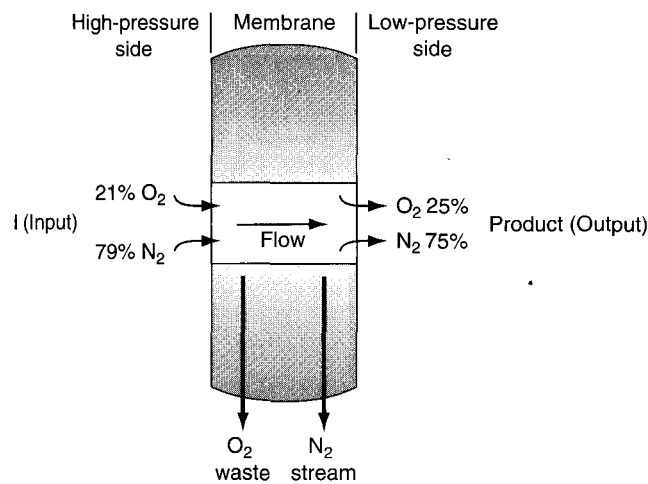
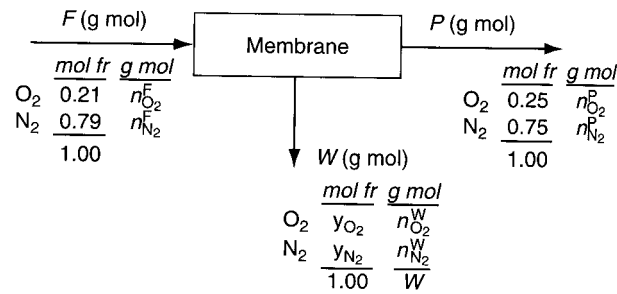


Figure E8.2a

Solution

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



Basis: 100 g mol = F

Basis: F = 100

Specifications:

$$n_{O_2}^F = 0.21(100) = 21$$

$$n_{N_2}^F = 0.79(100) = 79$$

$$y_{O_2}^P = n_{O_2}^P/P = 0.25 \quad n_{O_2}^P = 0.25P$$

$$y_{N_2}^P = n_{N_2}^P/P = 0.75 \quad n_{N_2}^P = 0.75P$$

$$W = 0.80(100) = 80$$

Material balances: O₂ and N₂

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

	<u>In</u>	<u>Out</u>		<u>In</u>	<u>Out</u>
O ₂ :	0.21 (100)	= 0.25P + y _{O₂} ^W (80)	or	0.21 (100)	= 0.25P + n _{O₂} ^W
N ₂ :	0.79 (100)	= 0.75P + y _{N₂} ^W (80)	or	0.79 (100)	= 0.75P + n _{N₂} ^W
	1.00	= y _{O₂} ^W + y _{N₂} ^W	or	80	= n _{O₂} ^W + n _{N₂} ^W

The solution of these equations is

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

Check: total balance 100 = 20 + 80 OK

❖ Another method for solution

The overall balance is easy to solve because

$$F = P + W \quad \text{or} \quad 100 = P + 80$$

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

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

$$n_{O_2}^W = 16 \text{ g mol, and } n_{N_2}^W = 80 - 16 = 64 \text{ g mol.}$$

Note (Example 10)

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

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

Example 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.

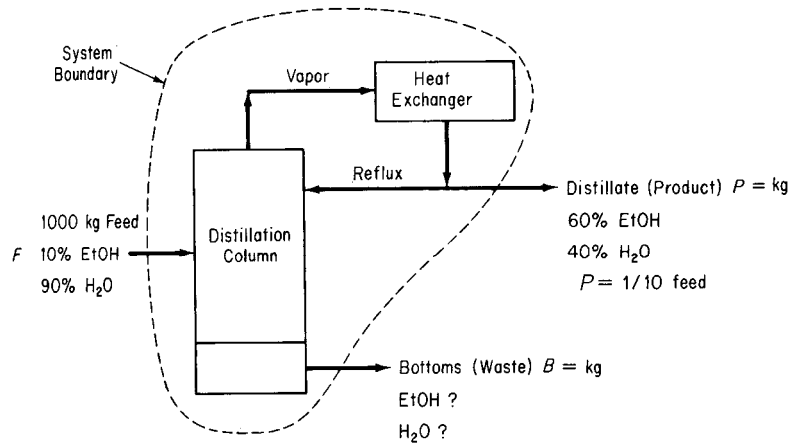


Figure E8.3

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: $m_{EtOH}^F = 1000(0.10) = 100$

$$m_{H_2O}^F = 1000(0.90) = 900$$

$$m_{EtOH}^P = 0.60P$$

$$m_{H_2O}^P = 0.40P$$

$$P = (0.1) (F) = 100 \text{ kg}$$

Material balances: EtOH and H₂O

Implicit equations: $\sum m_i^B = B$ or $\sum \omega_i^B = 1$

The total mass balance: $F = P + B$

$$B = 1000 - 100 = 900 \text{ kg}$$

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 ₂ O balance:	0.90(1000)	0.40(100)	= <u>860</u>	<u>0.956</u>
			900	1.000

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

$$m_{EtOH}^B + m_{H_2O}^B = B \quad \text{or} \quad \omega_{EtOH}^B + \omega_{H_2O}^B = 1$$

$$40 + 860 = 900 = B$$

Example 12

You are asked to prepare a batch of 18.63% battery acid as follows. A tank of old weak battery acid (H₂SO₄) solution contains 12.43% H₂SO₄ (the remainder is pure water). If 200 kg of 77.7% H₂SO₄ is added to the tank, and the final solution is to be 18.63% H₂SO₄, how many kilograms of battery acid have been made? See Figure E8.4.

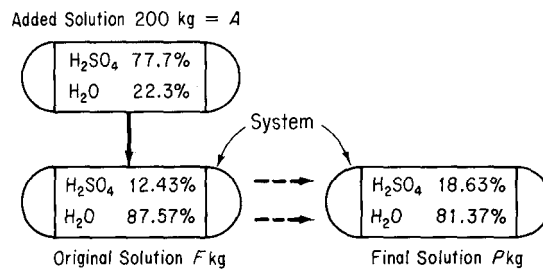


Figure E8.4

Solution

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

$$\text{Accumulation} = \text{In} - \text{Out}$$

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

$$\text{In} = \text{Out} \quad (\text{Because no accumulation occurs in the tank})$$

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

$$\text{Basis} = 200 \text{ kg of A}$$

Material balances: H₂SO₄ and H₂O

The balances will be in **kilograms**.

Type of Balance	Accumulation in Tank		In	Out
	Final	Initial		
H ₂ SO ₄	$P(0.1863)$	$F(0.1243)$	$= 200(0.777)$	$- 0$
H ₂ O	$P(0.8137)$	$F(0.8757)$	$= 200(0.223)$	$- 0$
Total	P	F	$= 200$	$- 0$

Note that any **pair** of the three equations is **independent**. $P = 2110 \text{ kg acid}$ & $F = 1910 \text{ kg acid}$.

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

	<u>A in</u>		<u>F in</u>		<u>P out</u>
H ₂ SO ₄	200(0.777)	+	F(0.1243)	=	P(0.1863)
H ₂ O	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.

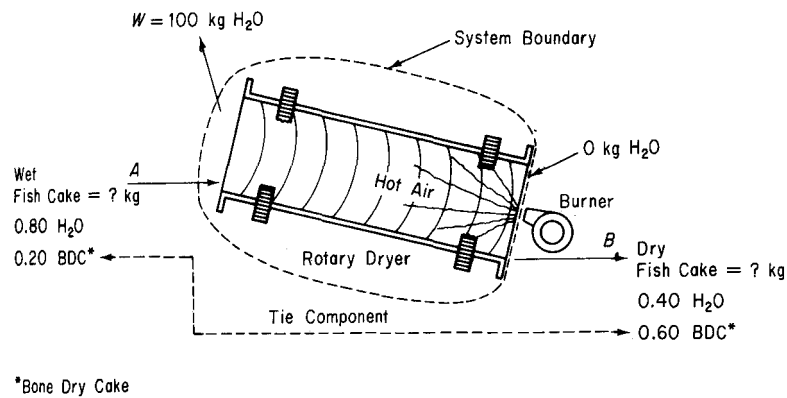


Figure E8.5

Solution

This is a steady-state process without reaction.

Basis: 100 kg of water evaporated = W

	<u>In</u>	=	<u>Out</u>	
Total balance:	A		B + W = B + 100	}
BDC balance:	0.20A		= 0.60B	

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) ≈ 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**.

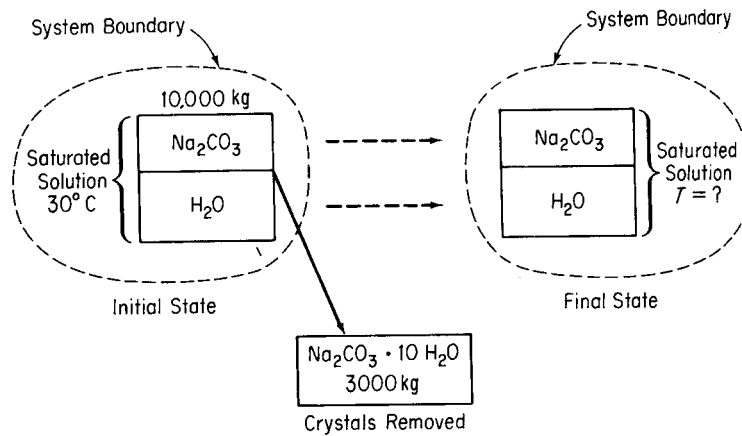
Example 14

A tank holds 10,000 kg of a saturated solution of Na₂CO₃ at 30°C. You want to crystallize from this solution 3000 kg of Na₂CO₃.10 H₂O without any accompanying water. To what temperature must the solution be cooled? You definitely need solubility data for Na₂CO₃ as a function of the temperature:

Temp.(°C)	Solubility (g Na ₂ CO ₃ /100 g H ₂ O)
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:

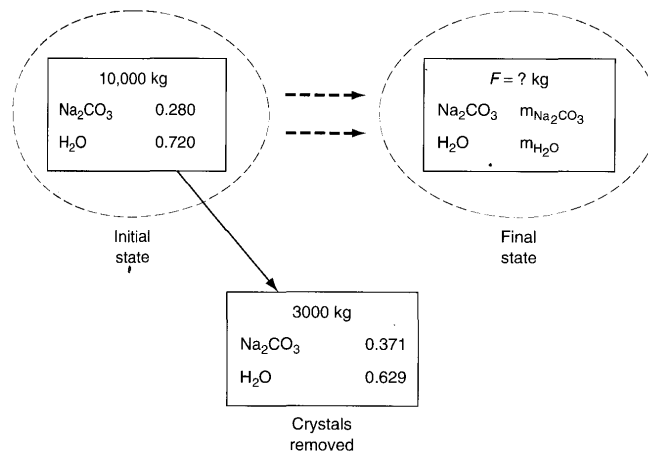
$$\frac{38.8 \text{ g Na}_2\text{CO}_3}{38.8 \text{ g Na}_2\text{CO}_3 + 100 \text{ g H}_2\text{O}} = 0.280 \text{ mass fraction Na}_2\text{CO}_3$$

Next, you should calculate the composition of the crystals.

Basis: 1 g mol Na₂CO₃·10 H₂O

Comp.	Mol	Mol wt.	Mass	Mass fr
Na ₂ CO ₃	1	106	106	0.371
H ₂ O	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)

$$\text{Accumulation} = \text{In} - \text{Out}$$

Basis: I = 10,000 kg

Material balances: Na₂CO₃, H₂O

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

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

Also redundant are equations such as $\sum \omega_i = 1$ and $\sum m_i = m_{\text{total}}$.

M.B.:

Accumulation in Tank					
	<u>Final</u>		<u>Initial</u>		<u>Transport out</u>
Na ₂ CO ₃	$m_{\text{Na}_2\text{CO}_3}^F$	-	10,000(0.280)	=	-3000(0.371)
H ₂ O	$m_{\text{H}_2\text{O}}^F$	-	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
$m_{\text{Na}_2\text{CO}_3}^F$	1687
$m_{\text{H}_2\text{O}}^F$	5313
F (total)	7000

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

To find the temperature of the final solution,

$$\frac{1,687 \text{ kg Na}_2\text{CO}_3}{5,313 \text{ kg H}_2\text{O}} = \frac{31.8 \text{ g Na}_2\text{CO}_3}{100 \text{ g H}_2\text{O}}$$

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

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

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**

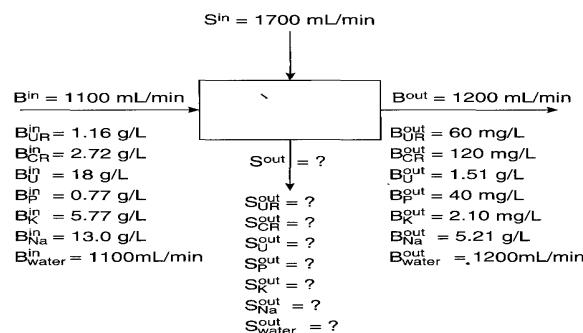


Figure E8.7b

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

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

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

The component balances in grams are:

	<i>g/L</i>
UR: $1.1(1.16) + 0 = 1.2(0.060) + 1.6 S_{\text{UR}}^{\text{out}}$	$S_{\text{UR}}^{\text{out}} = 0.75$
CR: $1.1(2.72) + 0 = 1.2(0.120) + 1.6 S_{\text{CR}}^{\text{out}}$	$S_{\text{CR}}^{\text{out}} = 1.78$
U: $1.1(18) + 0 = 1.2(1.51) + 1.6 S_{\text{U}}^{\text{out}}$	$S_{\text{U}}^{\text{out}} = 11.2$
P: $1.1(0.77) + 0 = 1.2(0.040) + 1.6 S_{\text{P}}^{\text{out}}$	$S_{\text{P}}^{\text{out}} = 0.50$
K: $1.1(5.77) + 0 = 1.2(0.120) + 16 S_{\text{K}}^{\text{out}}$	$S_{\text{K}}^{\text{out}} = 3.8$
Na: $1.1(13.0) + 0 = 1.2(3.21) + 1.6 S_{\text{Na}}^{\text{out}}$	$S_{\text{Na}}^{\text{out}} = 6.53$

Questions

- Answer the following questions true or false:
 - 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.
 - All open processes involving two components with three streams involve zero degrees of freedom.
 - An unsteady-state process problem can be analyzed and solved as a steady-state process problem.
 - If a flow rate is given in kg/min, you should convert it to kg mol/min.
- Under what circumstances do equations or specifications become redundant?

Answers:

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

Problems

- 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%?
- 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?
- If 100 g of Na_2SO_4 is dissolved in 200 g of H_2O and the solution is cooled until 100 g of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ 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.
- 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:

- 33.3 kg
- 178 kg/hr
- (a) 28% Na₂SO₄ ; (b) 33.3
- Salt: 0.00617; Oil: 0.99393.

2.4 The Chemical Reaction Equation and Stoichiometry**Stoichiometry**

- The stoichiometric coefficients in the chemical reaction equation

$$\text{C}_7\text{H}_{16}(\ell) + 11 \text{O}_2(\text{g}) \rightarrow 7 \text{CO}_2(\text{g}) + 8 \text{H}_2\text{O}(\text{g})$$

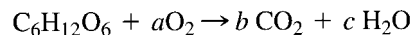
$$\text{C}_7\text{H}_{16}, 11 \text{ for O}_2 \text{ and so on.}$$
- Another way to use the chemical reaction equation is to indicate that **1 mole of CO₂** is formed from each **(1/7) mole of C₇H₁₆**, and **1 mole of H₂O** is formed with each **(7/8) mole of CO₂**. The latter ratios indicate the use of **stoichiometric ratios** in determining the relative proportions of products and reactants.

For example how many kg of CO₂ will be produced as the product if 10 kg of C₇H₁₆ react completely with the **stoichiometric quantity** of O₂? On the basis of 10 kg of C₇H₁₆

$$\frac{10 \text{ kg C}_7\text{H}_{16}}{100.1 \text{ kg C}_7\text{H}_{16}} \left| \frac{1 \text{ kg mol C}_7\text{H}_{16}}{1 \text{ kg mol C}_7\text{H}_{16}} \right| \left| \frac{7 \text{ kg mol CO}_2}{1 \text{ kg mol C}_7\text{H}_{16}} \right| \left| \frac{44.0 \text{ kg CO}_2}{1 \text{ kg mol CO}_2} \right| = 30.8 \text{ kg CO}_2$$

Example 15

The primary energy source for cells is the aerobic catabolism (oxidation) of glucose (C₆H₁₂O₆, a sugar). The overall oxidation of glucose produces CO₂ and H₂O by the following reaction



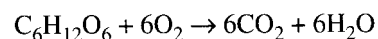
Determine the values of a, b, and c that balance this chemical reaction equation.

Solution**Basis: The given reaction**

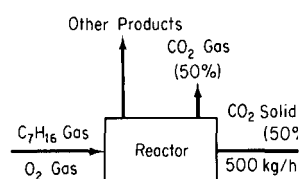
By inspection, the carbon balance gives b = 6, the hydrogen balance gives c = 6, and an oxygen balance

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

Gives a = 6. Therefore, the balanced equation is

**Example 16**

In the combustion of heptane, CO₂ is produced. Assume that you want to produce 500 kg of dry ice per hour, and that 50% of the CO₂ can be converted into dry ice, as shown in Figure E9.2. How many kilograms of heptane must be burned per hour? (MW: CO₂ = 44 and C₇H₁₆ = 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:

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

Example 17

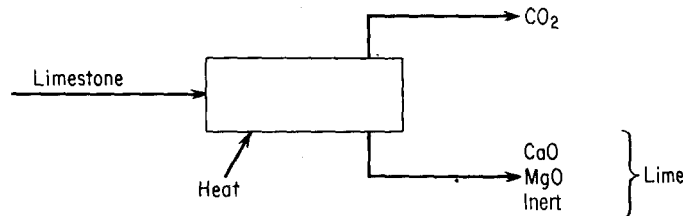
A limestone analyses (weight %): $CaCO_3$ 92.89%, $MgCO_3$ 5.41% and Inert 1.70%

By heating the limestone you recover oxides known as lime.

