SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I - Introduction – SCHA1304

1.INTRODUCTION

"Chemical engineers" use math, physical sciences (physics, chemistry), life sciences (biology, microbiology and biochemistry), and economics to solve practical problems. The difference between chemical engineers and other types of engineers is that they apply a knowledge of chemistry in addition to other engineering disciplines. Chemical engineers may be called "universal engineers" because their scientific and technical mastery is so extensive.

Chemical engineering is a branch of engineering that uses principles of chemistry, physics, mathematics, biology, and economics to efficiently use, produce, design, transport and transform energy and materials. The work of chemical engineers can range from the utilization of nano-technology and nano-materials in the laboratory to large-scale industrial processes that convert chemicals, raw materials, living cells, microorganisms, and energy into useful forms and products.

Chemical engineers are involved in many aspects of plant design and operation, including safety and hazard assessments, process design and analysis, modeling, control engineering, chemical reaction engineering, nuclear engineering, biological engineering, construction specification, and operating instructions.

1.1 CONCEPTS OF UNITS AND CONVERSION FACTORS

Any value that you'll run across as an engineer will either be unitless or, more commonly, will have specific types of units attached to it. In order to solve a problem effectively, all the types of units should be consistent with each other, or should be in the same system. A system of units defines each of the basic unit types with respect to some measurement that can be easily duplicated, so that for example 5 ft. is the same length in Australia as it is in the United States.

There are five commonly-used base unit types or dimensions that one might encounter (shown with their abbreviated forms for the purpose of dimensional analysis): Length (L), or the physical distance between two objects with respect to some standard distance Time (t), or how long something takes with respect to how long some natural phenomenon takes to occur Mass (M), a measure of the inertia of a material relative to that of a standard Temperature (T), a measure of the average kinetic energy of the molecules in a material relative to a standard Electric Current (E), a measure of the total charge that moves in a certain amount of time. There are several different consistent systems of units one can choose from. Which one should be used depends on

the data available.

1.2   UNIT AND DIMENSIONS

Unit

The "unit" indicates what the measured quantity represents,

➢ A measured or counted quantity has a numerical value and a unit

➢ Measurable units are specific values of dimensions that have been defined by convention,

Example: grams for mass, seconds for time, and centimeters for length

Dimensions

➢ The "dimension" is the measurable quantity that the unit represents. Example: length, mass, time, and temperature,

➢ It also be calculated by multiplying or dividing other dimensions,

Example: length/time = velocity,

$length^3$ = volume, and mass/length^3 =

density

NOTE: Chemical engineers, like many other engineers, use values, units, and dimensions all the time

Systems of Units

➢ There are several systems of units, but two primary systems that engineers use are:

➢ The International System of Units (SI system) and

➢ The American Engineering System of Units (AES).

➢ Other systems are:

- Centimeter–Gram–Second (CGS)
- Foot–Pound–Second (FPS)
- The British System of Units (British)

Units Associated with Systems

System	Mass (m)	Length (l)	Time (t)	Temperature (T)
SI	Kilogram (kg)	Meter (m)	Second (s)	Kelvin (K)
AES Degree	Pound mass (lbm)	Foot (ft)	Second (s)	Fahrenheit (°F)
CGS	Gram (g)	Centimeter (cm)	Second (s)	Kelvin (K)
FPS*	Pound mass (lbm)	Foot (ft)	Second (s)	Degree Fahrenheit (°F)
British	Slug	Foot (ft)	Second (s)	Degree Celsius (°C)

*Imperial system units are sometimes referred to as FPS.

1.3   CONVERSION FACTOR

To convert a quantity expressed in terms of one unit to its equivalent in terms of another unit, you will need to multiply the given quantity by the conversion factor (new unit/old unit)

A unit conversion expresses the same property as a different unit of measurement. For instance, time can be expressed in minutes instead of hours, while distance can be converted from miles to kilometers, or feet, or any other measure of length. Often measurements are given in one set of units, such as feet, but are needed in different units, such as chains. A conversion factor is a numeric expression that enables feet to be changed to chains as an equal exchange.

A conversion factor is a number used to change one set of units to another, by multiplying or dividing. When a conversion is necessary, the appropriate conversion factor to an equal value must be used. For example, to convert inches to feet, the appropriate conversion value is 12 inches equal 1 foot. To convert minutes to hours, the appropriate conversion value is 60 minutes equal 1 hour. A unit cancellation table is developed by using known units, conversion factors, and the fact that a unit of measure ÷ the same unit of measure cancels out that unit. The table is set up so all the units cancel except for the unit desired. To cancel a unit, the same unit must be in the numerator and in the denominator. When you multiply across the table, the top number will be divided by the bottom number, and the result will be the answer in the desired

units.

Unit Conversion Factors

Quantity	Equivalent Values
Mass	$1\ \text{kg} = 1000\ \text{g} = 0.001\ \text{metric ton} = 2.20462\ \text{lb}_m = 35.27392\ \text{oz}$ $1\ \text{lb}_m = 16\ \text{oz} = 5\times10^{-4}\ \text{ton} = 453.593\ \text{g} = 0.453593\ \text{kg}$
Length	$1\ \text{m} = 100\ \text{cm} = 1000\ \text{mm} = 10^6\ \mu\text{m} = 10^{10}\ \text{Å}$ $1\ \text{m} = 39.37\ \text{in} = 3.2808\ \text{ft} = 1.0936\ \text{yd} = 0.0006214\ \text{mile}$ $1\ \text{ft} = 12\ \text{in} = 1/3\ \text{yd} = 0.3048\ \text{m} = 30.48\ \text{cm}$
Volume	$1\ \text{m}^3 = 1000\ \text{liters} = 10^6\ \text{cm}^3 = 10^6\ \text{ml}$ $1\ \text{m}^3 = 35.3145\ \text{ft}^3 = 220.83\ \text{imperial gallons} = 264.17\ \text{gal} = 1056.68\ \text{qt}$ $1\ \text{ft}^3 = 1728\ \text{in}^3 = 7.4805\ \text{gal} = 0.028317\ \text{m}^3 = 28.317\ \text{liters} = 28317\ \text{cm}^3$
Force	$1\ \text{N} = 1\ \text{kg·m/s}^2 = 10^5\ \text{dynes} = 10^5\ \text{g·cm/s}^2 = 0.22481\ \text{lb}_f$ $1\ \text{lb}_f = 32.174\ \text{lb}_m\text{·ft/s}^2 = 4.4482\ \text{N}$
Pressure	$1\ \text{atm} = 1.01325\times10^5\ \text{N/m}^2\ (\text{Pa}) = 101.325\ \text{kPa} = 1.01325\ \text{bars}$ $1\ \text{atm} = 1.01325\times10^6\ \text{dynes/cm}^2$ $1\ \text{atm} = 760\ \text{mmHg at }0°\text{C (torr)} = 10.333\ \text{m H}_2\text{O at }4°\text{C} = 14.696\ \text{lb}_f/\text{in}^2\ (\text{psi})$ $1\ \text{atm} = 33.9\ \text{ft H}_2\text{0 at }4°\text{C} = 29.921\ \text{inHg at }0°\text{C}$
Energy	$1\ \text{J} = 1\ \text{N·m} = 10^7\ \text{ergs} = 10^7\ \text{dyne·cm} = 2.778\times10^{-7}\ \text{kW·h}$ $1\ \text{J} = 0.23901\ \text{cal} = 0.7376\ \text{ft-lb}_f = 9.486\times10^{-4}\ \text{Btu}$
Power	$1\ \text{W} = 1\ \text{J/s} = 1.341\times10^{-3}\ \text{hp}$

Problem 1.1

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

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

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

Another way is to use conversion factors you know

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

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

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.

Problem 1.2

    In biological systems, enzymes are used to accelerate the rates of certain biological reactions. Glucoamylase is an enzyme that aids in the conversion of starch to glucose (a sugar that cells use for energy). Experiments show that 1 μg mol of glucoamylase in a 4% starch solution results in a production rate of glucose of 0.6 μg mol/(mL)(min). Determine the production rate of glucose for this system in the units of lb mol/(ft³)(day).