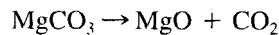
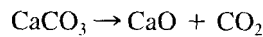
- (a) How many pounds of calcium oxide can be made from 1 ton of this limestone?
- (b) How many pounds of CO_2 can be recovered per pound of limestone?
- (c) How many pounds of limestone are needed to make 1 ton of lime?

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

Solution



Chemical Equation:



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:

$$\frac{92.89 \text{ lb } CaCO_3}{100.1 \text{ lb } CaCO_3} \left| \frac{1 \text{ lb mol } CaCO_3}{1 \text{ lb mol } CaCO_3} \right| \left| \frac{1 \text{ lb mol } CaO}{1 \text{ lb mol } CaCO_3} \right| \left| \frac{56.08 \text{ lb } CaO}{1 \text{ lb mol } CaO} \right| = 52.04 \text{ lb } CaO$$

$$\frac{5.41 \text{ lb } MgCO_3}{84.32 \text{ lb } MgCO_3} \left| \frac{1 \text{ lb mol } MgCO_3}{1 \text{ lb mol } MgCO_3} \right| \left| \frac{1 \text{ lb mol } MgO}{1 \text{ lb mol } MgCO_3} \right| \left| \frac{40.32 \text{ lb } MgO}{1 \text{ lb mol } MgO} \right| = 2.59 \text{ lb } MgO$$

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 $CO_2 = 0.9280 + 0.0642 = 0.992 \text{ lb mol } CO_2$

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

Alternately, you could have calculated the **lb CO₂** from a total balance: **100 - 56.33 = 44.67**.

Now, to calculate the quantities originally asked for:

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

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

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

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:

$$\xi = \frac{n_i - n_{i0}}{v_i} \quad \dots 9.1$$

Where:

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

n_{i0} = 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)

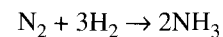
- The **coefficients** of the **products** in a chemical reaction are assigned **positive** values and the **reactants** assigned **negative** values. Note that $(n_i - n_{i0})$ is equal to the **generation** or **consumption** of component i by reaction.

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



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 :

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

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

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

Equation 9.2 can be used to determine the g mol of N₂ and H₂ in the products of the reaction

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

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

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

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

$$n_{\text{H}_2} = 25 + (-3)(2.5) = 17.5 \text{ g mol H}_2$$

$$m_{\text{H}_2} = \frac{17.5 \text{ g mol H}_2}{1 \text{ g mol H}_2} \left| \frac{2 \text{ g H}_2}{1 \text{ g mol H}_2} \right. = 35 \text{ g H}_2$$

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 k th reaction, the total number of moles of species i is

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

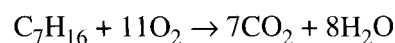
Where R is the total number of independent reactions.

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**.

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

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



If **1 g mol of C₇H₁₆** and **12 g mol of O₂** 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**,

$$\begin{array}{ccc} & \textit{Ratio in feed} & \textit{Ratio in chemical equation} \\ \frac{O_2}{C_7H_{16}}: & \frac{12}{1} = 12 & > \quad \frac{11}{1} = 11 \end{array}$$

❖ 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

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

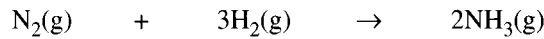
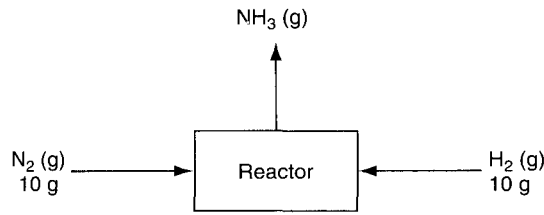
We conclude that **B** is the **limiting reactant relative to A**, and that **A** is the **limiting reactant relative to C**, hence **B** is the **limiting reactant** among the set of **three reactant**. In symbols we have **B < A**, **C > A** (i.e., **A < C**), so that **B < A < C**.

Example 19

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

- What is the maximum number of grams of NH_3 that can be produced?
- What is the limiting reactant?
- What is the excess reactant?

Solution



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 $\text{H}_2 = 4.960 - 3(0.357) = 3.89 \text{ g mol}$. To answer question (a), the maximum amount of NH_3 that can be produced is based on assuming **complete conversion** of the limiting reactant

$$\frac{0.357 \text{ g mol N}_2}{1 \text{ g mol N}_2} \left| \frac{2 \text{ g mol NH}_3}{1 \text{ g mol N}_2} \right| \frac{17.02 \text{ g NH}_3}{1 \text{ g mol NH}_3} = 12.2 \text{ g NH}_3$$

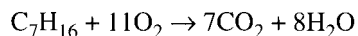
Conversion and degree of completion

- ☒ **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:



$$\text{C}_7\text{H}_{16} \text{ equivalent to CO}_2 \text{ in the product} \quad \frac{14.4 \text{ kg CO}_2}{44.0 \text{ kg CO}_2} \left| \frac{1 \text{ kg mol CO}_2}{7 \text{ kg mol CO}_2} \right| \frac{1 \text{ kg mol C}_7\text{H}_{16}}{1 \text{ kg mol C}_7\text{H}_{16}} = 0.0468 \text{ kg mol C}_7\text{H}_{16}$$

$$\text{C}_7\text{H}_{16} \text{ in the reactants} \quad \frac{10 \text{ kg C}_7\text{H}_{16}}{100.1 \text{ kg C}_7\text{H}_{16}} \left| \frac{1 \text{ kg mol C}_7\text{H}_{16}}{1 \text{ kg mol C}_7\text{H}_{16}} \right| = 0.0999 \text{ kg mol C}_7\text{H}_{16}$$

$$\% \text{ conversion} = \frac{0.0468 \text{ mol reacted}}{0.0999 \text{ kg mol fed}} \times 100 = 46.8\% \text{ of the C}_7\text{H}_{16}$$

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

Conversion is equal to the extent of reaction based on CO₂ formation (i.e., the **actual extent of reaction**) divided by the extent of reaction assuming **complete reaction** of C₇H₁₆ (i.e., the **maximum possible extent of reaction**).

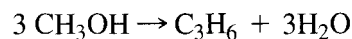
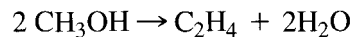
$$\text{Conversion} = \frac{\text{extent of reaction that actually occurs}}{\text{extent of reaction that would occur if complete reaction took place}}$$

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

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 (CH₃OH) can be converted into ethylene (C₂H₄) or propylene (C₃H₆) by the reactions



What is the selectivity of C₂H₄ relative to the C₃H₆ at 80% conversion of the CH₃OH? At 80% conversion: C₂H₄ 19 mole % and for C₃H₆ 8 mole %. Because the basis for both values is the same, **the selectivity = 19/8 = 2.4 mol C₂H₄ per mol C₃H₆**.

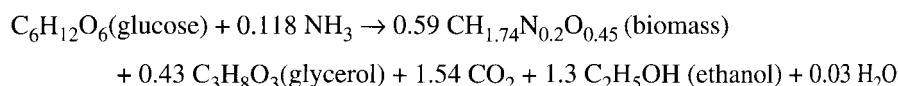
Yield

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



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

Solution

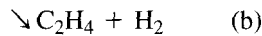
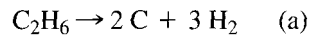
Basis: 0.59 g mol of biomass

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

$$\frac{1.3 \text{ g mol C}_2\text{H}_5\text{OH}}{1 \text{ g mol glucose}} \left| \frac{46 \text{ g C}_2\text{H}_5\text{OH}}{1 \text{ g mol C}_2\text{H}_5\text{OH}} \right| \frac{1 \text{ g mol glucose}}{180 \text{ g glucose}} = 0.332 \text{ g C}_2\text{H}_5\text{OH/g glucose}$$

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



If you collect 3 g mol of H₂ and 0.50 g mol of C₂H₄, what is the selectivity of C relative to C₂H₄?

Solution

Basis: 3 g mol H₂ by Reaction (a)

0.50 g mol C₂H₄ by Reaction (b)

The 0.5 g mol of C₂H₄ corresponds to 0.50 g mol of H₂ produced in Reaction (b).

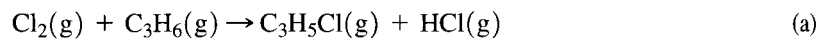
The H₂ produced by Reaction (a) = 3 - 0.50 = 2.5 g mol.

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 C₂H₄

Example 22

The two reactions of interest for this example are



C₃H₆ is propylene (propene) (MW = 42.08)

C₃H₅Cl is allyl chloride (3-chloropropene) (MW = 76.53)

C₃H₆Cl₂ 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 ₃ H ₆	C ₃ H ₅ Cl	C ₃ H ₆ Cl 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:

- How much Cl₂ and C₃H₆ were fed to the reactor in g mol?
- What was the limiting reactant?
- What was the excess reactant?
- What was the fraction conversion of C₃H₆ to C₃H₅Cl?
- What was the selectivity of C₃H₅Cl relative to C₃H₆Cl₂?
- What was the yield of C₃H₅Cl expressed in g of C₃H₅Cl to the g of C₃H₆ fed to the reactor?
- 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.

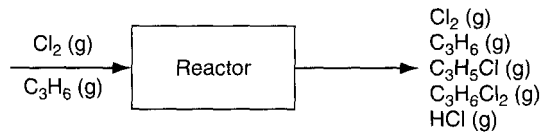


Figure E9.8

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

Reaction (a)

$$\frac{4.6 \text{ g mol C}_3\text{H}_5\text{Cl}}{1 \text{ g mol C}_3\text{H}_5\text{Cl}} \left| \frac{1 \text{ g mol Cl}_2}{1 \text{ g mol C}_3\text{H}_5\text{Cl}} \right. = 4.6 \text{ g mol Cl}_2 \text{ reacts}$$

Reaction (b)

$$\frac{24.5 \text{ g mol C}_3\text{H}_6\text{Cl}_2}{1 \text{ g mol C}_3\text{H}_6\text{Cl}_2} \left| \frac{1 \text{ g mol Cl}_2}{1 \text{ g mol C}_3\text{H}_6\text{Cl}_2} \right. = 24.5 \text{ g mol Cl}_2 \text{ reacts}$$

Total = 4.6 + 24.5 = 29.1 g mol Cl₂ reacts

Cl₂ in product = 141.0 from Table E9.8

(a) Total Cl₂ fed = 141.0 + 29.1 = 170.1 g mol Cl₂

Total C₃H₆ fed = 651.0 + 29.1 = 680.1 g mol of C₃H₆

(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

$$\xi^{\max} \text{ (based on C}_3\text{H}_6) = \frac{-680.1 \text{ g mol C}_3\text{H}_6}{-1 \text{ g mol C}_3\text{H}_6/\text{moles reacting}} = 680.1 \text{ moles reacting}$$

$$\xi^{\max} \text{ (based on Cl}_2) = \frac{-170.1 \text{ g mole Cl}_2}{-1 \text{ g mol Cl}_2/\text{moles reacting}} = 170.1 \text{ moles reacting}$$

Thus, **C₃H₆** was the **excess reactant** and **Cl₂** the **limiting reactant**.

(d) The fraction conversion of C₃H₆ to C₃H₅Cl was

$$\frac{4.6 \text{ g mol C}_3\text{H}_6 \text{ that reacted}}{680.1 \text{ g mol C}_3\text{H}_6 \text{ fed}} = 6.76 \times 10^{-3}$$

(e) The selectivity was

$$\frac{4.6 \text{ g mol C}_3\text{H}_5\text{Cl}}{24.5 \text{ g mol C}_3\text{H}_6\text{Cl}_2} = 0.19 \frac{\text{g mol C}_3\text{H}_5\text{Cl}}{\text{g mol C}_3\text{H}_6\text{Cl}_2}$$

(f) The yield was

$$\frac{(76.53)(4.6) \text{ g C}_3\text{H}_5\text{Cl}}{(42.08)(680.1) \text{ g C}_3\text{H}_6} = 0.012 \frac{\text{g C}_3\text{H}_5\text{Cl}}{\text{g C}_3\text{H}_6}$$

(g) Because **C₃H₅Cl** is produced only by the **first reaction**, the **extent of reaction** of the first reaction is

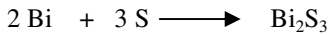
$$\xi_1 = \frac{n_i - n_{i0}}{v_i} = \frac{4.6 - 0}{1} = 4.6$$

Because **C₃H₆Cl₂** is produced only by the **second reaction**, the **extent of reaction** of the second reaction is

$$\xi_2 = \frac{n_i - n_{i0}}{v_i} = \frac{24.5 - 0}{1} = 24.5$$

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



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

Solution

a. Find the Limiting reactant

Ratio in the feed

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

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

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

b. % Excess reactant

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

$$\% \text{ excess Bi} = \frac{(0.0239 - 0.0208)}{0.0208} \times 100 = 14.9 \%$$

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%.

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

$$\begin{aligned} \% \text{ Conversion} &= \frac{\text{moles of feed that react}}{\text{moles of feed introduced}} \times 100 \\ &= \frac{0.0313 - 0.00938}{0.0313} \times 100 = 70.0 \% \end{aligned}$$

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.

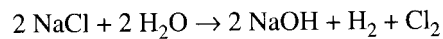
Q.4 All other reactants than the limiting reactant.

Q.5 For a species in

$$\text{Open system: } \xi = \frac{n_{\text{out},i} - n_{\text{in},i}}{v_i} \quad \text{Closed system: } \xi = \frac{n_{\text{final},i} - n_{\text{initial},i}}{v_i}$$

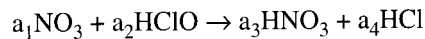
Problems

- Write balanced reaction equations for the following reactions:
 - C_9H_{18} and oxygen to form carbon dioxide and water.
 - FeS_2 and oxygen to form Fe_2O_3 and sulfur dioxide.
- 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 ?
- The electrolytic manufacture of chlorine gas from a sodium chloride solution is carried out by the following reaction:

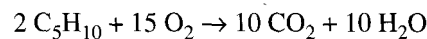


How many kilograms of Cl_2 can be produced from $10 m^3$ of brine solution containing 5% by weight of $NaCl$? The specific gravity of the solution relative to that of water at $4^\circ C$ is 1.07.

- Can you balance the following chemical reaction equation?

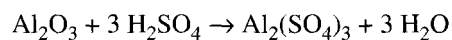


- For the reaction in which stoichiometric quantities of the reactants are fed



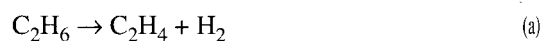
and the reaction goes to completion, what is the maximum extent of reaction based on C_5H_{10} ? On O_2 ? Are the respective values different or the same? Explain the result.

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



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.

- Identify the excess reactant.
 - What percentage of the excess reactant was consumed?
 - What was the degree of completion of the reaction?
- Two well-known gas phase reactions take place in the dehydration of ethane:



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%

- What species was the limiting reactant?
- What species was the excess reactant?
- What was the conversion of C_2H_6 to CH_4 ?
- What was the degree of completion of the reaction?
- What was the selectivity of C_2H_4 relative to CH_4 ?
- What was the yield of C_2H_4 expressed in kg mol of C_2H_4 produced per kg mol of C_2H_6 ?
- What was the extent of reaction of C_2H_6 ?

Answers:

- $C_9H_{18} + \frac{27}{2} O_2 \rightarrow 9 CO_2 + 9 H_2O;$ $4 FeS_2 + 11 O_2 \rightarrow 2Fe_2O_3 + 8 SO_2$
 - 3.08
 - 323
 - No
 - 1,
 - 1,
 - The same,
 - The extent of reaction depends on the reaction equation as a whole and not on one species in the equation.
 - $CaCO_3$: 43.4%, CaO : 56.4%; (b) 0.308
 - H_2SO_4
 - 79.2%;
 - 0.89
 - C_2H_6 (the hydrogen is from reaction No.2, not the feed);
 - None;
 - Fraction conversion = 0.184;
 - 0.45;
 - 1.22
 - Based on reactant in the feed: 0.45, based on reactant consumed: 0.84, based on theory: 0.50;
 - 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.

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

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:

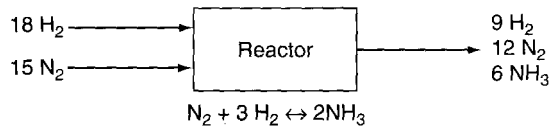


Figure 10.1. A reactor to produce NH_3 .

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

$$\xi = \frac{n_i^{\text{out}} - n_i^{\text{in}}}{v_i} \quad i = 1, \dots, N \quad (10.2)$$

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

$$v_{\text{NH}_3} = 2$$

$$v_{\text{H}_2} = -3$$

$$v_{\text{N}_2} = -1$$

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

$$\xi = \frac{n_{\text{NH}_3}^{\text{out}} - n_{\text{NH}_3}^{\text{in}}}{v_{\text{NH}_3}} = \frac{6 - 0}{2} = 3$$

$$\xi = \frac{n_{\text{H}_2}^{\text{out}} - n_{\text{H}_2}^{\text{in}}}{v_{\text{H}_2}} = \frac{9 - 18}{-3} = 3$$

$$\xi = \frac{n_{\text{N}_2}^{\text{out}} - n_{\text{N}_2}^{\text{in}}}{v_{\text{N}_2}} = \frac{12 - 15}{-1} = 3$$

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

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

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

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

$$\xi = \frac{(-f)n_{\text{limiting reactant}}^{\text{in}}}{v_{\text{limiting reactant}}} \quad \dots 10.3$$

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 $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$

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.

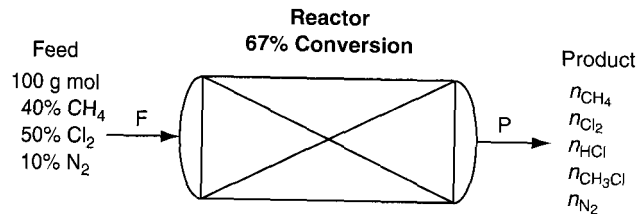


Figure E10.1

Basis 100 g mol feed

Limiting reactant:

$$\xi^{\max}(\text{CH}_4) = \frac{-n_{\text{CH}_4}^{\text{in}}}{v_{\text{CH}_4}} = \frac{-40}{(-1)} = 40$$

$$\xi^{\max}(\text{Cl}_2) = \frac{-n_{\text{Cl}_2}^{\text{in}}}{v_{\text{Cl}_2}} = \frac{-50}{(-1)} = 50$$

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

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

$$\xi = \frac{-f n_{lr}^{\text{in}}}{v_{lr}} = \frac{(-0.67)(40)}{-1} = 26.8 \text{ g moles reacting}$$

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

$$\begin{aligned} n_{\text{CH}_4}^{\text{out}} &= 40 - 1(26.8) = 13.2 \\ n_{\text{Cl}_2}^{\text{out}} &= 50 - 1(26.8) = 23.2 \\ n_{\text{CH}_3\text{Cl}}^{\text{out}} &= 0 + 1(26.8) = 26.8 \\ n_{\text{HCl}}^{\text{out}} &= 0 + 1(26.8) = 26.8 \\ n_{\text{N}_2}^{\text{out}} &= 10 - 0(26.8) = \underline{10.0} \\ &100.0 = P \end{aligned}$$

Therefore, the **composition** of the product stream is: **13.2% CH_4 , 23.2% Cl_2 , 26.8% CH_3Cl , 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 : $2 \text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) \rightarrow 3\text{S}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$

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 $\text{S}(\text{s})$, and in the product gas the ratio of SO_2 to H_2S was equal to 3, and the ratio of H_2O to

H₂S was 10. You are asked to determine the fractional conversion of the limiting reactant, and the feed rates of the H₂S and SO₂ streams.

Solution

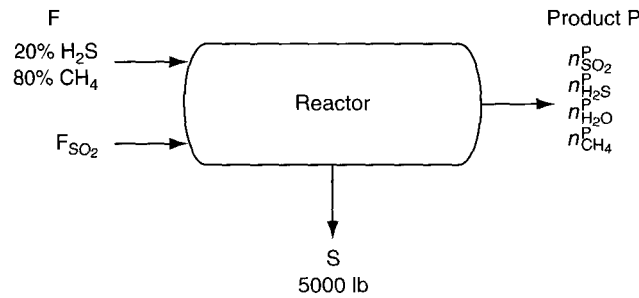


Figure E10.2

Basis is 5000 lb S (156.3 lb mol S)

Basis: S = 5000 lb (156.3 lb mol)

$$x_{\text{H}_2\text{S}}^F = 0.20 \text{ or } x_{\text{CH}_4}^F = 0.80, (n_{\text{SO}_2}^P/n_{\text{H}_2\text{S}}^P) = 3, (n_{\text{H}_2\text{O}}^P/n_{\text{H}_2\text{S}}^P) = 10$$

Specifications: 4 (3 independent)

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

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

$$\text{H}_2\text{S: } n_{\text{H}_2\text{S}}^P = 0.20F - 2\xi \quad (\text{b})$$

$$\text{SO}_2: n_{\text{SO}_2}^P = F_{\text{SO}_2} - 1\xi \quad (\text{c})$$

$$\text{H}_2\text{O: } n_{\text{H}_2\text{O}}^P = 0 + 2\xi \quad (\text{d})$$

$$\text{CH}_4: n_{\text{CH}_4}^P = 0.80F + 0 (\xi) \quad (\text{e})$$

The remaining specifications are

$$n_{\text{SO}_2}^P = 3n_{\text{H}_2\text{S}}^P \quad (\text{f})$$

$$n_{\text{H}_2\text{O}}^P = 10n_{\text{H}_2\text{S}}^P \quad (\text{g})$$

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

$$n_{\text{H}_2\text{O}}^P = 2(52.1) = 104.2 \text{ lb mol H}_2\text{O}$$

$$n_{\text{H}_2\text{S}}^P = \frac{1}{10}n_{\text{H}_2\text{O}}^P = 10.4 \text{ lb mol H}_2\text{S}$$

Next, Equation (g) gives

$$n_{\text{SO}_2}^P = 3(10.4) = 31.2 \text{ lb mol SO}_2$$

And Equation (f) gives

If you solve the rest of the equations in the order (b), (c), and (e), you find

$$F = 573 \text{ lb mol} \qquad F_{\text{SO}_2} = 83.3 \text{ lb mol} \qquad n_{\text{CH}_4}^F = 458 \text{ lb mol}$$

Finally, you can identify H₂S as the **limiting reactant** because the **molar ratio** of SO₂ to H₂S 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 H₂S divided by the total feed of H₂S

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

Processes Involving Multiple Reactions

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

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

Where:

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

ξ_j is the extent of reaction for the *j*th reaction in the minimal set.

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

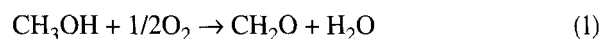
An equation analogous to Equation 10.4 can be written for a **closed, unsteady-state** system. The total moles, **N**, exiting a reactor are

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

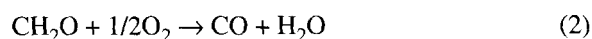
Where *S* is the number of species in the system.

Example 26

Formaldehyde (CH₂O) is produced industrially by the catalytic oxidation of methanol (CH₃OH) according to the following reaction:



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 H₂O, that is,



Assume that methanol and twice the stoichiometric amount of air needed for complete conversion of the CH₃OH to the desired products (CH₂O and H₂O) 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 CH₂O by Reaction 1. Determine the composition of the product gas leaving the reactor.

Solution

Figure E10.3 is a sketch of the process with y_i indicating the **mole fraction** of the respective components in P (a gas).

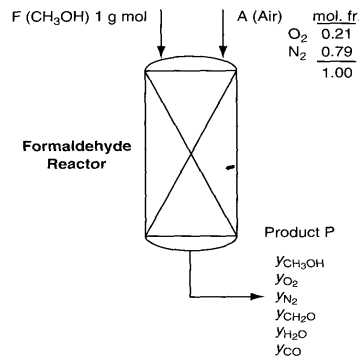


Figure E10.3

Basis: 1 gmol F

The **limiting** reactant is CH₃OH.

Use the fraction conversion, Equation 10.3:

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

The yield is related to ξ_i as follows

$$n_{\text{CH}_2\text{O}}^{\text{out},1} = n_{\text{CH}_2\text{O}}^{\text{in},1} + 1(\xi_1) = 0 + \xi_1 = \xi_1$$

By reaction 1:

$$n_{\text{CH}_2\text{O}}^{\text{out},2} = n_{\text{CH}_2\text{O}}^{\text{in},2} - 1(\xi_2) = n_{\text{CH}_2\text{O}}^{\text{out},1} - \xi_2 = \xi_1 - \xi_2$$

By reaction 2:

$$\frac{n_{\text{CH}_2\text{O}}^{\text{out},2}}{F} = \frac{\xi_1 - \xi_2}{1} = 0.75$$

The yield is

$\xi_2 = 0.15$ g moles reacting

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

$$n_{\text{O}_2}^A = 2\left(\frac{1}{2}F\right) = 2\left(\frac{1}{2}\right)(1.00) = 1.00 \text{ g mol}$$

$$A = \frac{n_{\text{O}_2}^A}{0.21} = \frac{1.00}{0.21} = 4.76 \text{ g mol}$$

$$n_{\text{N}_2}^A = 4.76 - 1.00 = 3.76 \text{ g mol}$$

Implicit equation: $\sum y_i^P = 1$

Calculate P using Equation 10.5:

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

The material balances:

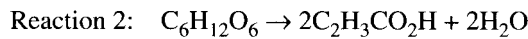
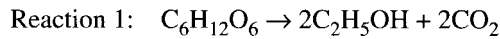
$$\begin{aligned}
 n_{\text{CH}_3\text{OH}}^{\text{out}} &= y_{\text{CH}_3\text{OH}} (6.28) = 1 - (0.9) + 0 = 0.10 \\
 n_{\text{O}_2}^{\text{out}} &= y_{\text{O}_2} (6.28) = 1.0 - (1/2)(0.9) - (1/2)(0.15) = 0.475 \\
 n_{\text{CH}_2\text{O}}^{\text{out}} &= y_{\text{CH}_2\text{O}} (6.28) = 0 + 1 (0.9) - 1 (0.15) = 0.75 \\
 n_{\text{H}_2\text{O}}^{\text{out}} &= y_{\text{H}_2\text{O}} (6.28) = 0 + 1 (0.9) + 1 (0.15) = 1.05 \\
 n_{\text{CO}}^{\text{out}} &= y_{\text{CO}} (6.28) = 0 + 0 + 1 (0.15) = 0.15 \\
 n_{\text{N}_2}^{\text{out}} &= y_{\text{N}_2} (6.28) = 3.76 - 0 - 0 = 3.76
 \end{aligned}$$

The six equations can be solved for the y_i :

$$\begin{aligned}
 y_{\text{CH}_3\text{OH}} &= 1.6\%, & y_{\text{O}_2} &= 7.6\%, & y_{\text{N}_2} &= 59.8\%, \\
 y_{\text{CH}_2\text{O}} &= 11.9\%, & y_{\text{H}_2\text{O}} &= 16.7\%, & y_{\text{CO}} &= 2.4\%.
 \end{aligned}$$

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 ($\text{C}_6\text{H}_{12}\text{O}_6$) from plants to form the products ethanol ($\text{C}_2\text{H}_5\text{OH}$) and propenoic acid ($\text{C}_2\text{H}_3\text{CO}_2\text{H}$) by the following overall reactions:



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

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

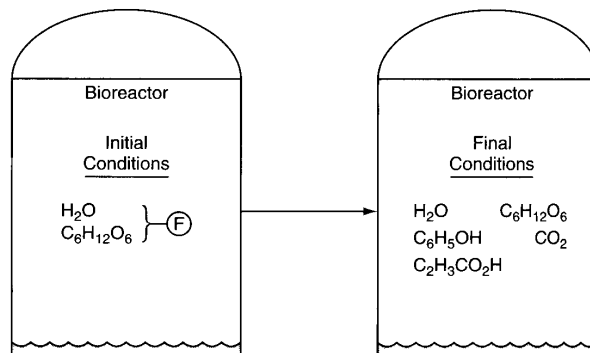


Figure E10.4

Basis: 4000 kg F

$$n_{\text{H}_2\text{O}}^{\text{Initial}} = \frac{4000(0.88)}{18.02} = 195.3$$

$$n_{\text{C}_6\text{H}_{12}\text{O}_6}^{\text{Initial}} = \frac{4000(0.12)}{180.1} = 2.665$$

Specifications: 4 (3 independent)

$$n_{\text{H}_2\text{O}}^{\text{Initial}} = 195.3 \text{ or } n_{\text{C}_6\text{H}_{12}\text{O}_6}^{\text{Initial}} = 2.665$$

(one is independent, the sum is F in mol)

$$n_{\text{C}_6\text{H}_{12}\text{O}_6}^{\text{Final}} = \frac{90}{180.1} = 0.500 \quad n_{\text{CO}_2}^{\text{Final}} = \frac{120}{44} = 2.727.$$

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

$$\text{H}_2\text{O}: \quad n_{\text{H}_2\text{O}}^{\text{Final}} = 195.3 + (0)\xi_1 + (2)\xi_2 \quad (\text{a})$$

$$\text{C}_6\text{H}_{12}\text{O}_6: \quad 0.500 = 2.665 + (-1)\xi_1 + (-1)\xi_2 \quad (\text{b})$$

$$\text{C}_2\text{H}_5\text{OH}: \quad n_{\text{C}_2\text{H}_5\text{OH}}^{\text{Final}} = 0 + 2\xi_1 + (0)\xi_2 \quad (\text{c})$$

$$\text{C}_2\text{H}_3\text{CO}_2\text{H}: \quad n_{\text{C}_2\text{H}_3\text{CO}_2\text{H}}^{\text{Final}} = 0 + (0)\xi_1 + (2)\xi_2 \quad (\text{d})$$

$$\text{CO}_2 \quad 2.727 = 0 + (2)\xi_1 + (0)\xi_2 \quad (\text{e})$$

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

$$\xi_1 = 1.364 \text{ kg moles reacting} \quad \xi_2 = 0.801 \text{ kg moles reacting}$$

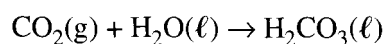
<u>Species</u>	<u>Results</u>	<u>Conversion to mass percent</u>		
	<u>kg kmol</u>	<u>MW</u>	<u>kg</u>	<u>Mass %</u>
H ₂ O	196.9	18.01	3546.1	88.7
C ₂ H ₅ OH	2.728	46.05	125.6	3.1
C ₂ H ₃ CO ₂ H	1.602	72.03	115.4	2.9
CO ₂	2.277	44.0	120.0	3.0
C ₆ H ₁₂ O ₆	0.500	180.1	90.1	2.3
			<u>3997</u>	<u>1.00</u>

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 10.1 to 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



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]

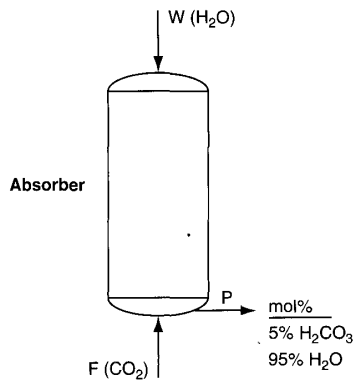


Figure 10.2 Schematic of the CO₂ absorber.

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

$$H: W(2) + F(0) = [0.05(2) + 0.95(2)]P = 2P$$

$$O: W(1) + F(2) = [0.05(3) + 0.95(1)]P = 1.10P$$

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:

$$C: 100 (0.40) = n_{CH_4}^{out}(1) + n_{CH_3Cl}^{out}(1)$$

$$H: 100 (0.40)(4) = n_{CH_4}^{out}(4) + n_{HCl}^{out}(1) + n_{CH_3Cl}^{out}(3)$$

$$Cl: 100 (0.50)(2) = n_{Cl_2}^{out}(2) + n_{HCl}^{out}(1) + n_{CH_3Cl}^{out}(1)$$

$$2N: 100 (0.10)(1) = n_{N_2}^{out}(1)$$

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

2. Example 25

The element balances are:

$$C: 1(1) + 4.76(0) = P[y_{CH_3OH}^P(1) + y_{CH_2O}^P(1) + y_{CO}^P(1)]$$

$$H: 1(4) + 4.76(0) = P[y_{CH_3OH}^P(4) + y_{CH_2O}^P(2) + y_{H_2O}^P(2)]$$

$$O: 1(1) + 1.00 = P[y_{CH_3OH}^P(1) + y_{O_2}^P(2) + y_{CH_2O}^P(1) + y_{H_2O}^P(1) + y_{CO}^P(1)]$$

$$2N: 1(0) + 3.76 = P[y_{N_2}^P(1)]$$

The solution of the problem will not change.

$$y_i^P P = n_i^P$$

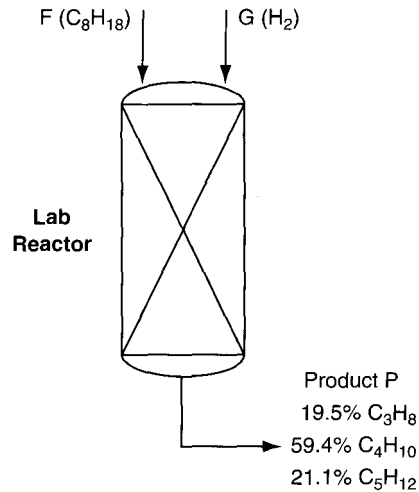
Note: It would be easier to use the term y_i^P and P.

in the equations above in place of the product of two variables,

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

Example 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 $F = 50.2 \text{ g mol}$ $G = 49.8 \text{ g mol}$

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

- ⌘ **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 .
- ⌘ 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).

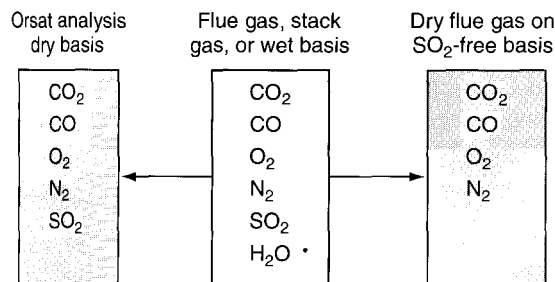


Figure 10.4 Comparison of a gas analysis on different bases.

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 **CO₂**, the excess air (or oxygen) is computed as if the process of combustion went to completion and produced only **CO₂**.

The **percent excess air** is identical to the percent **excess O₂**:

$$\% \text{ excess air} = \frac{\text{excess air}}{\text{required air}} \times 100 = \frac{\text{excess O}_2 / 0.21}{\text{required O}_2 / 0.21} \times 100 \quad \dots 10.6$$

Note that the ratio **1/0.21** of air to **O₂** cancels out in Equation 10.6. **Percent excess air** may also be computed as

$$\% \text{ excess air} = \frac{\text{O}_2 \text{ entering process} - \text{O}_2 \text{ required}}{\text{O}_2 \text{ required}} \times 100 \quad \dots 10.7$$

Or

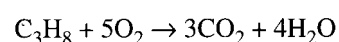
$$\% \text{ excess air} = \frac{\text{excess O}_2}{\text{O}_2 \text{ entering} - \text{excess O}_2} \times 100 \quad \dots 10.8$$

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



Basis: 20 kg of C_3H_8

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

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

The percentage of excess air is
$$\% \text{ excess air} = \frac{O_2 \text{ entering process} - O_2 \text{ required}}{O_2 \text{ required}} \times 100$$

$$\% \text{ excess air} = \frac{2.90 \text{ lb mol } O_2 - 2.27 \text{ lb mol } O_2}{2.27 \text{ lb mol } O_2} \left| \frac{100}{1} \right| = 28\%$$

Note:

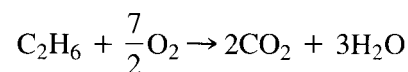
In calculating the amount of excess air, remember that the excess is the amount of air that enters the combustion process over and above that required for complete combustion.

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



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 :

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

Example 31

Figure E10.8 is a sketch of a fuel cell in which a continuous flow of methane (CH₄) and air (O₂ plus N₂) produce electricity plus CO₂ and H₂O. Special membranes and catalysts are needed to promote the reaction of CH₄. Based on the data given in Figure E10.8, you are asked to calculate the composition of the products in P.