Solution

Basis: 1 min

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

$$= 0.0539 \frac{lb \ mol}{(ft^3)(day)}$$

Problem 1.3

Convert the following quantities to the ones designated :
a. 42 ft²/hr to cm²/s.
b. 25 psig to psia.
c. 100 Btu to hp-hr.

Solution

a. $\dfrac{42.0 \ ft^2}{hr} \left(\dfrac{1.0 \ m}{3.2808 \ ft} \right)^2 \dfrac{10^4 cm^2}{1.0 \ m^2} \left| \dfrac{1 \ hr}{3600 \ s} \right.$ $=$ 10.8 cm²/s

b. $\dfrac{100 \ Btu}{} \left| \dfrac{3.93 \times 10^{-4} \ hp\text{-}hr}{1 \ Btu} \right.$ $=$ 3.93 × 10⁻² hp-hr

c. $\dfrac{80.0 \ lb_f}{} \left| \dfrac{32.174 \ (lb_m)(ft)}{(lb_f)(s)^2} \right| \dfrac{1 \ kg}{2.20 \ lb_m} \left| \dfrac{1 \ m}{3.2808 \ ft} \right| \dfrac{1 \ N}{1 \ (kg)(m)(s)^{-2}}$ = 356 N

Problem 1.4

Convert the ideal gas constant : $R = 1.987 \ \dfrac{cal}{(gmol)(K)}$ to $\dfrac{Btu}{(lb \ mol)(^{\circ}R)}$

Solution

$$\frac{1.987 \text{ cal}}{(\text{gmol})(\text{K})} \left| \frac{1 \text{ Btu}}{252 \text{ cal}} \right| \frac{454 \text{ gmol}}{1 \text{ lb mol}} \left| \frac{1\text{K}}{1.8 \,^{\circ}\text{R}} \right. = 1.98 \frac{\text{Btu}}{(\text{lb mol})(^{\circ}\text{R})}$$

1.5 FUNDAMENTAL AND DERIVED UNITS

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. By attaching units to all numbers that are not fundamentally dimensionless, you get the following very practical benefits:

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.

1.6 BASIC CHEMICAL CALCULATIONS

mole

A mole is a unit of measurement that is associated with the mass of a chemical substance. The mole is a specific measurement of the number of atoms or molecules in a substance, based on the number of atoms in 12 grams of carbon-12. The mole exists to give scientists an easy way to convert between grams and molecules and back again in chemistry.

The usage of the mole occurs when measuring the number of grams would not make much sense, but measuring down to exact numbers of atoms and molecules would

not make sense either. The mole was created as a middle ground to measure a large number of atoms in a substance. It is not an exact measurement, merely an easy way to say that a substance has an approximate number of atoms or molecules.

a mole is a quantity used relate reactants to products in stoichiometric equations. A mole of any substance is equal to 6.02×10^{23} particles -- usually atoms or molecules -- of that substance. For a given element, the mass (grams) of one mole is given by its mass number on the periodic table; the "molar mass" of a molecule is the sum of the molar masses of the elements in the molecule in the correct ratios. It is simple to determine the molar mass of elements and molecules using the periodic table, as well as convert between grams and moles.

Mass

Mass is a property that reflects the quantity of matter within a sample. Mass usually is reported in grams (g) and kilograms (kg).

Mass may also be considered to be the property of matter that gives it a tendency to resist acceleration. The more mass an object has, the harder it is to accelerate it.

Mass Versus Weight

The weight of an object depends on its mass, but the two terms don't mean the same thing. Weight is the force exerted on mass by a gravitational field:

$$W = mg$$

Molecular weight

Molecular weight is a measure of the sum of the atomic weight values of the atoms in a molecule. Molecular weight is used in chemistry to determine stoichiometry in chemical reactions and equations. Molecular weight is commonly abbreviated by M.W. or MW. Molecular weight is either unitless or expressed in terms of atomic mass units (amu) or Daltons (Da).

Both atomic weight and molecular weight are defined relative to the mass of the isotope carbon-12, which is assigned a value of 12 amu. The reason the atomic weight of carbon is not precisely 12 is that it is a mixture of isotopes of carbon.

Sample Molecular Weight Calculation

The calculation for molecular weight is based on the molecular formula of a compound (i.e., not the simplest formula, which only includes the ratio of types of atoms and not the number). The number of each type of atom is multiplied by its atomic weight and then added to the weights of the other atoms.

For example, the molecular formula of hexane is C_6H_{14}. The subscripts indicate the number of each type of atom, so there are 6 carbon atoms and 14 hydrogen atoms in each hexane molecule. The atomic weight of carbon and hydrogen may be found on a periodic table.

Atomic weight of carbon:

12.01 Atomic weight of

hydrogen: 1.01

molecular weight = (number of carbon atoms) (C atomic weight) + (number of H

atoms) (H atomic weight) so we calculate as follows:

molecular weight = (6 x 12.01) + (14 x 1.01) molecular weight of hexane = 72.06 + 14.14 molecular weight of hexane = 86.20

One important calculation you should become skilled at is to convert the number of moles to mass and the mass to moles. To do this you 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

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

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

For example

$$\frac{100.0 \text{ g } H_2O}{} \left| \frac{1 \text{ g mol } H_2O}{18.0 \text{ g } H_2O} \right. = 5.56 \text{ g mol } H_2O$$

$$\frac{6.0 \text{ lb mol } O_2}{} \left| \frac{32.0 \text{ lb } O_2}{1 \text{ lb mol } O_2} \right. = 192 \text{ lb } O_2$$

Problem .1.5 Use of molecular weight to convert mass to mole

If a bucket holds 2.00 lb of NaOH, how many

(a) Pound moles of NaOH does it contain?
(b) Gram moles of NaOH does it contain?

Solution

You want to convert pounds to pound moles, and then convert respective values to the SI system of units.

Look up the molecular weight of NaOH, or calculate it from the atomic weights. It is 40.0.

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

(b$_1$) $\dfrac{2.00 \text{ lb NaOH}}{} \left| \dfrac{1 \text{ lb mol NaOH}}{40.0 \text{ lb NaOH}} \right| \dfrac{454 \text{ g mol}}{1 \text{ lb mol}} = 22.7 \text{ g mol}$

(b$_2$) $\dfrac{2.00 \text{ lb NaOH}}{} \left| \dfrac{454 \text{ g}}{1 \text{ lb}} \right| \dfrac{1 \text{ g mol NaOH}}{40.0 \text{ g NaOH}} = 22.7 \text{ g mol}$

Check your answer. Convert the 2.00 lb of NaOH to the SI system first, and then make the calculation.

Problem 1.6 Use of molecular weight to convert mole to mass

How many pounds of NaOH are in 7.50 g mol of NaOH?

Solution

The problem concerns converting g mol to lb.
From Example 2.2, the MW of NaOH is 40.0.

Basis: 7.50 g mol of NaOH

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

Note the conversion between lb mol and g mol converts the value of 7.50 g mol from the SI to the AE system of units. Could you first convert 7.50 g mol NaOH to g of NaOH, and then use the conversion of 454 g = 1 lb to get lb NaOH? Of course.

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

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

Specific gravity

Specific gravity is commonly thought of as a dimensionless ratio. Actually, it should be considered as the ratio of two densities—that of the substance of interest, A, to that of a reference substance—each of which has associated units. In symbols:

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

The reference substance for liquids and solids normally is water. Thus, the specific gravity is the ratio of the density of the substance in question to the density of water, which is 1.000 g/cm^3, 1000 kg/m^3, or 62.43 lb/ft^3 at 4°C. The specific gravity of gases frequently is referred to air, but may be referred to other gases.