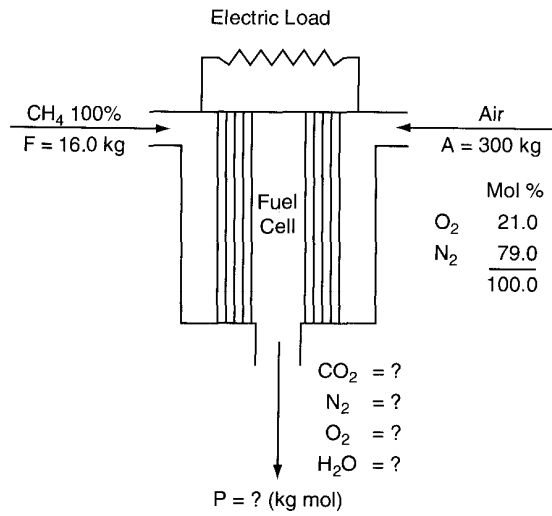


Figure E10.8

Solution

Assume a **complete reaction** occurs because no CH₄ appears in P. The system is the fuel cell (open, steady state). The necessary preliminary conversions as follows:

$$\frac{300 \text{ kg A}}{29.0 \text{ kg A}} \left| \frac{1 \text{ kg mol A}}{29.0 \text{ kg A}} \right. = 10.35 \text{ kg mol A in}$$

$$\frac{16.0 \text{ kg CH}_4}{16.0 \text{ kg CH}_4} \left| \frac{1 \text{ kg mol CH}_4}{16.0 \text{ kg CH}_4} \right. = 1.00 \text{ kg mol CH}_4 \text{ in}$$

$$\frac{10.35 \text{ kg mol A}}{1 \text{ kg mol A}} \left| \frac{0.21 \text{ kg mol O}_2}{1 \text{ kg mol A}} \right. = 2.17 \text{ kg mol O}_2 \text{ in}$$

$$\frac{10.35 \text{ kg mol A}}{1 \text{ kg mol A}} \left| \frac{0.79 \text{ kg mol N}_2}{1 \text{ kg mol A}} \right. = 8.18 \text{ kg mol N}_2 \text{ in}$$

Basis: 16.0 kg CH₄ entering = 1 kg mol CH₄

$$n_{\text{O}_2}^A = 2.17, n_{\text{N}_2}^A = 8.18$$

Specifications and calculated quantities: 2

$$\sum n_i^P = P$$

Implicit equation:

The element material balances are (in moles):

	Out	In
C:	$n_{\text{CO}_2}^P(1)$	= 1(1)
H:	$n_{\text{H}_2\text{O}}^P(2)$	= 1(4)
O:	$n_{\text{CO}_2}^P(2) + n_{\text{O}_2}^P(2) + n_{\text{H}_2\text{O}}^P(1)$	= 2.17(2)
2N:	$n_{\text{N}_2}^P$	= 8.18

The species material balances are:

Compound	Out	In	$v_i \xi$	g mol
CH ₄ :	$n_{\text{CH}_4}^P$	= 1.0	- 1 × 1	= 0
O ₂ :	$n_{\text{O}_2}^P$	= 2.17	- 2 × 1	= 0.17
N ₂ :	$n_{\text{N}_2}^P$	= 8.18	- 0 × 1	= 8.18
CO ₂ :	$n_{\text{CO}_2}^P$	= 0	+ 1 × 1	= 1.0
H ₂ O:	$n_{\text{H}_2\text{O}}^P$	= 0	+ 2 × 1	= 2.0

The **solution** of **either** set of **equations** gives

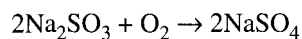
$$n_{\text{CH}_4}^P = 0, n_{\text{O}_2}^P = 0.17, n_{\text{N}_2}^P = 8.18, n_{\text{CO}_2}^P = 1.0, n_{\text{H}_2\text{O}}^P = 2.0, P = 11.35$$

The mole percentage composition of P is

$$y_{\text{O}_2} = 1.5\%, y_{\text{N}_2} = 72.1\%, y_{\text{CO}_2} = 8.8\%, \text{ and } y_{\text{H}_2\text{O}} = 17.6\%$$

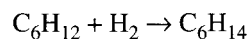
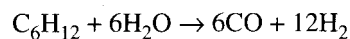
Problems

- Hydrofluoric acid (HF) can be manufactured by treating calcium fluoride (CaF₂) with sulfuric acid (H₂SO₄). A sample of fluorospar (the raw material) contains 75% by weight CaF₂ 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 CaSO₄, inerts, and unreacted sulfuric acid is also removed from the reaction chamber. Assume complete conversion of the CaF₂ occurs. How many kilograms of cake are produced per 100 kg of fluorospar charged to the process?
- 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:



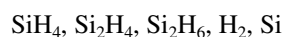
How many pounds of sodium sulfite are theoretically required (for complete reaction) to remove the oxygen from 8,330,000 lb of water (10⁶ gal) containing 10.0 parts per million (ppm) of dissolved oxygen and at the same time maintain a 35% excess of sodium sulfite?

- Consider a continuous, steady-state process in which the following reactions take place:



In the process 250 moles of C₆H₁₂ and 800 moles of H₂O are fed into the reactor each hour. The yield of H₂ is 40.0% and the selectivity of H₂ relative to C₆H₁₄ is 12.0. Calculate the molar flow rates of all five components in the output stream.

- Consider a system used in the manufacture of electronic materials (all gases except 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 mol%, CO 14 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 11.1a illustrates a serial combination of mixing and splitting stages. In a **mixer**, two or more entering streams of different **compositions are combined**. In a **splitter**, two or more streams exit, all of which have the **same composition**. In a **separator**, the exit streams can be of **different compositions**.

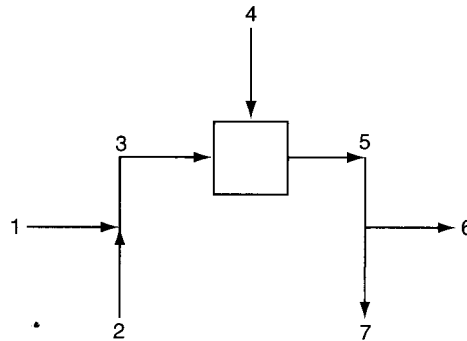


Figure 11.1a serial mixing and splitting in a system without reaction. Streams 1 plus 2 mix to form Stream 3, and Stream 5 is split into Streams 6 and 7.

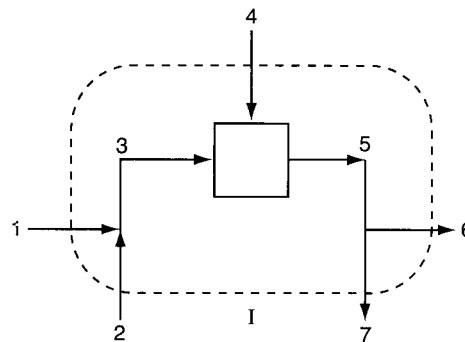


Figure 11.1b the dashed line I designates the boundary for overall material balances made on the process in Figure 11.1a.

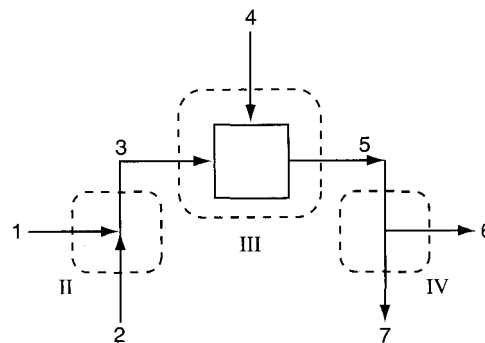


Figure 11.1c Dashed lines II, III and IV designate the boundaries for material balances around each of the individual units comprising the overall process.

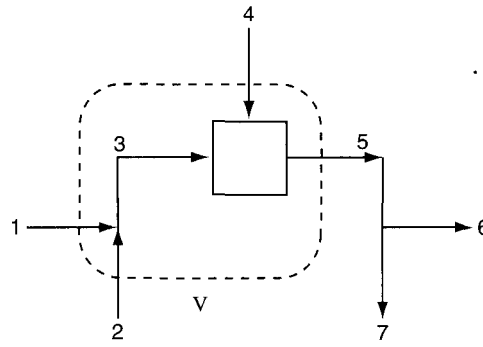


Figure 11.1d the dashed line V designates the boundary for material balances around a system comprised of the mixing point plus the unit portrayed by the box.

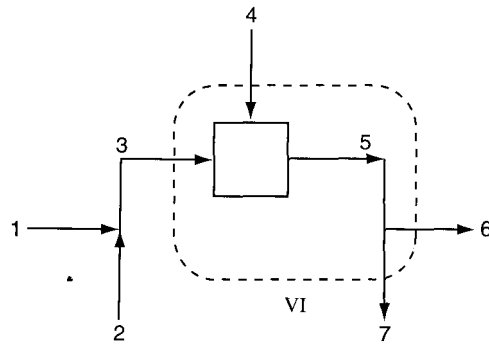


Figure 11.1e the dashed line VI designates the boundary for material balances about a system comprised of the unit portrayed by the box plus the splitter.

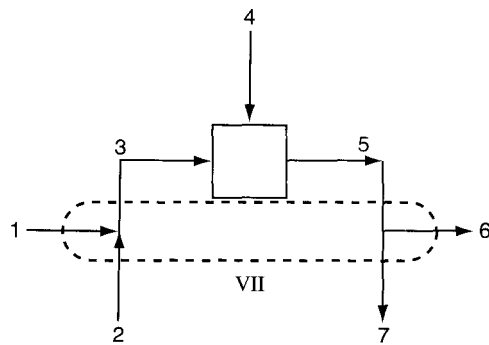


Figure 11.1f the dashed line VII designates the boundary for material balances about a system comprised of the mixer plus the splitter.

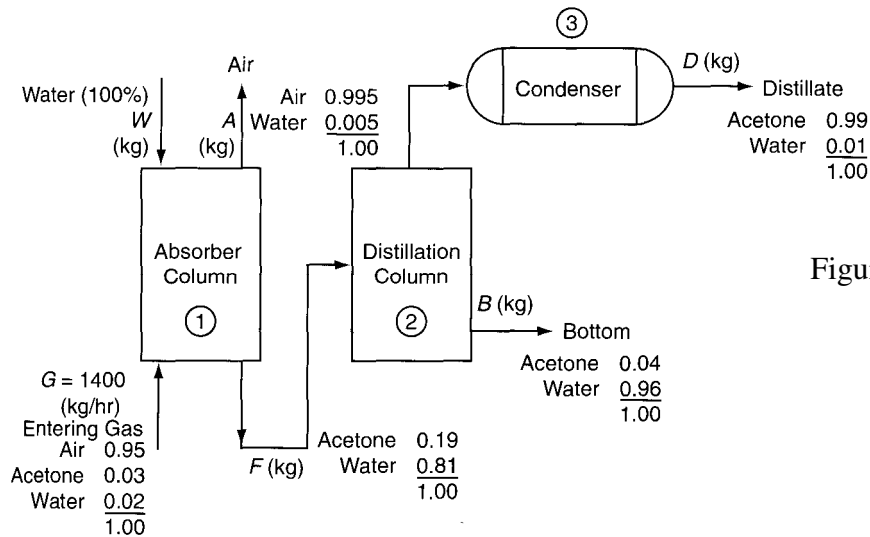
Example 32

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 E11.1. All the concentrations shown in E11.1 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. $G = 1400 \text{ kg/hr}$.

Solution

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

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



The mass balances for **Unit 1 (Absorber Column)**

	<i>In</i>	=	<i>Out</i>	
Air:	1400 (0.95)	=	A(0.995)	(a)
Acetone:	1400 (0.03)	=	F(0.19)	(b)
Water:	1400 (0.02) + W(1.00)	=	F(0.81) + A(0.005)	(c)

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).

$$\begin{array}{r}
 G + W = A + F \\
 1400 \quad 157.7 = 1336.7 \quad 221.05 \\
 1557.7 \cong 1557.7
 \end{array}$$

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

$$\text{Acetone: } 221.05(0.19) = D(0.99) + B(0.04) \tag{d}$$

$$\text{Water: } 221.05(0.81) = D(0.01) + B(0.96) \tag{e}$$

Solve Equations (d) and (e) simultaneously to get D = 34.90 kg/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**

	<u>In</u>	=	<u>Out</u>			
Air:	$G(0.95)$	=	$A(0.995)$			(f)
Acetone:	$G(0.03)$	=		$D(0.99)$	+ $B(0.04)$	(g)
Water:	$G(0.02) + W$	=	$A(0.005)$	+ $D(0.01)$	+ $B(0.96)$	(h)
Total	$G + W$	=	A	+ D	+ B	(i)

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: O₂, 20%; N₂, 76%; and CO₂, 4%. The stack gases go up a common stack, See Figure E11.2.

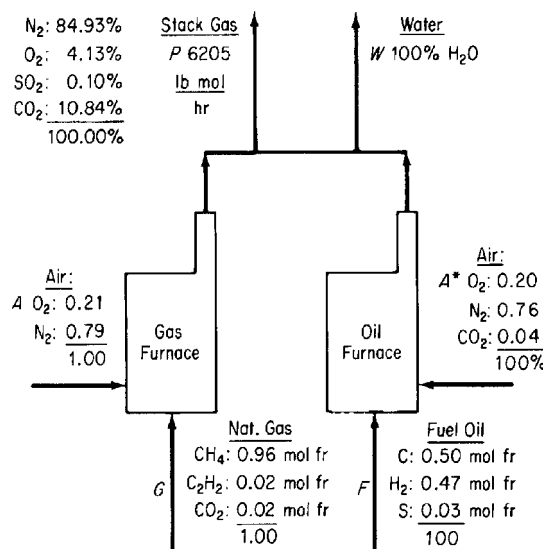


Figure E11.2

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)

	In	=	Out
2H:	G(1.94) + F(0.47)	=	W(1)
2N:	A(0.79) + A*(0.76)	=	6205(0.8493)
2O:	A(0.21) + A*(0.20 + 0.04) + G(0.02)	=	6205(0.0413 + 0.001 + 0.1084) + W(1/2)
S:	F(0.03)	=	6205(0.0010)
C:	G(0.96) + (2)(0.02) + 0.02 + F(0.50) + 0.04A*	=	6205(0.1084)

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:

$$F = 207 \text{ lb mol/hr and } G = 499 \text{ lb mol/hr}$$

Finally, the fuel oil consumption is

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

If the fuel oil reserves were only 560 bbl,

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

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.

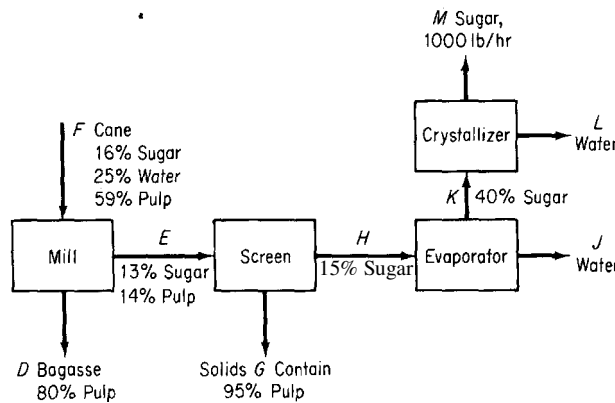


Figure E11.3

Solution

Basis: 1 hour (M= 1000lb)

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:

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

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 F1 is 1000 lb/hr, calculate the value of F2 and the composition of F2.

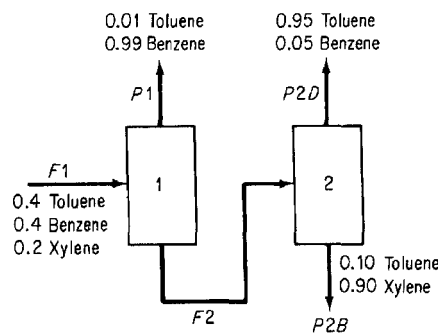


Figure SAT11P1

2. A simplified process for the production of SO₃ 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 SO₂ is achieved in the burner. In the converter, the conversion of SO₂ to SO₃ 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.

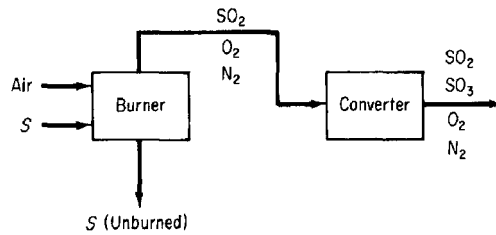
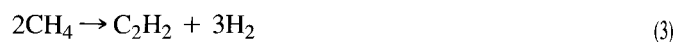
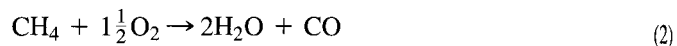
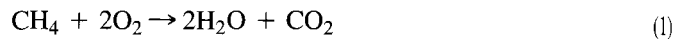


Figure SAT11P2

3. In the process for the production of pure acetylene, C₂H₂ (see Figure SAT11P3), pure methane (CH₄), and pure oxygen are combined in the burner, where the following reactions occur:



- Calculate the ratio of the moles of O₂ to moles of CH₄ fed to the burner.
- On the basis of 100 lb mol of gases leaving the condenser, calculate how many pounds of water are removed by the condenser.
- What is the overall percentage yield of product (pure) C₂H₂, based on the carbon in the natural gas entering the burner?

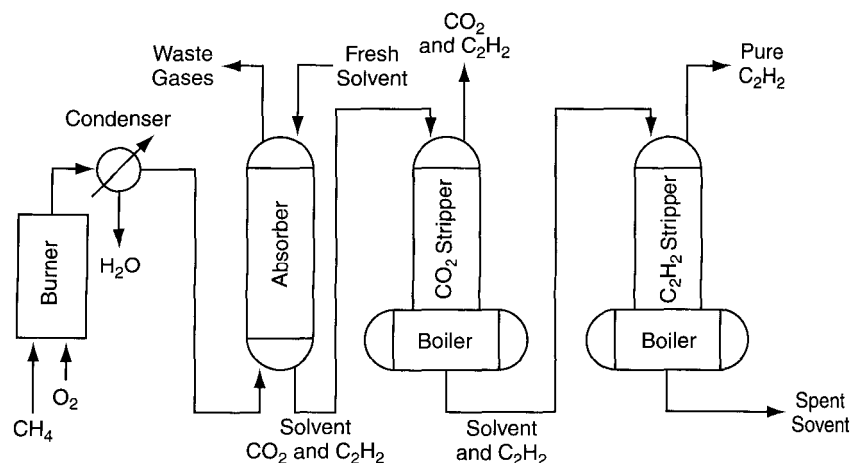


Figure SAT11P3

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 ₂ H 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 C₂H₂ and essentially all the CO₂ are removed with the solvent. The solvent from the absorber is sent to the CO₂ stripper, where all the CO₂ is removed. The analysis of the gas stream leaving the top of the CO₂ stripper is as follows:

	Mol %
C ₂ H ₂	7.5
CO ₂	92.5
Total	100.0

The solvent from the CO₂ stripper is pumped to the C₂H₂ stripper, which removes all the C₂H₂ 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 12.1c. 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.

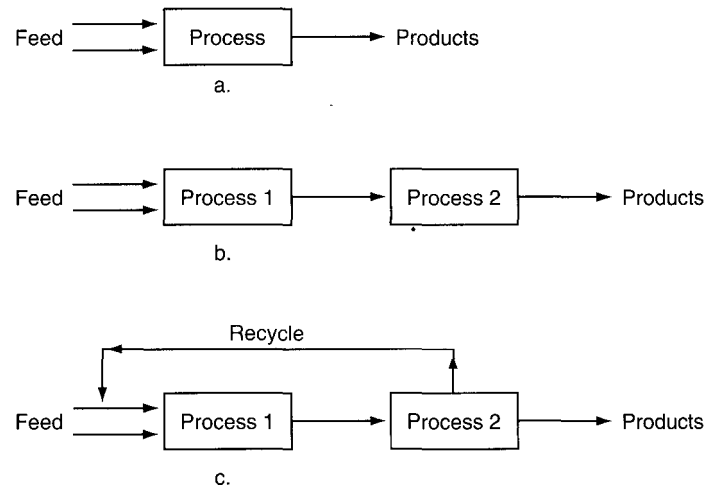


Figure 12.1: Figure 12.1a shows a single unit with serial flows. Figure 12.1b shows multiple units but still with serial flows. Figure 12.1c shows the addition of recycle.

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)**.

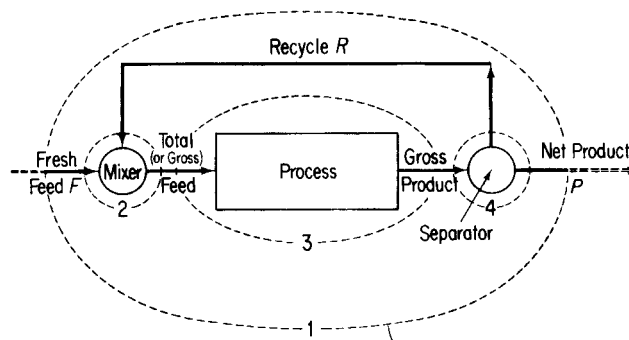


Figure 12.2 Process with recycle (the numbers designate possible system boundaries for the material balances).

Example 35

Figure E12.1a 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).

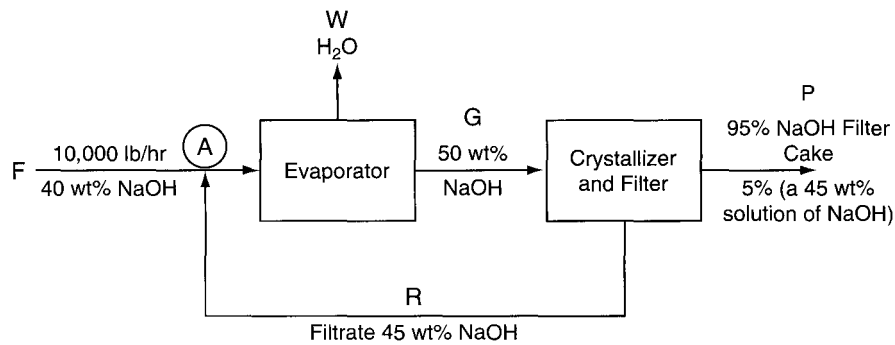


Figure E12.1a

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.

- You are asked to determine the flow rate of water removed by the evaporator, and the recycle rate for this process.
- 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 H₂O 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 $[(0.95) + (0.45)(0.05)](4113) = 4000 \text{ lb}$

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

H₂O 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 E12.1b.

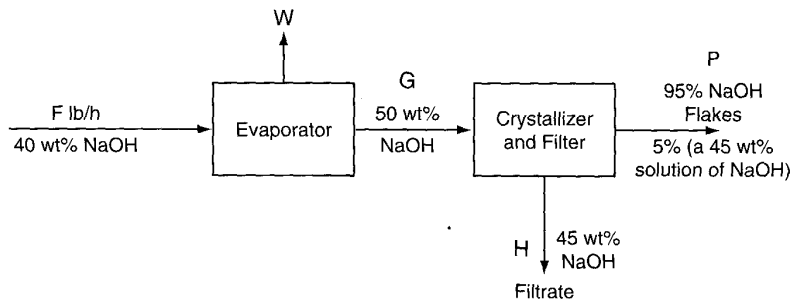


Figure E12.1b

The basis is now $P = 4113 \text{ lb}$ (the same as 1 hour)

The unknowns are now F , W , G , and H .

NaOH balance on the **crystallizer**

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

H₂O 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

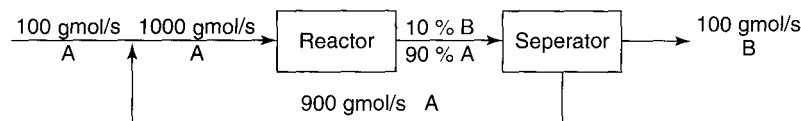


Figure 12.3 A simple recycle system with chemical reaction.

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 $A = 900 \text{ g mol}$
 $B = 100 \text{ g mol}$

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:

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

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

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

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** .

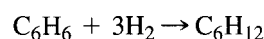
$$\text{Overall conversion of species A} = f_{\text{OA}} = \frac{-v_{\text{A}}\xi}{n_{\text{A}}^{\text{fresh feed}}} \quad (12.1)$$

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

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

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:



For the process shown in Figure E12.2, 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.

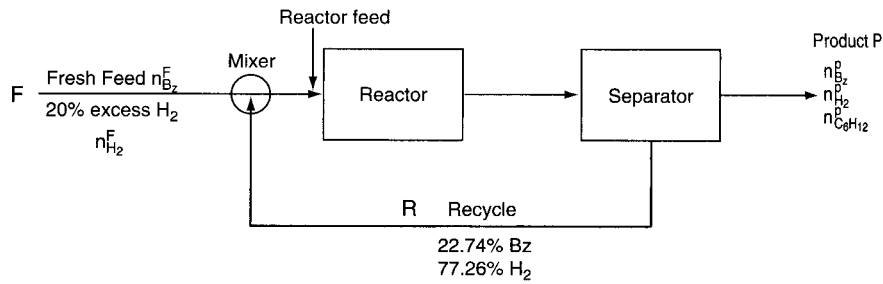


Figure E12.2 Schematic of a recycle reactor.

Solution

The process is **open** and **steady state**.

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

Excess H₂ = (in – required)/ required **(for complete reaction)**

In H₂ (Feed):

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

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

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

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

$$\xi = 95 \text{ reacting moles.}$$

The unknowns are R , n_{Bz}^P , $n_{H_2}^P$, and $n_{C_6H_{12}}^P$.

The species **overall balances** are

$$n_1^{out} = n_1^{in} + v_i \xi_{overall}$$

$$\text{Bz: } n_{Bz}^P = 100 + (-1)(95) = 5 \text{ mol}$$

$$\text{H}_2: n_{H_2}^P = 360 + (-3)(95) = 75 \text{ mol}$$

$$\text{C}_6\text{H}_{12}: n_{C_6H_{12}}^P = 0 + (1)(95) = \underline{95 \text{ mol}}$$

$$P = 175 \text{ mol}$$

The amount of the **Bz** feed to the **reactor** is **100 + 0.2274 R**, and $\xi = 95$. Thus, for benzene

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

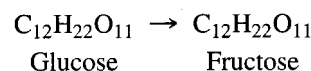
and $R = 1649 \text{ mol}$

Finally, the ratio of **recycle** to **fresh feed** is

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

Example 37

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 E12.3a, 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



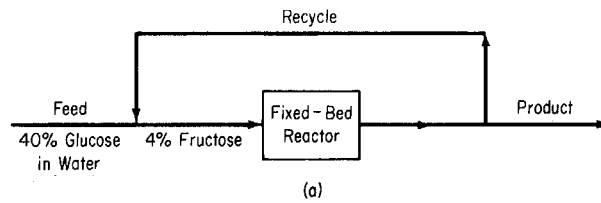


Figure E12.3a

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.

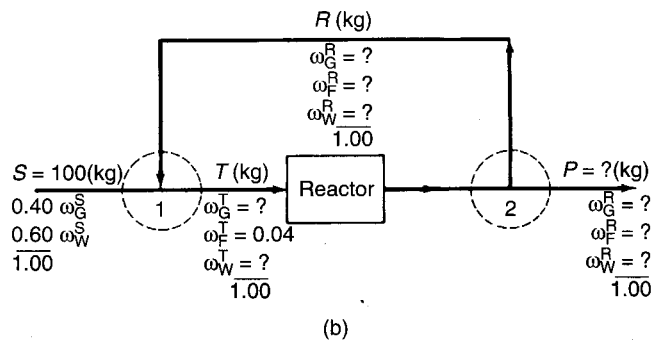


Figure E12.3b

Pick as a basis $S = 100 \text{ kg}$

Overall balances

Total: $P = S = 100 \text{ kg}$

Consequently,

$$R = \frac{100}{8.33} = 12.0 \text{ kg } \textit{R} = 8.33]$$

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

Total: $100 + 12 = T = 112$

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

Fructose: $0 + 12\omega_F^R = 112(0.04)$

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)

$$\begin{aligned} \text{Glucose: } \omega_G^T T - (R + P)(\omega_G^R) &= (f)(\omega_G^T T) \\ (0.360)(112) - (112)(0.027) &= f(0.360)(112) \\ 40.3 - 3.02 &= f(40.32) \\ f &= 0.93 \end{aligned}$$

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.

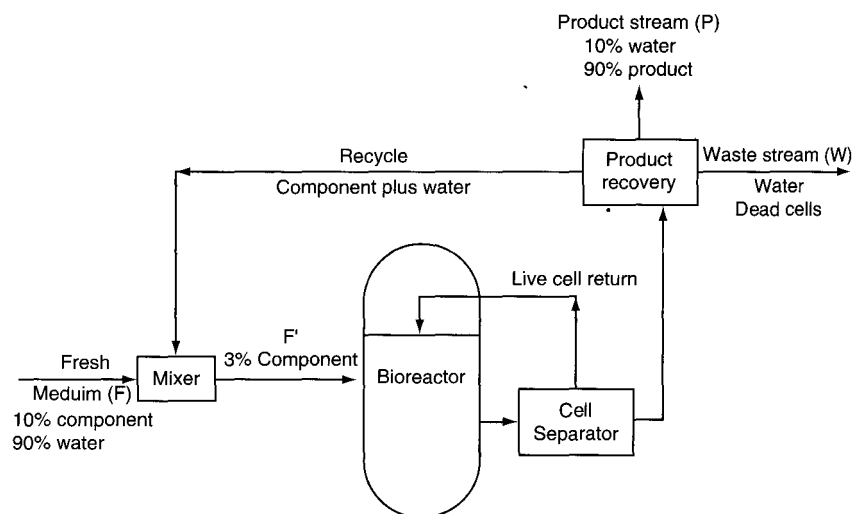


Figure E12.4

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: $0.10(100) = 0.90 P$

$P = 11.1 \text{ kg}$

$W = 88.9 \text{ kg}$

The reactor plus the product recovery unit balance

$$\begin{array}{ccccc}
 \text{Accumulation} & \text{Input} & \text{Output} & \text{Generation} & \text{Consumption} \\
 0 & = [100 (0.10) + R\omega] & - R\omega & + 0 & - 0.40 [100 (0.10) + R\omega] \\
 & & & & R\omega = 15 \text{ kg of component in the recycle stream}
 \end{array}$$

Mixer balance

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

Total balance: $R + 100 = F' \longrightarrow R = 833 - 100 = 733 \text{ kg}$

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

Bypass and Purge

- a. A **bypass** stream—a stream that skips one or more stages of the process and **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.

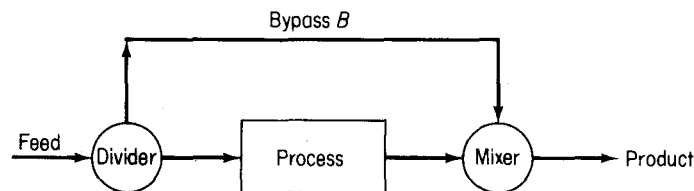


Figure 12.4 A process with a bypass stream.

- 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).

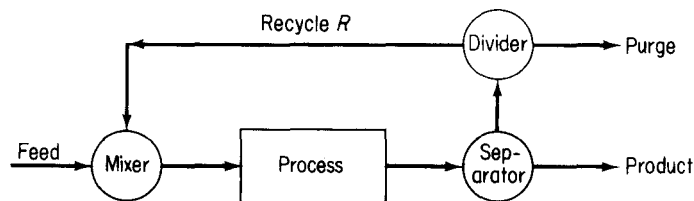


Figure 12.5 A process with a recycle stream with purge.

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.

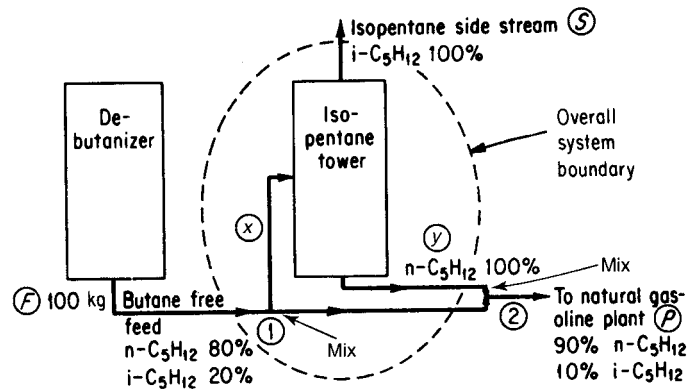


Figure E12.5

Solution**Basis: 100 kg feed****Overall balances**

Total material balance:

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

Component balance for n-C₅ (tie component)

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

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-C₅H₁₂ stream leaving the isopentane tower.

Total material balance:
$$\frac{In}{x} = \frac{Out}{11.1 + y} \quad (c)$$

Component balance for n-C₅
$$x(0.80) = y \quad (d)$$

Consequently, combining (c) and (d) yields $x = 55.5 \text{ kg}$, 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: $(100 - x) + y = 88.9 \quad (e)$

Component (iso-C₅): $(100 - x)(0.20) + 0 = 88.9(0.10) \quad (f)$

Solving yields $x = 55.5 \text{ kg as before}$

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.

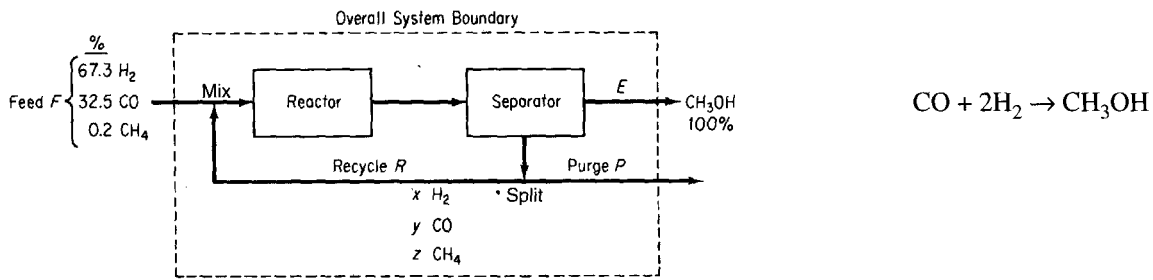


Figure E12.6

Note in Figure E12.6 that some CH₄ enters the process, but does not participate in the reaction. A purge stream is used to maintain the CH₄ 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, CH₃OH, 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 H₂, CO, and CH₄, respectively.

Basis: F = 100 mol

The variables whose values are unknown are x, y, z, E, P, and R.

$$z = 0.032 \tag{a}$$

The implicit mole fraction balance in the recycle stream $x + y + z = 1 \tag{b}$

The **overall element balances** are (in moles):

$$2\text{H: } 67.3 + 0.2(2) = E(2) + P(x + 2z) \tag{c}$$

$$\text{C: } 32.5 + 0.2 = E(1) + P(y + z) \tag{d}$$

$$\text{O: } 32.5 = E(1) + P(y) \tag{e}$$

Reactor plus the Separator

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

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 ₃ OH	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 SAT12.1P1?

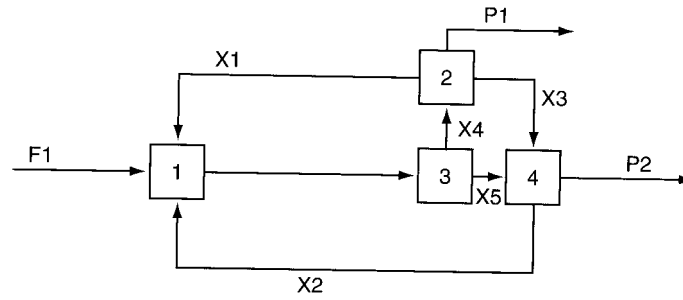


Figure SAT12.1P1

2. The Hooker Chemical Corporation operates a process in Michigan for the purification of HCl. Figure SAT12.1P2 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 (hexachlorobutadiene). The various stream compositions are shown in Figure SAT12.1P2.

How many recycle streams are there in the Hooker process?