Flow Rate

For continuous processes the **flow rate** of a process stream is the rate at which material is transported through a pipe. In this book we usually use an overlay dot to denote a rate except for the volumetric flow rate F. 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** (n) rate of a process stream is the number of moles (n) of a substance transported through a line per unit time.

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

Use any consistent units in your calculation.

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. Although the mass fraction is the correct word, by custom ordinary engineering usage employs the term **weight fraction**. 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.

Problem 1.7

An industrial-strength drain cleaner contains 5.00 kg of water and 5.00 kg of NaOH. What are the mass (weight) fractions and mole fractions of each component in the drain cleaner container?

Component	kg	Weight fraction	Mol. Wt.	kg mol	Mole fraction
H_2O	5.00	$\dfrac{5.00}{10.0} = 0.500$	18.0	0.278	$\dfrac{0.278}{0.403} = 0.69$
NaOH	5.00	$\dfrac{5.00}{10.00} = 0.500$	40.0	0.125	$\dfrac{0.125}{0.403} = 0.31$
Total	10.00	1.000		0.403	1.00

The kilogram moles are calculated as follows:

$$\frac{5.00 \text{ kg } H_2O}{} \left| \frac{1 \text{ kg mol } H_2O}{18.0 \text{ kg } H_2O} \right. = 0.278 \text{ kg mol } H_2O$$

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

Adding these quantities together gives the total kilogram moles.

Problem 1.8 Phosphoric acid is a colorless deliquescent acid used in the manufacture of fertilizers and as a flavoring agent in drinks. For a given 10 wt. % phosphoric acid solution of specific gravity 1.10 determine:

a. the mol fraction composition of this mixture.

b. the volume (in gallons) of this solution which would contain 1 g mol H_3PO_4.

Solution

a.   Basis: 100 g of 10 wt% solution

	g	MW	g mol	mol fr
H_3PO_4	10	97.97	0.102	0.020
H_2O	90	18.01	5.00	0.980

b. Specific gravity $= \dfrac{\rho_{soln}}{\rho_{ref}}$ The ref. liquid is water

The density of the solution is $\dfrac{1.10 \text{ g soln/cm}^3 \text{ soln} \left| 1.00 \text{ g } H_2O/\text{cm}^3 \right.}{1.00 \text{ g } H_2O/\text{cm}^3} = 1.10 \dfrac{\text{g soln}}{\text{cm}^3}$

$\dfrac{1 \text{ cm}^3 \text{ soln}}{1.10 \text{ g soln}} \left| \dfrac{1 \text{ g soln}}{0.1 \text{ g } H_3PO_4} \right| \dfrac{97.97 \text{ g } H_3PO_4}{1 \text{ g mol } H_3PO_4} \left| \dfrac{264.2 \text{ gal}}{10^6 \text{ cm}^3} \right. = \textbf{0.24 gal/g mol}$

Problem 1.9 The density of a liquid is 1500 kg/m³ at 20 °C.

a. What is the specific gravity 20°C/4°C of this material.

b. What volume (ft³) does 140 lbm of this material occupy at 20°C.

Solution

Assume the reference substance is water which has a density of 1000 kg/m³ at 4°C.

a. Specific gravity $= \dfrac{\rho_{soln}}{\rho_{ref}} = \dfrac{(kg/m^3)soln}{(kg/m^3)ref} = \dfrac{1500\ kg/m^3}{1000\ kg/m^3} = 1.50$

b. $\dfrac{1\ m^3\ liquid}{1500\ kg}\left|\dfrac{1\ kg}{2.20\ lb}\right|\dfrac{35.31\ ft^3}{1\ m^3}\left|\dfrac{140\ lb_m}{}\right| = 1.50\ ft^3$

Problem 1.10 A liquified mixture of n-butane, n-pentane and n-hexane has the following composition in percent: n-C_4H_{10} -50, n - C_5H_{12} -30 , and n - C_6H_{14}-20

Calculate the weight fraction, mol fraction and mol percent of each component and also the average molecular weight of the mixture.

Solution

Note that the hydrocarbon mixture is liquid so that the composition is therefore in weight percent. It is convenient to use a weight basis and set up a table to make the calculations.

Basis: 100 kg

	% = kg	wt fr	MW	kg mol	mol fr
n - C_4H_{10}	50	0.50	58	0.86	0.57
n - C_5H_{12}	30	0.30	72	0.42	0.28
n - C_6H_{14}	20	0.20	86	0.23	0.15
	100	1.00		1.51	1.00

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

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The ideal gas obeys the ideal gas law expressed as follows PV=nRT

Where

P = the absolute pressure of the gas

V = the total volume occupied by the gas n =

the number of moles of the gas

R = the ideal gas constant in appropriate units T =

the absolute temperature of the gas

IDEAL GAS CONSTANT R

1.987 cal/(g mol)(K)
1.987 Btu/(lb mol)(°R)
10.73 (psia)(ft³)/(lb mol)(°R)
8.314 (kPa)(m³)/(kg mol)(K) = 8.314 J/(g mol)(K)
82.06 (cm³)(atm)/(g mol)(K)
0.08206 (L)(atm)/(g mol)(K)
21.9 (in Hg)(ft³)/(lb mol)(°R)
0.7302 (ft³)(atm)/(lb mol)("R)

Sometimes, the ideal gas law is written as follows:

$$PV = nRT \implies \boxed{Pv = RT} \qquad v = V/n$$

where v is the specific volume (volume per mole or mass) of a gas

Common Standard Conditions for the Ideal Gas

System	T	P	v
SI	273.15 K	101.325 kPa	22.415 m³/kmol
Universal scientific	0.0°C	760 mmHg	22.415 L/mol
Natural gas	60.0°F (15.0°C)	14.696 psia 101.325 kPa	379.4 ft³/lbmol
American engineering	32°F	1 atm	359.05 ft³/lbmol

Van der Waals Equation of State

Van der Waals equation:

$$(P + \frac{a}{v^2})(v - b) = RT$$

where v $(= 1/\rho)$ is the specific volume.

If a and b are both zero the equation of state reduces to the ideal-gas equation:

$$p = \rho RT$$

Note that R, a, b are in mass units and are related to the corresponding molar units (denoted by a *) by:

$$R = \frac{R*}{M}, \qquad a = \frac{a*}{M^2}, \qquad b = \frac{b*}{M}$$

a and b are related to the critical temperature and pressure by

$$P_c = \frac{1}{27}\frac{a}{b^2}, \qquad T_c = \frac{8}{27}\frac{a}{Rb}$$

or, conversely,

$$a = \frac{27}{64}\frac{R^2 T_c^2}{P_c}, \qquad b = \frac{1}{8}\frac{RT_c}{P_c}$$

The variables are:

      P = pressure;
      T = temperature;
      ρ = density;
      v = specific volume $(= 1/\rho)$;
      M = molar mass;
      R = gas constant;
      a, b = Van der Waals constants.

1.7 DIMENSIONAL ANALYSIS

Sometimes experiments cannot be possible to carry out on its full size of units where the experiments are carried out. Example: in Dam, river, channels or hydraulic machines such as turbines, large pumps etc.

For the shake of economy and convenience, it is required that small scale models are made for test purposes

Certain laws of similarity must be followed in order to ensure that the model test data can be applied to the prototype.

In order to apply these laws of similarity, one has to express the experimental results in terms of non-dimensional factors.

Uses of dimensional analysis

 It is useful to find whether an equation of any flow phenomenon is rational or not. Generally, dimensionally

homogeneous equation is called rational equation

By dimensional analysis, the relationship between various physical quantities in an equation can be obtained

 Rational formulae for a flow phenomenon can be derived

 It helps in making suitable smaller sized models in which experiments can be performed to predict the performance of the prototypes

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UNIT – II - Material Balance Without Chemical Reaction – SCHA1304

2. INTRODUCTION

Material balance involves calculations the quantities of all materials that enter and leave any system or process which are based on the principle of the "law of conversation of mass". This law states that matter is neither created nor destroyed in the process and the total mass remains unchanged. The general principle of material balance calculations is to put and solve a number of independent equations involve number of unknowns of compositions and mass flow rates of streams enter and leave the system or process.

The process can be defined as one or a series of operations in which physical and chemical treatments are carried out and a desired product is result in the end such as distillation, drying, absorption, etc.

The system can be defined as any arbitrary portion of a process that you want to consider for analysis such as a reactor. The system boundary must be fixed in each problem by drawing an imaginary boundary around it as shown in the following figure:
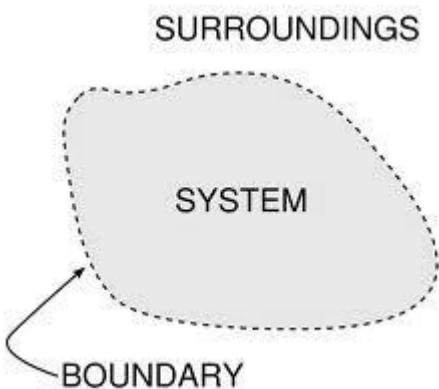
2.1 STEADY STATE PROCESS:

The steady state process can be defined as that process in which all the operating conditions (temperature, pressures, compositions, flow rate, etc.) remains constant with time. In such process there is no accumulation in the system, and the equation of material balance can be written as:

Input = Output

2.2 UNSTEADY STATE PROCESS:

For an unsteady state process, not all of the operating conditions in the process (e.g., temperature, pressure, compositions, flow rate, etc.) remain constant with time, and/or the flows in and out of the system can vary with time, hence the accumulation of materials within can be written as follows:
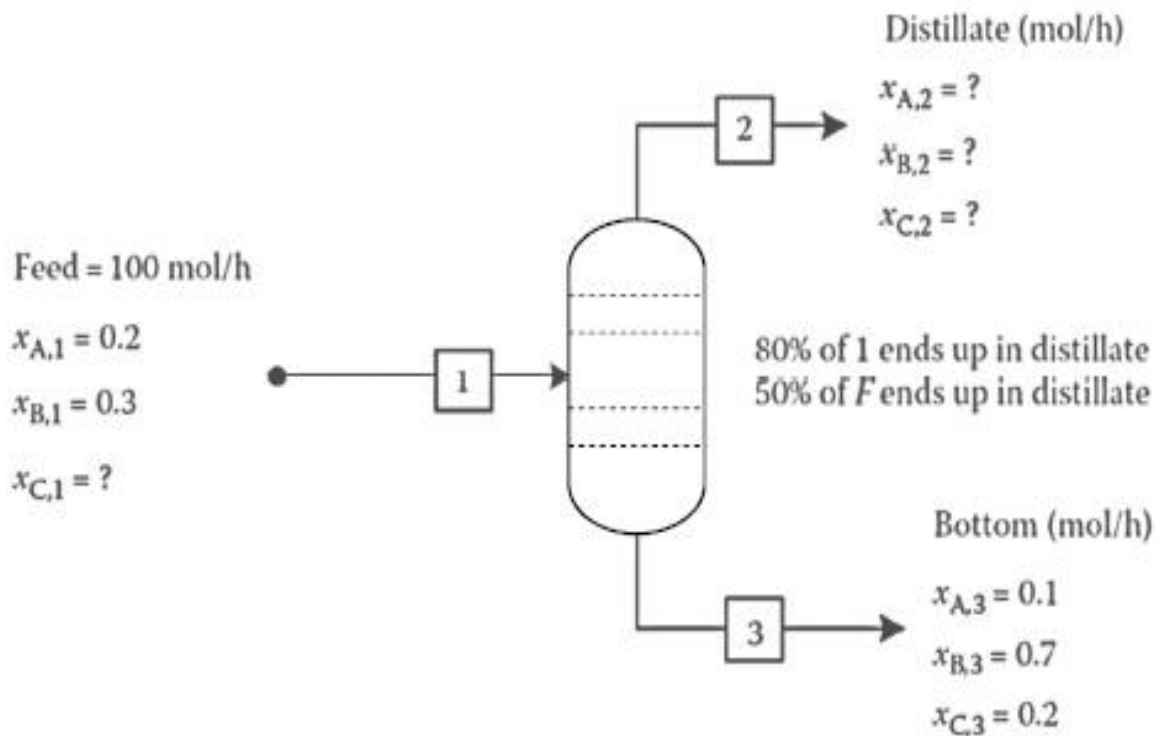
Input - Output = Accumulation

2.3 PROCESS FLOWSHEET OR FLOWCHART OR BLOCK DIAGRAM

➢ It is a sequence of process units connected by process streams. It shows the flow of materials and energy through the process units.

➢ A flowsheet is a convenient way of organizing process information for subsequent calculations.

➢ To obtain maximum benefit from the flowsheet in material balance calculations, you must:

- Write the values and units of all known stream variables at the locations of the streams on the sheet.

- Assign algebraic symbols to unknown stream variables and write these variable names and their associated units on the sheet

Feed = 100 mol/h

$x_{A,1} = 0.2$

$x_{B,1} = 0.3$

$x_{C,1} = ?$

Distillate (mol/h)

$x_{A,2} = ?$

$x_{B,2} = ?$

$x_{C,2} = ?$

80% of 1 ends up in distillate
50% of F ends up in distillate

Bottom (mol/h)

$x_{A,3} = 0.1$

$x_{B,3} = 0.7$

$x_{C,3} = 0.2$
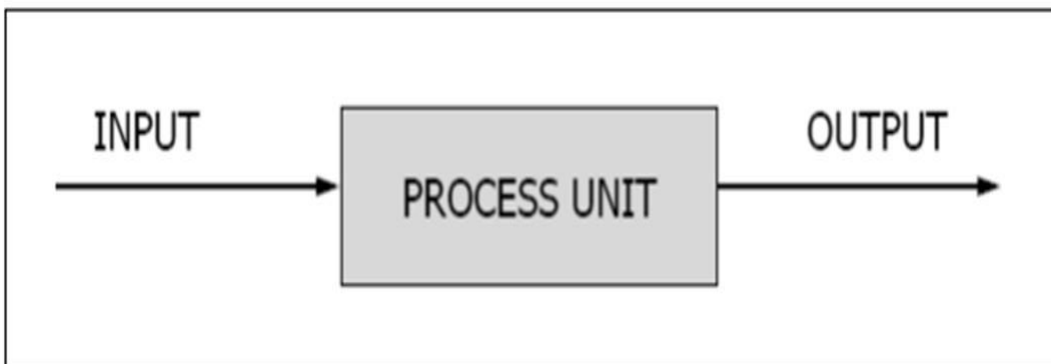
2.1 Flowchart of Distillation in a Distillation Column (Single Unit)

General Material Balance Equation

$$\begin{bmatrix} \text{Accumulation} \\ \text{within the defined} \\ \text{system} \end{bmatrix} = \begin{bmatrix} \text{Input through} \\ \text{system} \\ \text{boundary} \end{bmatrix} - \begin{bmatrix} \text{Output through} \\ \text{system} \\ \text{boundary} \end{bmatrix} + \begin{bmatrix} \text{Generation} \\ \text{within the} \\ \text{system} \end{bmatrix} - \begin{bmatrix} \text{Consumption} \\ \text{within the} \\ \text{system} \end{bmatrix}$$

$$[\text{ACCUMULATION}] = [\text{INPUT}] - [\text{OUTPUT}] + [\text{GENERATION}] - [\text{CONSUMPTION}]$$

Positive contributions to the system: Input & Generation
Negative contributions to the system: Output & Consumption

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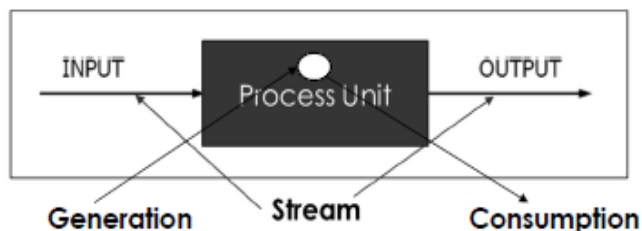
Simplified Equation

➢ No chemical reaction within process unit(s) – then mass cannot be generated or consumed; mass conservation simplifies to:

INPUT – OUTPUT= ACCUMULATION

➢ At steady state, there is no accumulation, so further simplifies to:

INPUT = OUTPUT

➢ For a given system, a material balance can be written in terms of the following conserved quantities:

- Total mass or moles., Mass or moles of a chemical compound., Mass or mole of an atomic species.