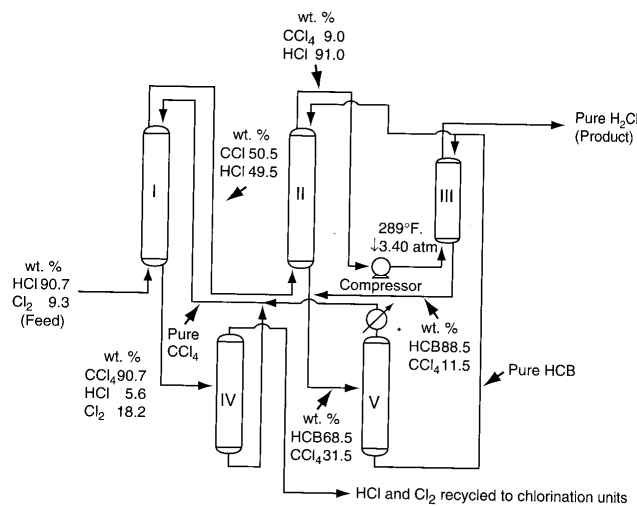


Figure SAT12.1P2

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

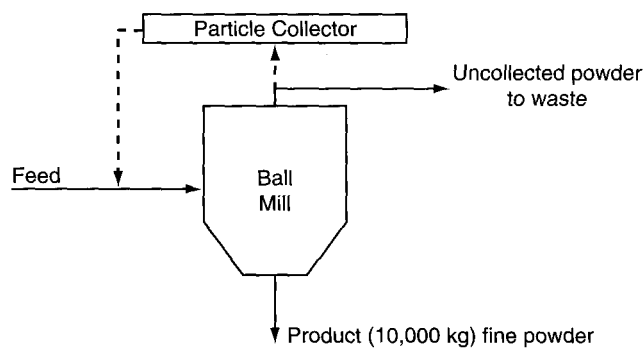


Figure SAT12.2P1

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?

- Sea water is to be desalinated by reverse osmosis using the scheme indicated in Figure SAT12.2P2. Use the data given in the figure to determine: (a) the rate of waste brine removal (B); (b) the rate of desalinated water production (P); (c) the fraction of the brine leaving the reverse osmosis cell (which acts in essence as a separator) that is recycled.

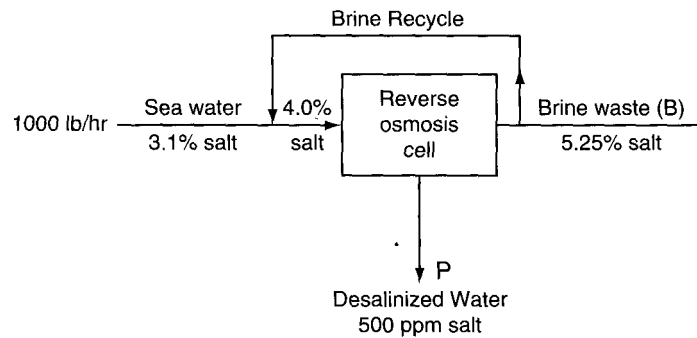


Figure SAT12.2P2

- 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).
 - What is the ratio of the recycle to the feed entering the granulator?
 - What is the rate of air flow to the dryer on a dry basis?
- Benzene, toluene, and other aromatic compounds can be recovered by solvent extraction with sulfur dioxide (SO₂). Figure SAT12.2P4 is the process schematic. As an example, a catalytic reformat stream containing 70% benzene and 30% nonbenzene material is passed through the countercurrent extractive recovery scheme shown in Figure SAT12.2P4. 1000 lb of reformat and 3000 lb of SO₂ are fed to the system per hour. The benzene product stream contains 0.15 lb of SO₂ 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 SO₂. How many lb of benzene are extracted in the product stream on an hourly basis? How many lb of raffinate are produced per hour?

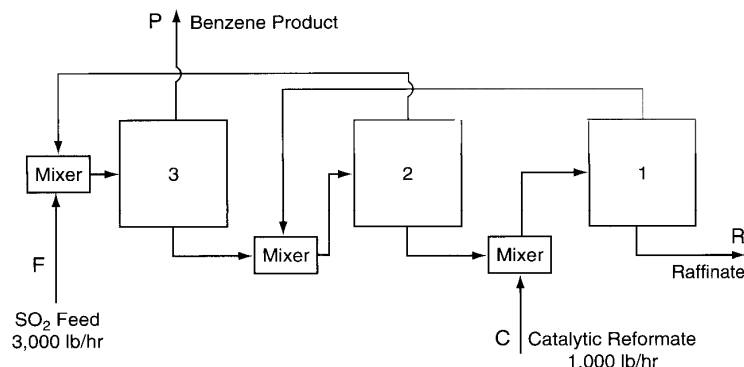


Figure SAT12.2P4

7. A catalytic dehydrogenation process shown in Figure SAT12.3P1, 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.

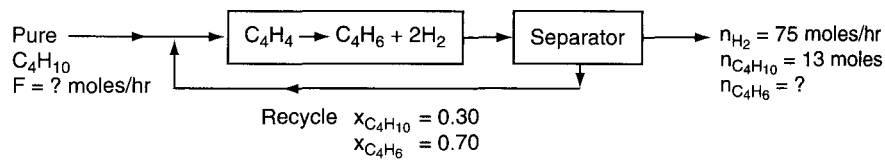


Figure SAT12.3P1

- (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 $140^\circ C$:

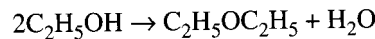


Figure SAT12.3P3 is a simplified process diagram. If 87% conversion of the alcohol fed to the reactor occurs per pass in the reactor, calculate: (a) kilograms per hour of fresh feed, and (b) kilograms per hour of recycle.

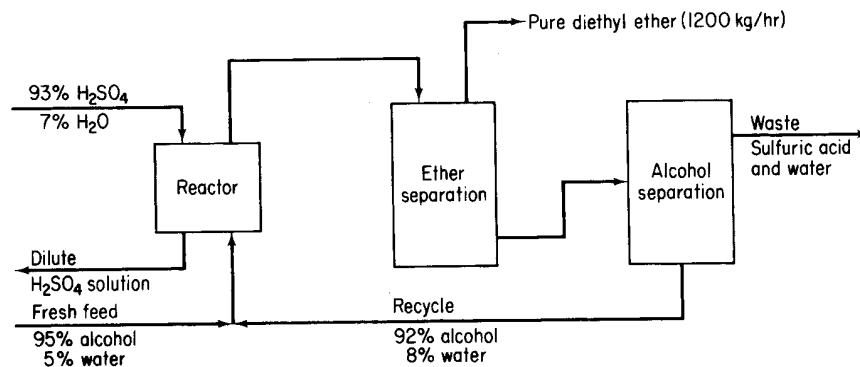


Figure SAT12.3P3

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 $600^\circ C$ 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.

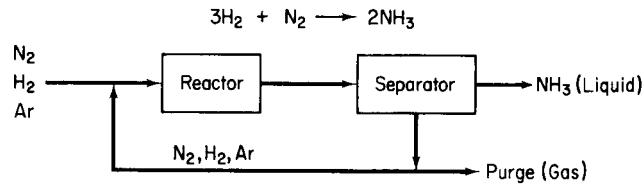


Figure SAT12.4P1

The fresh feed of gas composed of 75.16% H₂, 24.57% N₂, and 0.27% Ar is mixed with the recycled gas and enters the reactor with a composition of 79.52% H₂. The gas stream leaving the ammonia separator contains 80.01% H₂ 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 (C₂H₄Cl₂). The feed data have been placed on the figure. Ninety percent conversion of the C₂H₄ occurs on each pass through the reactor. The overhead stream from the separator contains 98% of the Cl₂ entering the separator, 92% of the entering C₂H₄, and 0.1% of the entering C₂H₄Cl₂. Five percent of the overhead from the separator is purged. Calculate (a) the flow rate and (b) the composition of the purge stream.

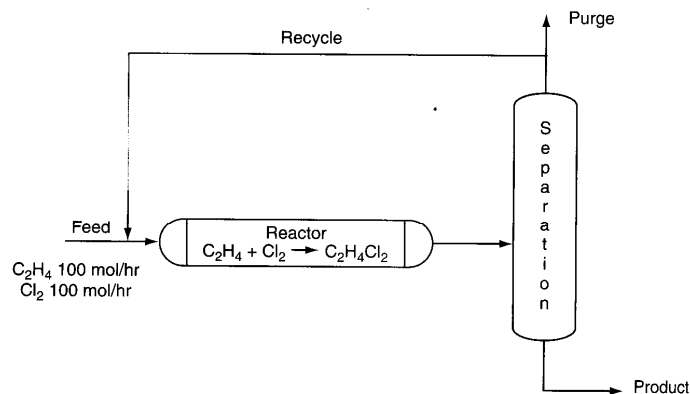


Figure SAT12.4P2

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 C₄H₆ = 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) Cl₂: 0.658; C₂H₄: 0.338; C₂H₄Cl₂: 0.0033.

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

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

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

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

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

Example 1

Calculate the volume, in cubic meters, occupied by 40 kg of CO₂ at standard conditions.

Solution

Basis: 40 kg of CO₂

40 kg CO ₂	1 kg mol CO ₂	22.42 m ³ CO ₂	= 20.4 m ³ CO ₂ at S.C.
	44 kg CO ₂	1 kg mol CO ₂	

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 cm³, and the temperature in K.

Solution

At standard conditions we will use the approximate values

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

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

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)

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

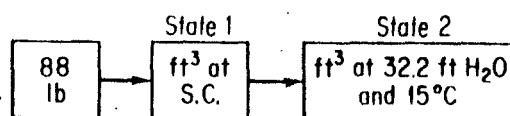
or

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

Example 3

Calculate the volume occupied by 88 lb of CO₂ 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 **n₁/n₂** 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 CO₂

88 lb CO ₂		359 ft ³	288	33.91	= 798 ft ³ CO ₂ at 32.2 ft H ₂ O and 15°C
	44 lb CO ₂	1 lb mol	273	32.2	
	1 lb mol CO ₂				

Calculation of V₁

Another solution

The same results can be obtained by using Eq. 1

$$R = \frac{pV}{T}$$

At S.C.,

$$p = 33.91 \text{ ft H}_2\text{O} \qquad V = 359 \text{ ft}^3/\text{lb mol} \qquad T = 273\text{K}$$

$$R = \frac{33.91}{273} \times \frac{359}{1} = 44.59 \frac{(\text{ft H}_2\text{O})(\text{ft}^3)}{(\text{lb mol})(\text{K})}$$

Basis: 88 lb of CO₂

$$V = \frac{nRT}{p} = \frac{88 \text{ lb CO}_2}{44 \text{ lb CO}_2} \times \frac{44.59 (\text{ft H}_2\text{O})(\text{ft}^3)}{(\text{lb mol})(\text{K})} \times \frac{288 \text{ K}}{32.2 \text{ ft H}_2\text{O}}$$

$$= 798 \text{ ft}^3 \text{ CO}_2 \text{ at } 32.2 \text{ ft H}_2\text{O and } 15^\circ\text{C}$$

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 N₂ at 27°C and 100 kPa in SI units?

SolutionBasis: 1 m³ of N₂ at 27°C and 100 kPa

$$\frac{1 \text{ m}^3}{300 \text{ K}} \left| \frac{273 \text{ K}}{100 \text{ kPa}} \right| \left| \frac{101.3 \text{ kPa}}{22.4 \text{ m}^3} \right| \left| \frac{28 \text{ kg}}{1 \text{ kg mol}} \right| = 1.123 \text{ kg}$$

density = 1.123 kg/m³ of N₂ 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 N₂ at 80°F and 745 mm Hg compared to air at 80°F and 745 mm Hg?

SolutionBasis: 1 ft³ of air at 80°F and 745 mm Hg

$$\frac{1}{540} \left| \frac{492}{745} \right| \left| \frac{760}{359} \right| \left| \frac{29}{1} \right| = 0.0721 \text{ lb/ft}^3 \text{ at } 80^\circ\text{F and } 745 \text{ mm Hg}$$

Basis: 1 ft³ of N₂ at 80°F and 745 mm Hg

$$\frac{1}{540} \left| \frac{492}{745} \right| \left| \frac{760}{359} \right| \left| \frac{28}{1} \right| = 0.0697 \text{ lb/ft}^3 \text{ at } 80^\circ\text{F and } 745 \text{ mm Hg}$$

$$(\text{sp. gr.})_{\text{N}_2} = \frac{0.0697}{0.0721} = 0.967 \frac{\text{lb N}_2/\text{ft}^3 \text{ at } 80^\circ\text{F, } 745 \text{ mm Hg}}{\text{lb air}/\text{ft}^3 \text{ air at } 80^\circ\text{F, } 745 \text{ mm Hg}}$$

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.

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

$$\text{Thus } \text{sp. gr.} = \frac{\rho_A}{\rho_B} = \left(\frac{p_A}{p_B} \right) \left(\frac{\text{mol. wt. A}}{\text{mol. wt. B}} \right) \left(\frac{T_B}{T_A} \right) \quad (3)$$

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

$$p_i V_{\text{total}} = n_i RT_{\text{total}} \quad (4)$$

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

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

or

$$p_i = p_{\text{total}} \frac{n_i}{n_{\text{total}}} = p_{\text{total}} y_i \quad (5)$$

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?

(6)

$$p_1 + p_2 + \dots + p_n = p_t \quad \dots 13.6$$

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% CO₂, 6.0% O₂, and 80.0% N₂. 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**.

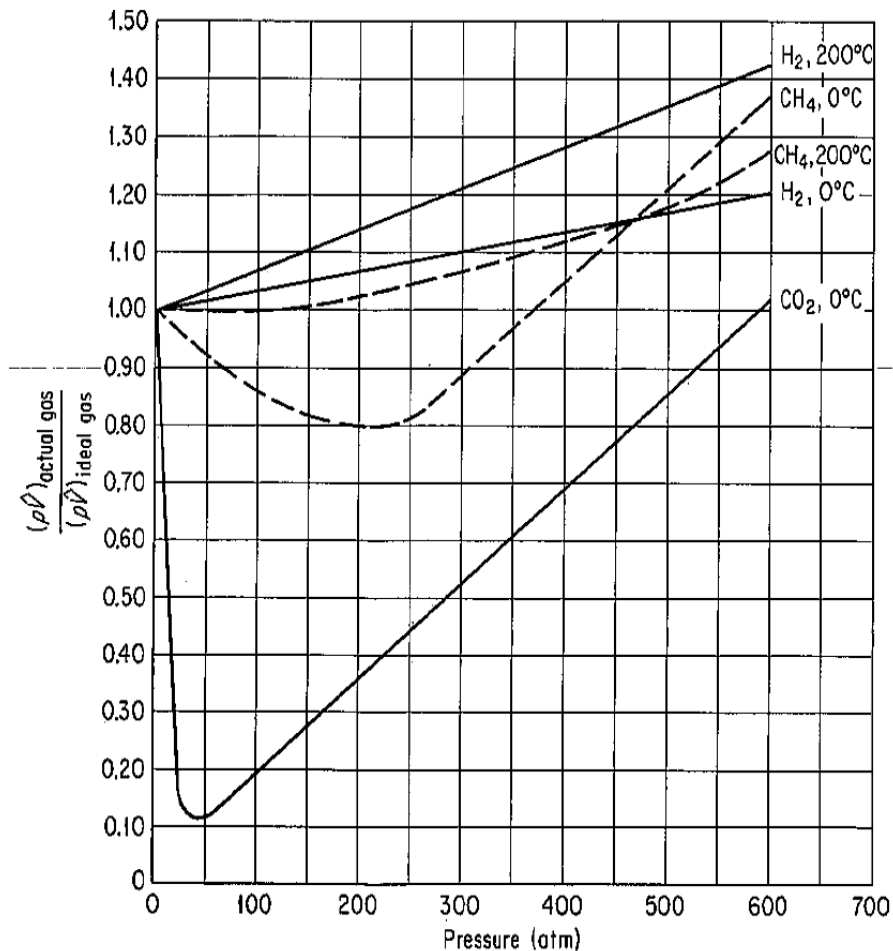


Figure 1 Deviation of real gases from the ideal gas law at high pressures.

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.

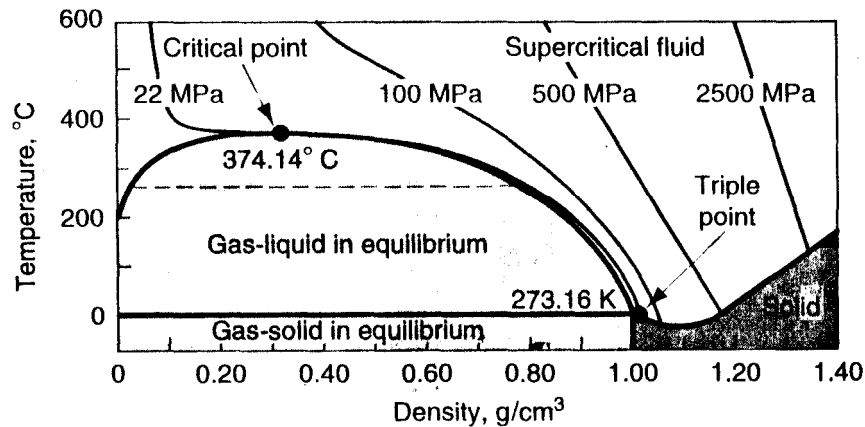


Figure 2 The regions of existence of solid, liquid, gaseous, and supercritical water. At the triple point solid, liquid, and gas are all in equilibrium.

- ❖ 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.

$$p V = z n R T \quad (7)$$

- ❖ 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-and-error 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_{ci} the ideal critical volume (not the experimental value of the critical volume), or

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

Both V_{ri} and \hat{V}_{ci} are easy to calculate since T_c and p_c are presumed known.