2.4 PROCEDURE FOR MATERIAL BALANCE EQUATION

1. Read and understand the problem statement

This mean read the problem carefully so that you know what is given and what is to be accomplished.

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

Draw a simplified imaginary sketch (block diagram) or a flow sheet or process flow diagram (PFD) consists of boxes which represent equipment's, and lines which indicate all streams enter and leaves each equipment.

3. Label the flow of each stream and the associated compositions with symbols

Put a letter as a symbol stream such as (F) for feed stream, (P) for product stream, etc. Furthermore, put all the known values of compositions and stream flows on the figure by each stream; calculate additional compositions from the given data as necessary.

4. Write additional data required to solve the problem and the chemical equations if the process involves chemical reaction.

5. Select a suitable basis of calculations.

6. List by symbols each of the unknown values of the stream flows and compositions

7. **Make a number of independent material balances equations** equal to unknown quantities to be calculated. It is important to put these equations in proper sequence so that the first one content only one unknown in order to avoid complicated solution of the simultaneous equations. Three type of material balance equations can be formulated:

a. Equation for total quantities which is called **(total material balance) or (over all material balance).**

b. Equation for each component which is called **(component material balance).** If there is no chemical reaction the number of equations that can be written is equal to the number of components in the system.

c. Equation for each element which is called **(element material balance)** if there is a chemical reaction.

8. The existence of a substance that enters in one inlet stream and leaves in one outlet stream with known compositions and it passes unchanged through the process unit **(inert for chemical reaction)** is greatly simplified material balance calculations. This substance is termed as **(tie component).** It is important to search for the existence of a tie component and formulate a material balance equation. Nitrogen is considered as a tie component in handling of combustion calculations. Since it is input within air stream unreacted, and out with the exit flue gases. If there are more than on tie component in the same input and output streams, these components can be made on **(over all tie components material balance).**

9. Check your answers by introducing them, or some of them, into the material balance equations. Are the equations satisfied? Are the answers reasonable?

Remember

For a given system, a material balance can be written in terms of the following conserved quantities:

- Total overall mass or moles balance.
- Mass or moles of each chemical compound balance. or
- Mass or mole of an atomic species balance.

Sources of independent equations relating unknown process stream variables

➢ Material balance: Balance equations from number of species or compounds or atoms

➢ An energy balance: Energy balance equations from conservation of energy law

➢ Process specifications: The equations for relating process variables (Like: $m_1 = k*m_2$)

➢ Physical properties and laws: Like equation of state, Henry's law, Raoult's law

➢ Physical constraints: sum of mole fractions of components is one

$$(x_A + x_B + x_C = 1; \ y_A + y_B + y_C = 1).$$

Overall Balance:
$P + Q + R + S = T + U + V + W$

Component 1 balance:
$Py_1 + Qy_1 = Ty_1 + Wy_1$

Component 2 balance:
$Py_2 = Ty_2 + Uy_2$

Component 3 balance:
$Py_3 + Qy_3 = Vy_3$

Component 4 balance:
$Qy_4 = Vy_4$

Component 5 balance:
$Ry_5 = Uy_5 + Ty_5$

Component 6 balance:
$Ry_6 = Uy_6 + Vy_6$

Component 7 balance:
$Sy_7 = Wy_7 + Vy_7$

Component 8 balance:
$Sy_8 = Wy_8$
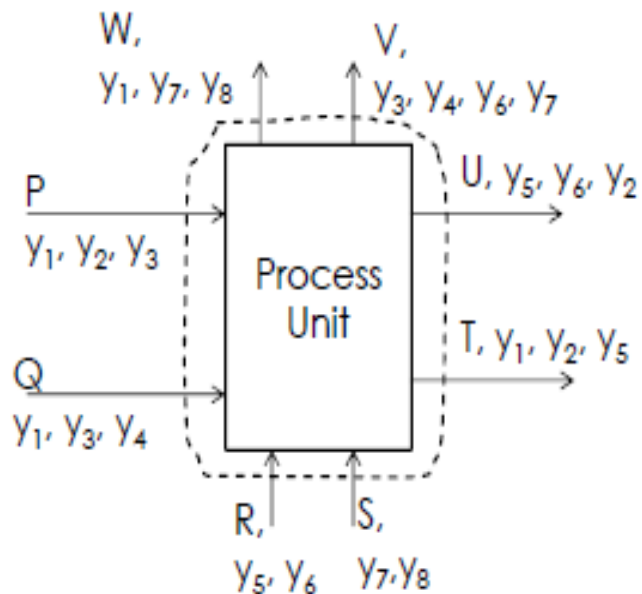
2.5 BASIS FOR CALCULATION

The amount or flow rate of one of the process streams can be used as a basis for calculation. It is recommended to keep the following in mind:

- ➤ If a stream amount or flow rate is given in the problem statement, use this as the basis for calculation.
- ➤ If no stream amounts or flow rates are known, assume one, preferably stream of known composition.
- ➤ If mass fractions are known, choose the total mass or mass flow rate of that stream (e.g., 100 kg or 100 kg/h) as the basis.
- ➤ If mole fractions are known, choose the total number of moles or the molar flow rate.

2.1 Separation of a Mixture of Ethanol and Water. A mixture containing 10% ethanol (E) and 90% H_2O (W) by weight is fed into a distillation column at the rate of 100 kg/h. The distillate contains 60% ethanol and the distillate is produced at a rate of one tenth that of the feed. Assumptions: steady state, no reactions. Consider Basis: 100 kg/h of feed.

1.Draw and label a flowchart of the process.2. Write a proper set of material balance equations.

3.Calculate all unknown stream flow rates and compositions.

Solution

$$[ACCUMULATION] = [INPUT] - [OUTPUT] + [GENERATION] - [CONSUMPTION]$$

Overall total material in the system

$$F = D + B$$
$$100 = D + B;$$

Since D = 10% of F = 10 kg/h
B = 90 kg/h

Component balance (ethanol):
$$F x_{E,1} = D x_{E,2} + B x_{E,3}$$
$$100 \times 0.1 = 10 \times 0.6 + 90 \times x_{E,3}$$
$$\Rightarrow x_{E,3} = 0.044$$

Component balance (water):
$$F x_{W,1} = D x_{W,2} + B x_{W,3}$$
$$100 \times 0.9 = 10 \times 0.4 + 90 \times x_{W,3}$$
$$\Rightarrow x_{W,3} = 0.956$$

D (kg/h)
60% E
40% W

100 kg/h
10% E
90% W

Distillation column

Bottoms, B

$E x_{E,3}$
$W x_{W,3}$
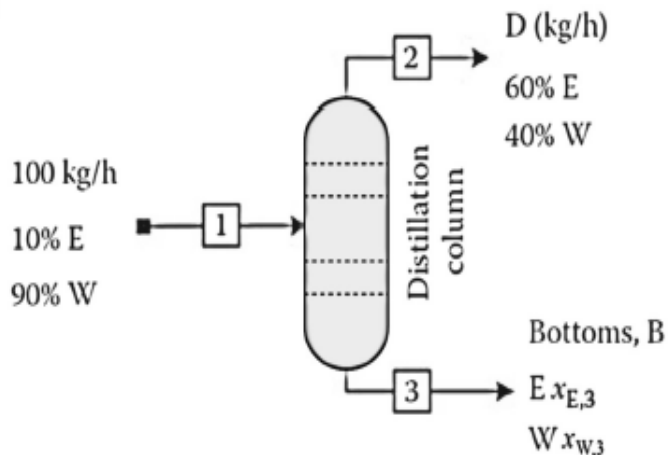
$$x_{W,3} = (1 - x_{E,3}) = 1 - 0.044 = 0.956$$

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Problem 2.2 A binary mixture consists of 35 % benzene and 65 % toluene are continuously fed to the distillation column at a rate of 1000 kg/hr. Whereas, the distillate flow rate was 10% from the feed flow rate. The distillate (top product) contains 85 % benzene. Calculate quantity and compositions of the waste stream.

Solution: Although the distillation unit shown in Figure below is comprised of more than one unit of equipment, you can select a system that includes all of the equipment inside the system boundary. Consequently, you can ignore all the internal streams for this problem.

Basis: 1 hr

F = 1000 kg

P = (10 /100) of Feed = 0.1 x (1000) = 100 kg

Overall Material Balance:

Input = Output

  F = P + W

1000 = 100 + W

  W = 900 kg
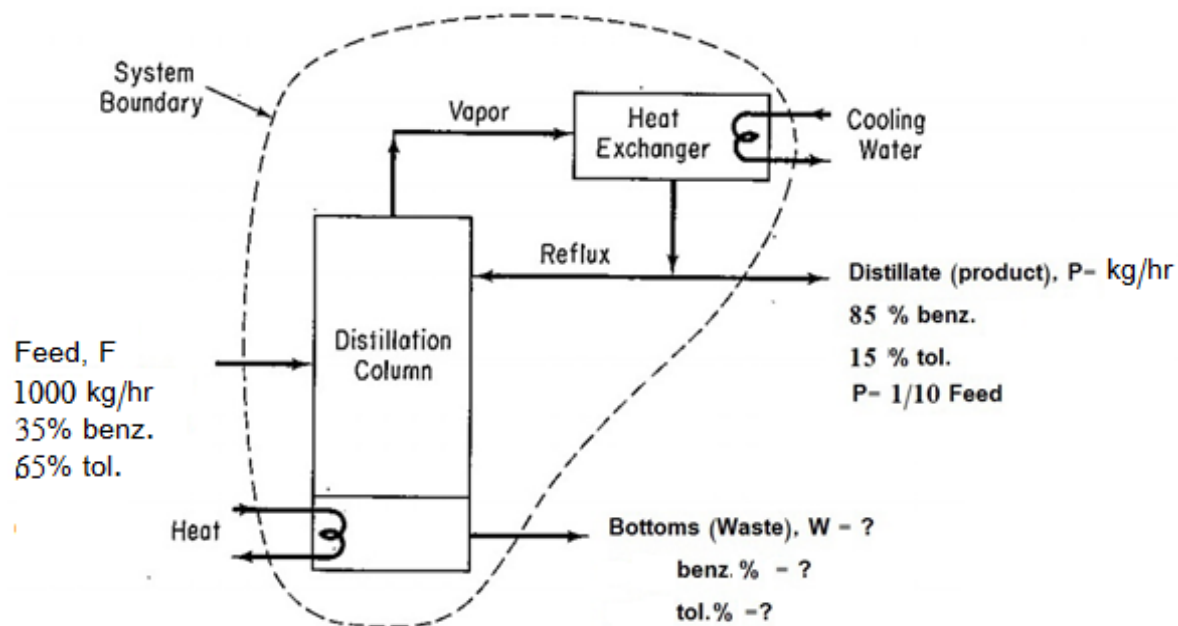
Benzene Material Balance:
$(0.35)\,(1000) = (0.85)\,(100) + $ Kg of benz. in (W)

$350 = 85 + $ Kg of benz. in (W) $\quad\Longrightarrow\quad$ Kg of benz. in (W) $= 265$ kg

Toluene Material Balance:
$(0.65)\,(1000) = (0.15)\,(100) + $ Kg of tol. in (W)

$650 = 15 + $ Kg of benz. in (W) $\quad\Longrightarrow\quad$ Kg of tol. in (W) $= 635$ kg

$W = $ Kg of benz. in (W) $+$ Kg of tol. in (W) $= 265 + 635 = 900$ kg

Mass fraction of benz. in waste $= \dfrac{265}{265+635} = 0.294$

Mass fraction of tol. in waste $= \dfrac{635}{265+635} = 0.706$

Problem 2.3 A solution composed of 50% ethanol (EtOH), 10% methanol (MeOH), and 40% water (H_2O) is fed at the rate of 100 kg/hr into a separator that produces one stream at the rate of 60 kg/hr with the composition of 80% EtOH, 15% MeOH, and 5% H_2O, and a second stream of unknown composition. Calculate the composition (in %) of the three compounds in the unknown stream and its flowrate in kg/hr.

The figure is shown with all known values entered as numbers (with units) and all unknown values entered as symbols.

F = 100 kg/hr	Separator	P = 60 kg/hr
mass fr		*mass fr*
EtOH 0.50		EtOH 0.80
MeOH 0.10		MeOH 0.15
H₂O 0.40	W = ? kg/hr	H₂O 0.05
1.00		1.00

	kg/hr	or	mass fr
EtOH	mEtOH		ωEtOH
MeOH	mMeOH		ωMeOH
H₂O	mH₂O		ωH₂O
	W		1.00
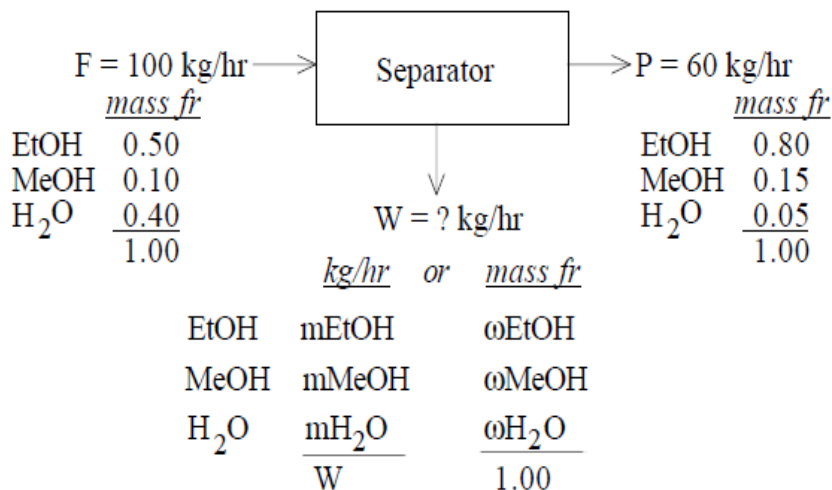
Four mass balances can be written for each set of variables, one total and three component balances, but only three of the balances are independent.

Total: $\quad F \; = \quad P \; + \; W$ $\qquad\qquad\qquad F \; = \quad P + \quad W$

EtOH: $\quad 0.50F \; = \; 0.80P \; + \; m_{EtOH}$ $\qquad\qquad 0.50F \; = \; 0.80P + \omega_{EtOH}W$

MeOH: $\;0.10F \; = \; 0.15P \; + \; m_{MeOH} \quad$ or $\quad 0.10F \; = \; 0.15P + \omega_{MeOH}W$

H_2O: $\quad 0.40F \; = \; 0.05P \; + \; m_{H2O}$ $\qquad\qquad 0.40F \; = \; 0.05P + \omega_{H2O}W$

In addition you know one more independent equation holds for the components in W

$$m_{EtOH} + m_{MeOH} + m_{H2O} = W \qquad \text{or} \qquad \omega_{EtOH} + \omega_{MeOH} + \omega_{H2O} = 1$$

Thus, we have four independent equations, and can get a unique solution.