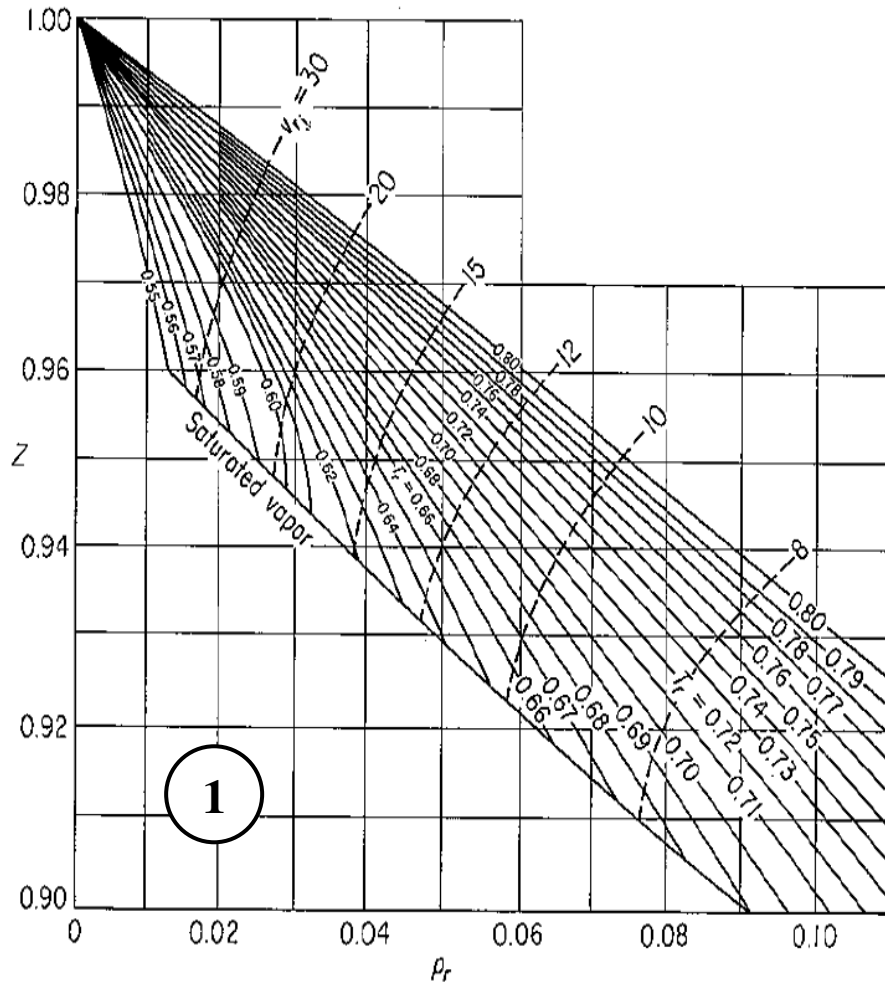


Figure 3(a) Generalized Compressibility Chart, Very Low Reduced Pressure.

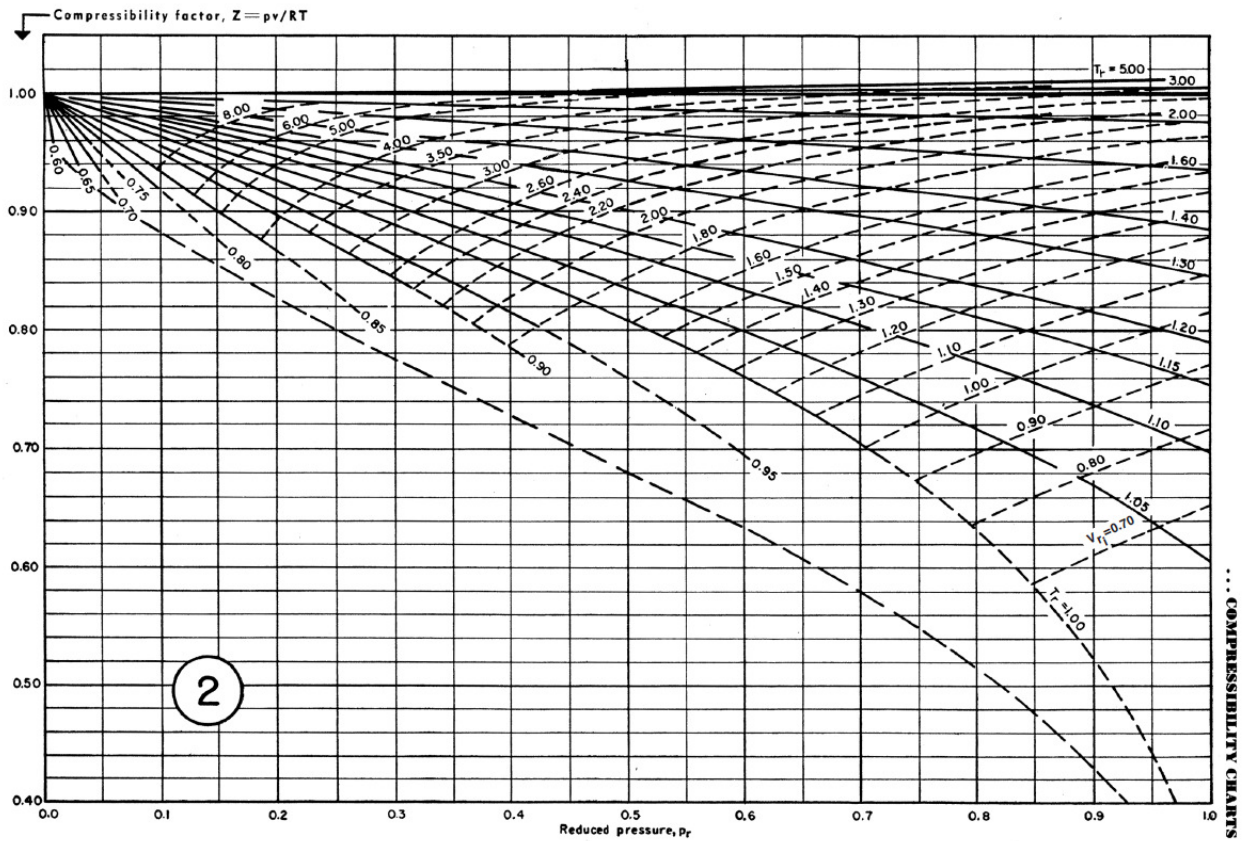


Figure 3(b) Generalized Compressibility Chart, Low Pressure.

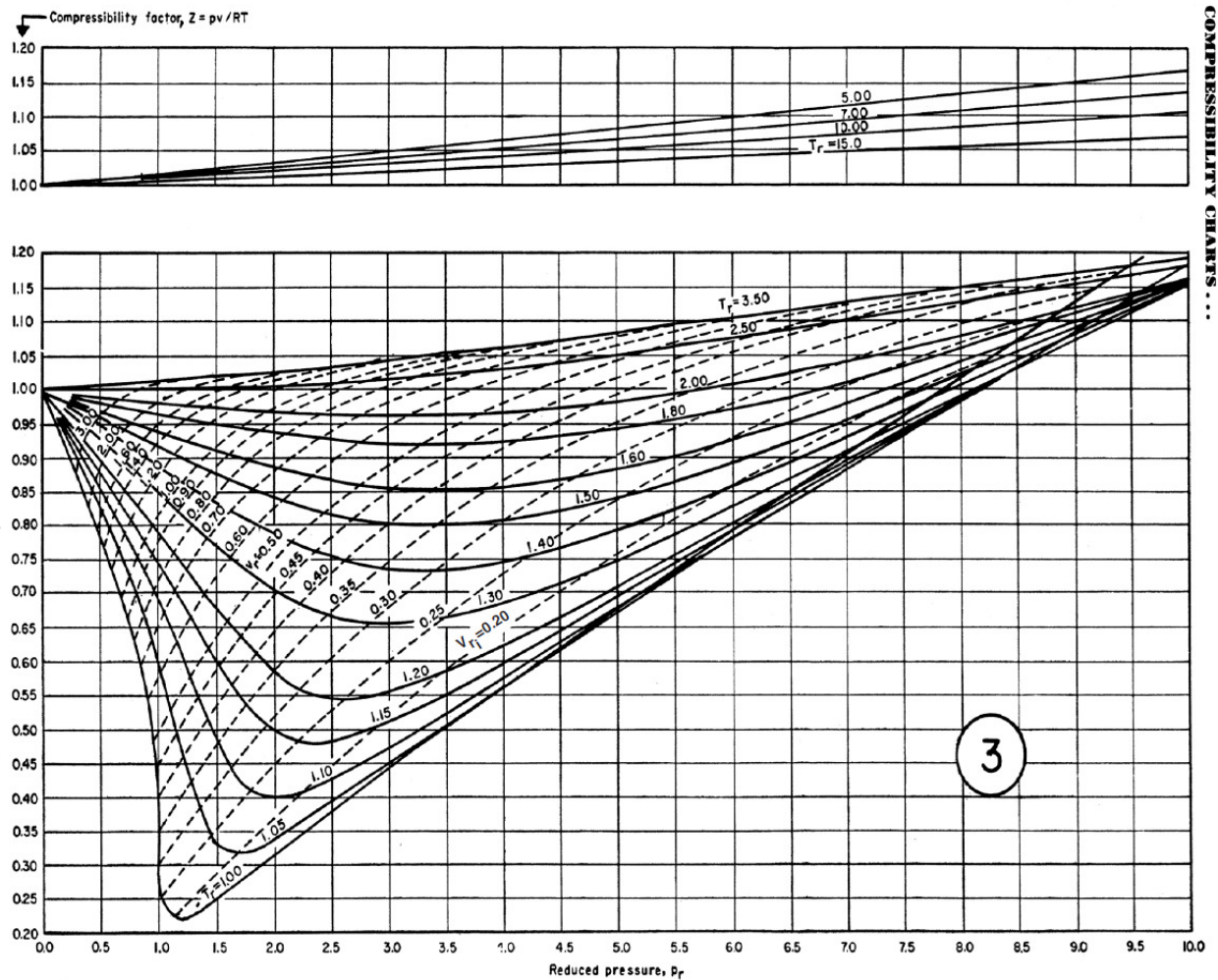


Figure 3(c) Generalized Compressibility Chart, Medium Pressure.

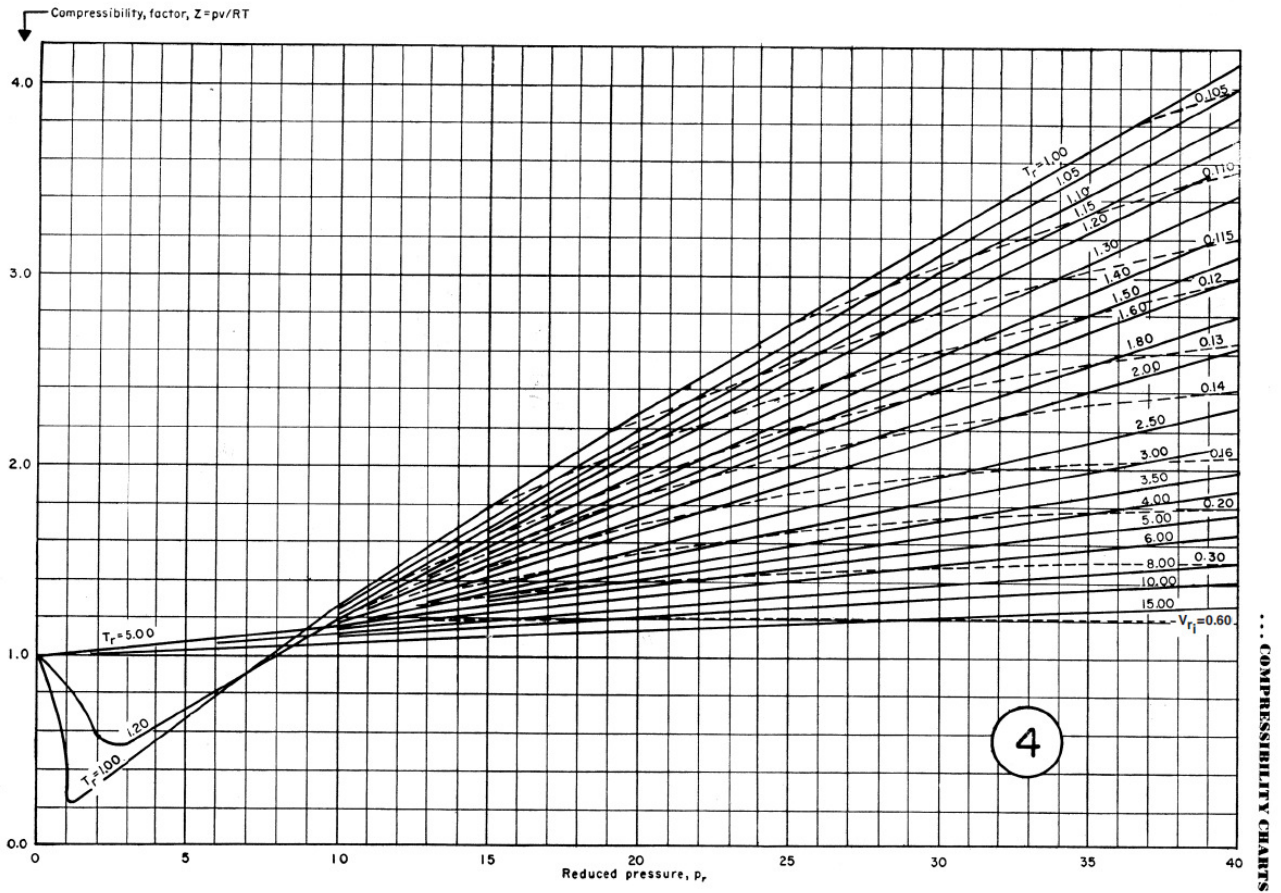


Figure 3(d) Generalized Compressibility Chart, High Pressure.

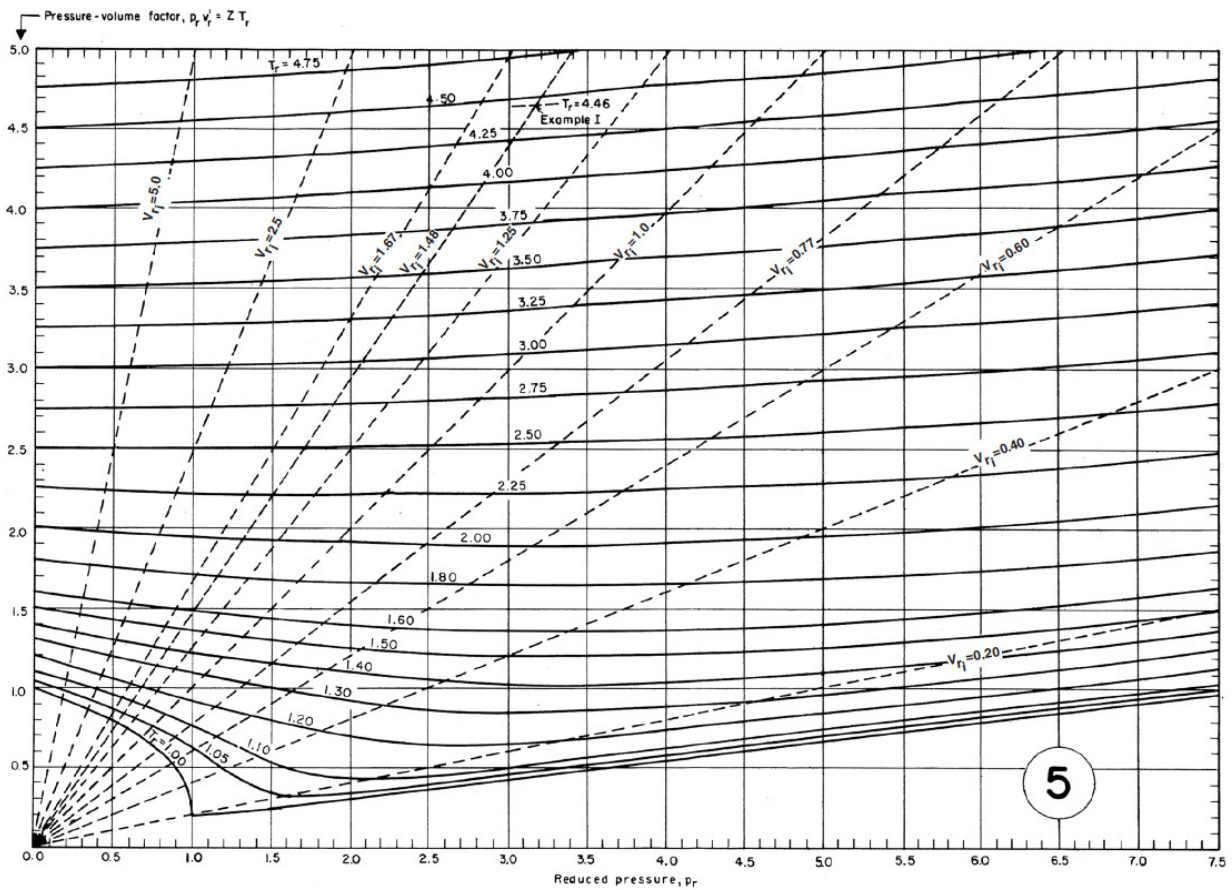


Figure 3 (e) Generalized Compressibility Chart, with Special Scales.

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 $1.20 \text{ ft}^3/\text{lb}$ and hence that there are only 100 lb of NH_3 in the tank. Could he be correct? See Figure E 3.7.

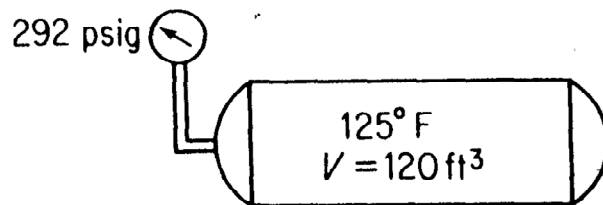


Figure E 3.7

Solution

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

$$R = 10.73 \frac{(\text{psia})(\text{ft}^3)}{(\text{lb mol})(^\circ\text{R})}$$

$$p = 292 + 14.7 = 306.7 \text{ psia}$$

$$T = 125^\circ\text{F} + 460 = 585^\circ\text{R}$$

$$u = \frac{1 \text{ lb}}{17 \text{ lb/lb mol}}$$

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

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:

$$T_c = 405.5\text{K} \approx 729.9\text{R}$$

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

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

$$\hat{V} = \frac{1.20 \text{ ft}^3 \text{ ideal}}{\text{lb}} \left| \frac{0.855}{1} \right. = 1.03 \text{ ft}^3/\text{lb NH}_3$$

$$\frac{1 \text{ lb NH}_3}{1.03 \text{ ft}^3} \left| \frac{120 \text{ ft}^3}{1} \right. = 117 \text{ lb NH}_3$$

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 $\hat{V} = 0.973 \text{ ft}^3/\text{lb}$, 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 (10^4 kPa)?

Solution

Basis: 3.500 kg O_2

We know from Appendix D that

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

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

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

Note that the *molar 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

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

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:

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

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

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

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:

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

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

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

Kammerlingh-Onnes:

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

Holborn:

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

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:

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

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

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

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

$$w = a\alpha$$

Peng-Robinson:

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

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

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

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

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

$$\omega = \text{acentric factor (see p. 275)}$$

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

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

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

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

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 m³ in volume containing 22.7 kg of propane C₃H₈ 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:

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

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

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

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

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

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:

$$p'_c = p_{cA} y_A + p_{cB} y_B + \dots \quad (8a)$$

$$T'_c = T_{cA} y_A + T_{cB} y_B + \dots \quad (8b)$$

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, CH₄ 20

Ethylene, C₂H₄ 30

Nitrogen, N₂ 50

at 90 atm pressure and 100°C. Compare the volume per mole as computed by the methods of:

- the perfect gas law
- 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 ₂ H 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

$$\begin{aligned} p'_c &= p_{cA}y_A + p_{cB}y_B + p_{cC}y_C = (45.8)(0.2) + (50.5)(0.3) + (33.5)(0.5) \\ &= 41.2 \text{ atm} \end{aligned}$$

$$\begin{aligned} T'_c &= T_{cA}y_A + T_{cB}y_B + T_{cC}y_C = (191)(0.2) + (283)(0.3) + (126)(0.5) \\ &= 186 \text{ K} \end{aligned}$$

Then we calculate the pseudo-reduced values for the mixture

$$p'_r = \frac{p}{p'_c} = \frac{90}{41.2} = 2.18, \quad T'_r = \frac{T}{T'_c} = \frac{373}{186} = 2.01$$

With the aid of these two parameters we can find from Figure 13.3(c) $z = 0.965$. Thus

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

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

$$\hat{V}_{c_i}' = \frac{RT_c'}{p_c'} \quad \text{and} \quad \hat{V}_{r_i}' = \frac{\hat{V}}{V_{c_i}'}$$

\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).

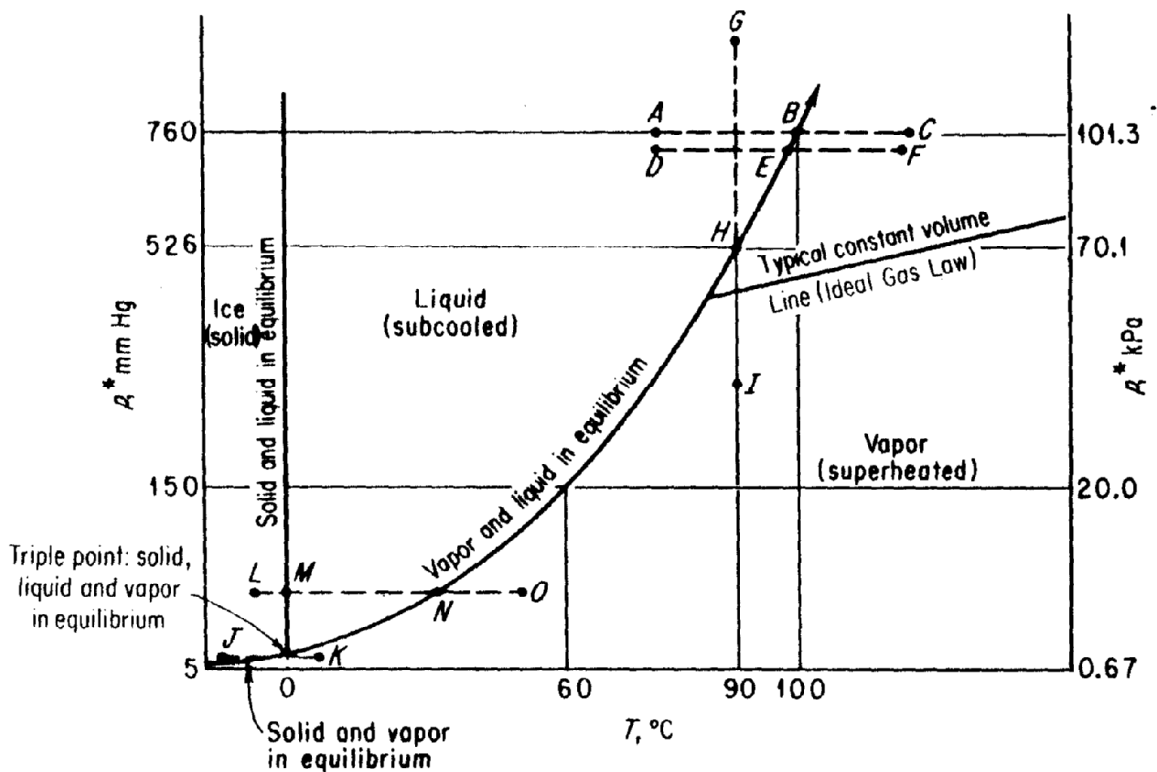


Figure 13.4 Vapor-pressure curve for water.

- ❖ Any substance has an infinite number of **boiling points**, but by custom we say the **“normal” boiling point** 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.

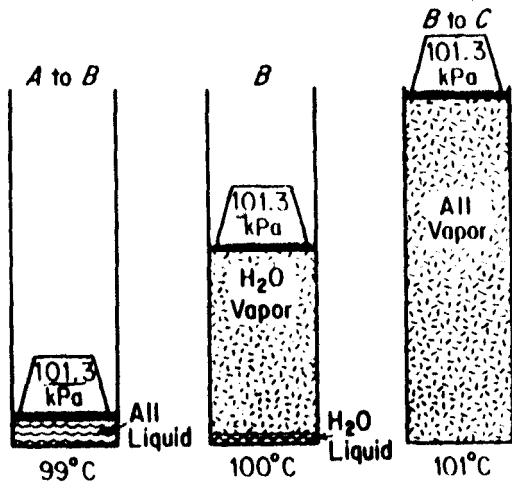


Figure 13.5 Transformation of liquid water into vapor at constant pressure. The 101.3 kPa exerted by the piston includes the force of the atmosphere above the piston.

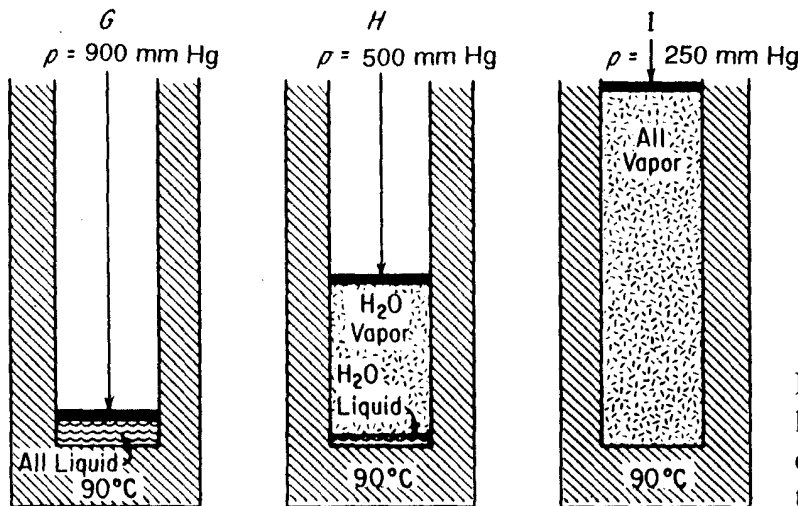


Figure 13.6 Transformation of liquid water into water vapor at a constant temperature by changing the imposed pressure.

- ❖ 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:

$$\ln p^* = A - \frac{B}{C + T} \quad (9)$$

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

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

From Appendix G in the text the coefficients are
 Benzene: $A = 15.9008$ $T = \text{K}$
 $B = 2788.51$ $p^* = \text{mmHg}$
 $C = -52.36$

- a. Vapor Pressure of benzene at 50°C

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

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

- 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, $T = 353.3\text{K}$

Liquid Properties

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

$$\rho = \rho_o - \beta(T - T_o) \quad (10)$$

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.

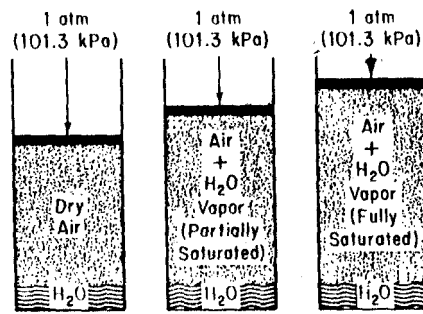
For compounds with like **molecular structures**, such as hydrocarbons of similar molecular weight, called **ideal liquids**, the density of a liquid mixture can be approximated by assuming that the weighted specific volumes are additive:

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

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**:

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

or

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

in a volume V at temperature T.

Example 12

What is the minimum number of cubic meters of dry air at 20°C and 100 kpa necessary to evaporate 6.0 kg of ethyl alcohol if the total pressure remains constant at 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

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

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

$$\frac{6.0 \text{ kg alcohol}}{46.07 \text{ kg alcohol}} \left| \frac{1 \text{ kg mol alcohol}}{46.07 \text{ kg alcohol}} \right| \frac{94.07 \text{ kg mol air}}{5.93 \text{ kg mol alcohol}} = 2.07 \text{ kg mol air}$$

$$V_{air} = \frac{2.07 \text{ kg mol air}}{1} \left| \frac{8.314 \text{ (kPa)(m}^3\text{)}}{(\text{kg mol})(\text{K})} \right| \frac{293 \text{ K}}{100 \text{ kPa}} = 50.3 \text{ m}^3 \text{ at } 20^\circ\text{C and } 100 \text{ kPa}$$

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

$$V \text{ m}^3 \text{ of alcohol at } 5.93 \text{ kPa and } 20^\circ\text{C}$$

$$V \text{ m}^3 \text{ of air at } 94.07 \text{ kPa and } 20^\circ\text{C}$$

$$V \text{ m}^3 \text{ of air plus alcohol at } 100 \text{ kPa and } 20^\circ\text{C}$$

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

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

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

$$V_{\text{air}} = \frac{53.5 \text{ m}^3 \left| \begin{array}{c} 94.07 \\ 100 \end{array} \right|}{100} = 50.3 \text{ m}^3 \text{ at } 100 \text{ kPa and } 20^\circ\text{C}$$

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.

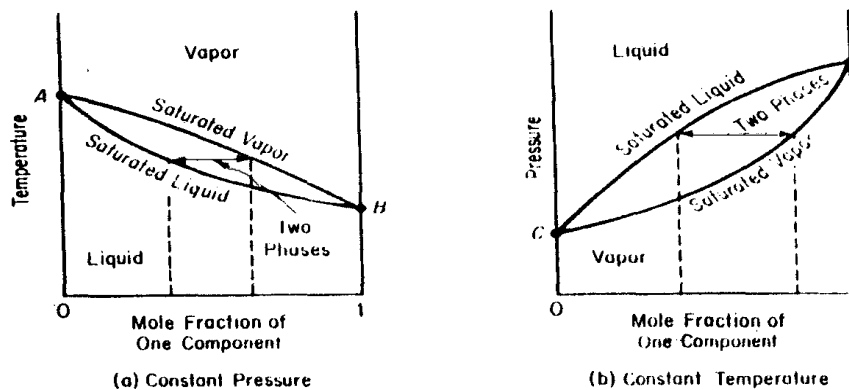


Figure 13.17 Vapor-liquid equilibrium for a binary mixture. The dashed lines show the equilibrium compositions.

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

$$p_i = H_i x_i \tag{12}$$

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

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

And since H_i 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 $x_i \equiv 1$, $p_i \equiv p_i^*$.

$$p_i = p_i^* x_i \quad (13)$$

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 ($p_i = p_i y_i$):

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

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.

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

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

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

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

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

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

$$1 = \sum_{i=1}^n \frac{y_i}{K_i} \quad (18)$$

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

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

Example 13

A gas containing nitrogen, benzene, and toluene is in equilibrium with 40 mole% benzene and 60 mole% toluene liquid mixtures at 100 °C 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

$$\ln p^* = A - \frac{B}{C+T} \Rightarrow p_B^* = \text{Exp} \left[15.9008 - \frac{2788.51}{-52.36+373} \right] = 1344.9 \text{ mm Hg}$$

$$p_T^* = \text{Exp} \left[16.0137 - \frac{3096.52}{-53.67+373} \right] = 553.8 \text{ mm Hg}$$

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

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

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

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. $p_{\text{H}_2\text{O}}^* (75^\circ \text{C}) = 289 \text{ mm Hg}$

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**:

$$y_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^*(75^\circ \text{C}) / P$$

$$y_{\text{H}_2\text{O}} = \frac{289 \text{ mm Hg}}{760 \text{ mm Hg}} = \boxed{0.380 \frac{\text{mol H}_2\text{O}}{\text{mol}}}$$

$$y_{\text{dry air}} = 1 - y_{\text{H}_2\text{O}} = \boxed{0.620 \frac{\text{mol dry air}}{\text{mol}}}$$

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 2.63×10^4 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.

$$x_{\text{C}_2\text{H}_6} = \frac{y_{\text{C}_2\text{H}_6} P}{H_{\text{C}_2\text{H}_6}} = \frac{(0.0100)(20.0 \text{ atm})}{2.63 \times 10^4 \text{ atm/mole fraction}} = \boxed{7.60 \times 10^{-6} \frac{\text{mol C}_2\text{H}_6}{\text{mol}}}$$

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

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

$$= 6.906 - \frac{1211}{T + 220.8} \xrightarrow{T = 30^\circ\text{C}} p_{\text{B}}^* = 119 \text{ mm Hg}$$

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

$$p_{\text{B}} = x_{\text{B}} p_{\text{B}}^* = (0.500)(119 \text{ mm Hg}) = 59.5 \text{ mm Hg}$$

$$p_{\text{T}} = x_{\text{T}} p_{\text{T}}^* = (0.500)(36.7 \text{ mm Hg}) = 18.35 \text{ mm Hg}$$

$$P = p_{\text{B}} + p_{\text{T}} = \boxed{77.9 \text{ mm Hg}}$$

$$y_{\text{B}} = p_{\text{B}}/P = \boxed{0.764 \text{ mole benzene/mole}}$$

$$y_{\text{T}} = p_{\text{T}}/P = \boxed{0.236 \text{ mole toluene/mole}}$$

Gibb's phase rule

The rule can be applied only to systems in **equilibrium**.

$$F = C - P + 2 \quad (20)$$

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:

- Pure liquid benzene.
- A mixture of ice and water only.
- A mixture of liquid benzene, benzene vapor, and helium gas.
- A mixture of salt and water designed to achieve a specific vapor pressure.

What variables might be specified in each case? **Solution**

$$F = C - P + 2$$

- $C = 1, P = 1$, hence $F = 1 - 1 + 2 = 2$. The temperature and pressure might be specified in the range in which benzene remains a liquid.
- $C = 1, P = 2$, hence $F = 1 - 2 + 2 = 1$. Once either the temperature or the pressure is specified, the other intensive variables are fixed.
- $C = 2, P = 2$, hence $F = 2 - 2 + 2 = 2$. A pair from temperature, pressure, or mole fraction can be specified.
- $C = 2, P = 2$, 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

- Calculate the volume in ft^3 of 10 lb mol of an ideal gas at 68°F and 30 psia.
- 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?
- 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?
- 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?
- What is the density of a gas that has a molecular weight of 0.123 kg/kg mol at 300 K and 1000 kPa?
- What is the specific gravity of CH_4 at 70°F and 2 atm compared to air at S.C.?
- 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

- What is the partial pressure of each component?
- 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 $20^\circ C$. Determine the mass in kilograms of CO_2 at 1 atm.
11. Calculate the pressure of 4 g mol CO_2 contained in a $6.25 \times 10^{-3} m^3$ fire extinguisher at $25^\circ C$.
12. You measure that 0.00220 lb mol of a certain gas occupies a volume of $0.95 ft^3$ at 1 atm and $32^\circ F$. 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 $71^\circ F$.
13. Calculate the temperature of 2 g mol of a gas using van der Waals' equation with $a = 1.35 \times 10^{-6} m^6(atm)(g mol^{-2})$, $b = 0.0322 \times 10^{-3} (m^3)(g mol^{-1})$ 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 $50^\circ C$ 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 $50^\circ C$, 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 $60^\circ C$ and equilibrium is reached, will there still be liquid water present? at $125^\circ C$?
19. A mixture of air and benzene contains 10 mole% benzene at $43^\circ C$ 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 $82^\circ F$. 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 $80^\circ F$. 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 $100^\circ F$ and (b) the liquid composition.

Component	Mole fraction	K values at psia of		
		190	200	210
C ₂ H ₆	0.218	3.22	3.07	2.92
C ₃ H ₈	0.665	1.005	0.973	0.92
<i>i</i> -C ₄ H ₁₀	0.1073	0.45	0.43	0.41
<i>n</i> -C ₄ H 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: N₂ (g), O₂ (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 N₂ plus ethanol vapor.

Answers:

- 1883 ft³
- 2.98 kg
- 1.32
- 28.3 m³/hr
- 0.0493 kg/m³
- 1.02 (lb CH₄/ft³ at 70 °F and 2 atm)/ (lb air/ ft³ at S.C.)
- N₂, 0.28 psia; CH₄, 10.9 psia; C₂H₆, 2.62 psia
- (a) 11.12 psia at 2 ft³ and 120°F; (b) 0.28 psia at 2 ft³ and 120°F
- $V_{ci} = R T_c/P_c$. It can be used to calculate V_{ri} , which is a parameter on the Nelson and Obert charts.
- 1.65 kg
- 14.9 atm
- $V = 0.60 \text{ ft}^3$
- 314 K
- (a) 50.7 atm; (b) 34.0 atm
- 262 atm
- predicted 220.9 mm Hg
- The partial pressure of the vapor equals the vapor pressure of the gas. Liquid and vapor are in equilibrium.
- Yes; yes
- 21°C; benzene
- 0.0373
- 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 is 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) $C = 2$, $P = 2$, $F = 2$