The solution of the equations is (using the total and first two component balances)

	m_i (kg/hr)	ω_i (mass fr)
EtOH	2	0.050
MeOH	1	0.025
H_2O	37	0.925
	40	1.00

Problem 2.4 Evaporation Process

An evaporator is feed continuously with 40000 kg/hr of a solution containing 15% NaOH, 15% NaCl and 70% water by weight. During the evaporation water is boiled off and NaCl is precipitates as a crystal and removed from the remaining liquor. The concentrated liquor leaving the evaporator contains 60% NaOH, 5% NaCl and 35% water. Assume the process is steady state.

1.Draw the process flowchart.

2.Calculate the amount of water evaporated per hour.

3.Calculate amount of salt precipitated per hour.

4.Calculate the amount of concentrated liquor produced per hour.

Solution

Water evaporated, E

F = 40000 kg

Evaporator

NaCl: 0.15
NaOH: 0.15
Water: 0.70

Liquor, L kg
NaCl crystal: C
NaOH: 0.60
Water: 0.35
NaCl: 0.05

Assumption: Steady state No reaction
Basis: One hour operation.
Let E = Evaporation, kg
   C = Crystals formed, kg
   L = Concentrated Liquor, kg
   F = Evaporator Feed, kg
MATERIAL BALANCE: IN = OUT
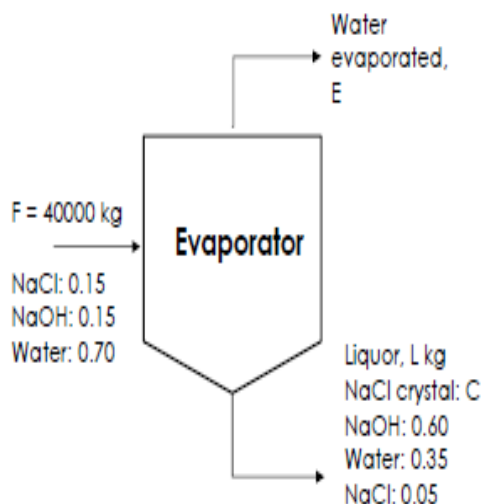
COMPONENT BALANCE:
NaCl: F (0.15) = C + L (0.05)
   40000(1.5) = L (0.05) ------------------ (1)
NaOH: 40000(1.5) = L (0.60) ----------------- (2)
Water: 40000(1.5) = L (0.35) + E ----------- (3)

Total Material Balance:
   40000 = E + C + L --------------------- (4)

From equation (2): L = 10000
From equation (1): C = 40000(0.15) – L(0.05)
        = 40000(0.15) – 10000(0.05)
        = 5500
From equation (3): E = 40000(0.70) – L(0.35)
        = 24500
From equation (4): E = 40000 – C – L
        = 40000 – 5500 – 10000
        = 24500 (Checked)

$$[ACCUMULATION] = [INPUT] - [OUTPUT] + [GENERATION] - [CONSUMPTION]$$

Problem 2.5: Crystallization: A tank holds 10,000 kg of a saturated solution of Na_2CO_3 at 30°C. You want to crystallize from this solution 3000 kg of $Na_2CO_3.10H_2O$ without any accompanying water. To what temperature must the solution be cooled? The solubility data of Na_2CO_3 as a function of the temperature is given as below:

Temp. (°C)	Solubility (g Na_2CO_3 / 100 g H_2O)
0	7
10	12.5
20	21.5
30	38.8
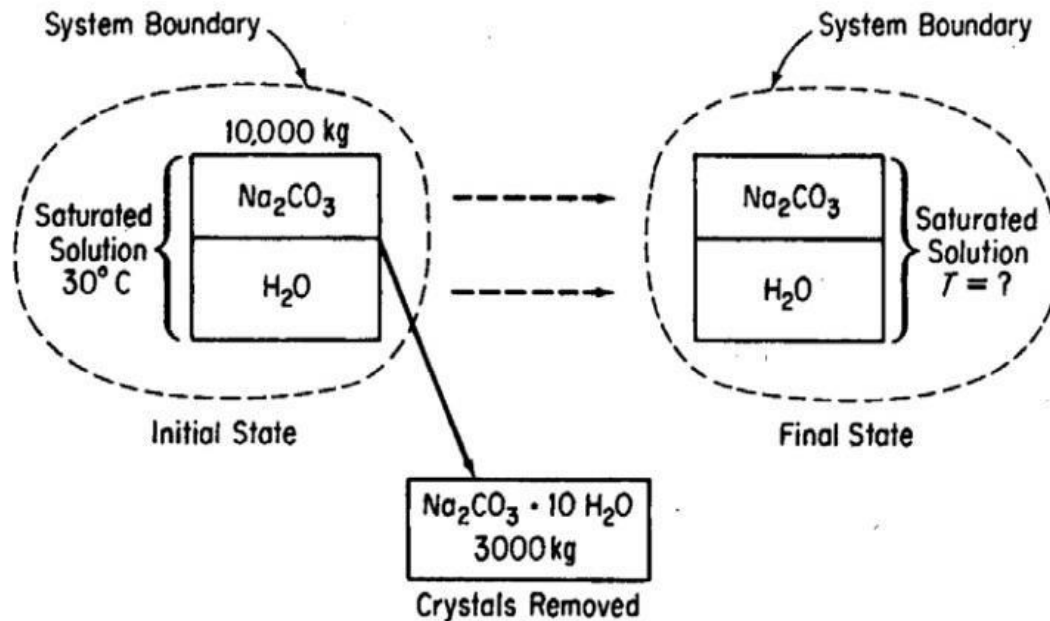
Since the initial solution is saturated at 30°C, you can calculate the composition of the initial

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

Basis: 1 g mol of Na$_2$CO$_3$.10H$_2$0

Comp.	Mol	Mol wt.	Mass	Mass fraction
Na$_2$CO$_3$	1	106	106	0.371
H$_2$0	10	18	180	0.629
Total			286	1.0

Basis: 10000 kg of saturated solution at 30°C
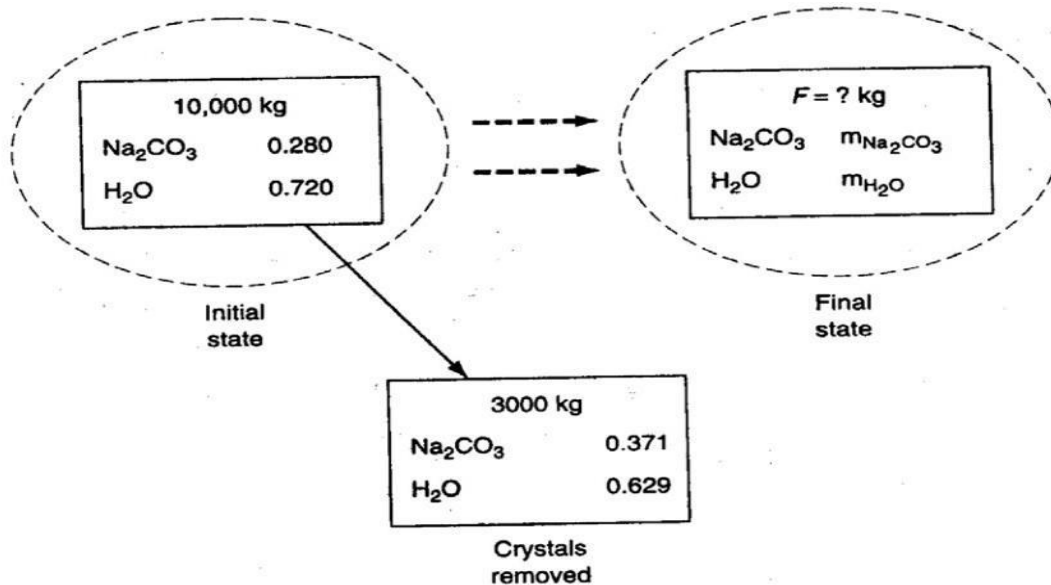
Because we are treated this problem as an unsteady-state problem (the flow = 0), the mass balance reduces to:

Overall material balance:

Initial state – Final state = Crystal removed

$10000 - F = 3000$

$F = 7000$ kg

$\underline{Na_2CO_3\ material\ balance:}$
$(0.28)\ (10000) - (M_{Na_2CO_3})\ (F) = (0.371)\ (3000)$.   where: M=mass fraction

$(0.28)\ (10000) - (M_{Na_2CO_3})\ (7000) = (0.371)\ (3000)$

$M_{Na_2CO_3} = 0.241$

Mass of Na_2CO_3 in the final state $= (M_{Na_2CO_3})\ (F) = (0.241)\ (7000) = \mathbf{1687\ kg}$

$\underline{H_2O\ material\ balance:}$
$(1-0.28)\ (10000) - (M_{H_2O})\ (F) = (0.629)\ (3000)$

$(0.72)\ (10000) - (M_{H_2O})\ (7000) = (0.629)\ (3000)$

$M_{H_2O} = 0.759$

Mass of H_2O in the final state $= (M_{H_2O})\ (F) = (0.759)\ (7000) = \mathbf{5313\ kg}$

To find the temperature of the final solution, calculate the composition of the final solution in terms of (g Na_2CO_3 / 100 g H_2O) so that you can use the tabulated solubility data listed above.

$$\frac{1687 \text{ kg } Na_2CO_3}{5313 \text{ kg } H_2O} = \frac{31.8 \text{ g } Na_2CO_3}{100 \text{ g } H_2O}$$

Na_2CO_3	H_2O
1687 kg	5313 kg
X	100 g

$\Rightarrow X=31.8$

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

$$(30°C) - \left[\frac{38.8 - 31.8}{38.8 - 21.5}\right](10°C) = 26°C$$

Slope 1 ($m1$) = Slope 2 ($m2$),

where, $m = \frac{y_2 - y_1}{x_2 - x_1}$

$$\left[\frac{38.8-31.8}{30-X}\right] = \left[\frac{38.8-21.5}{30-20}\right] \Rightarrow X=26°C$$

Problem 2.6 Absorption column: A gaseous mixture (F) consists of 16 mol% CS_2 and 84 mol% air are fed to the absorption column at a rate of 1000 Ibmole /hr. Most of the CS_2 input are absorbed by liquid benzene (L) which is fed to the top of the column. 1 % of benzene input are evaporated and out with the exit gas stream which consists of 96 mol% air, 2 mol% CS_2 and 2 mol% benzene. The product liquid stream (P) consists of benzene and CS_2. Calculate the mole flow rates of (G), (L) and (P) and the compositions.

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Solution:

Basis = 1 hr

F = 1000 Ibmole

Air material balance: (Tie component)

(0.84) (F) = (0.96) (G)

(0.84)(1000) = (0.96) (G)

G = 840/0.96 = 875 Ibmole

Benzene material balance:

Benzene in (G) = (875) (0.02) = 17.5 Ibmole

17.5 = 1% of benzene input

17.5 = (0.01) (L) ⟹ L = 1750 Ibmole

Benzene in (P) = 99% of benzene input = (0.99) (L) =(0.99) (1750) = 1732.5 Ibmole

Let x = mole fraction of benzene in (P) ⟹ P x = 1732.5 ....(1)

CS_2 material balance:

(0.16) (F) = (0.02) (G) + P (1-x)

(0.16) (1000) = (0.02) (875) + P – P x

160 =17.5 + P – 1732.5 ⟹ P = 1875 Ibmole

Sub. (P) in equation (1):

x = (1732.5) / (1875) = 0.924 mole fraction of benzene in (P)

mole fraction of CS_2 in (P) = 1- 0.924 = 0.076

Checking total material balance:

Input = F + L = 1000 + 1750 = 2750 Ibmole

Output = G + P = 875 + 1875 = 2750 Ibmole

G

96% air

2% CS_2

2% benzene

L

benzene

Absorption column

F = 1000 Ibmole/hr

16% CS_2

84% air

P

Benzene

CS_2
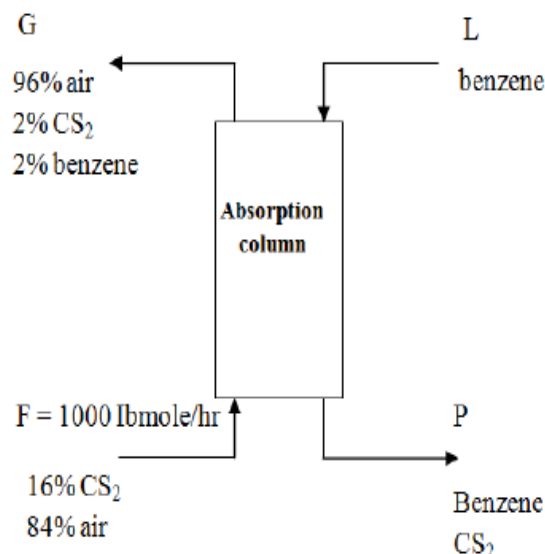
Problem 2.7 You are asked to measure the rate at which waste gases are being discharged from a stack. The gases entering contain 2.1 % carbon dioxide. Pure carbon dioxide is introduced into the bottom of the stack at a measured rate of 4.0 lb per minute. You measure the discharge of gases leaving the stack, and find the concentration of carbon dioxide is 3.2 %. Calculate the rate of flow, in lb mol/minute, of the entering waste gases.

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

$$\frac{4 \text{ lb } CO_2 \mid 1 \text{ lb mol } CO_2}{44 \text{ lb } CO_2} = 0.091 \text{ lb mol } CO_2$$

P (lb mol)

	mol fr.
carbon dioxide	0.032
other	0.968

Stack

F (lb mol)
waste gas

	mol fr.
carbon dioxide	0.021
other	0.979

C = 0.091 lb mol

pure carbon dioxide

mol fr.
1.00
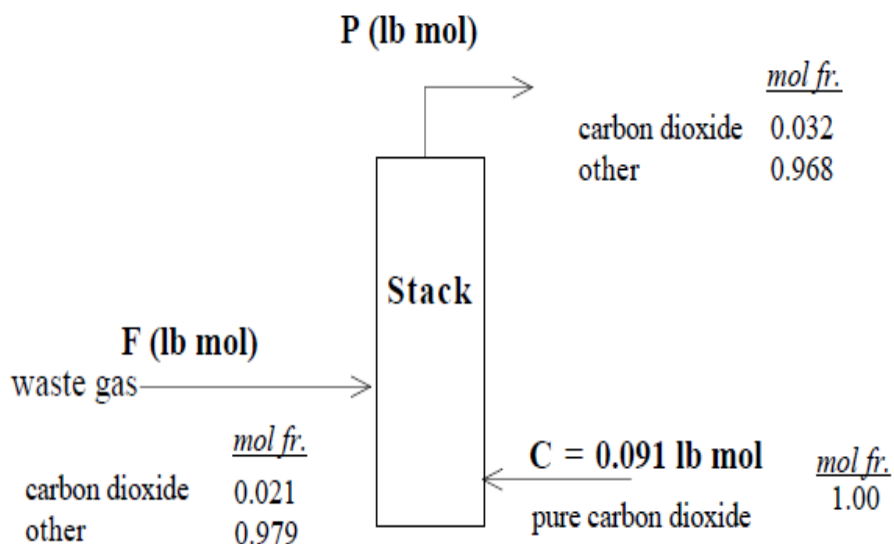
CO_2 balance : $0.021\,F \ + \ 0.091 \ = \ 0.032\,P$ (1)

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

Solving (1) and (2) $P \ = \ 8.10 \text{ lb mol/min}$ $F \ = \ 8.01 \text{ lb mol/min}$

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Problem 2.8 A crystallizer contains 6420 lb of aqueous solution of anhydrous sodium sulfate (concentration 29.6 wt %) at 104 °C. The solution is cooled to 20 °C to crystallize out the desired $Na_2SO_4 \cdot 10\ H_2O$. The remaining solution (the mother liquor) is found to contain 16.1 % anhydrous sodium sulfate. What is the weight of this mother liquor.

Basis : 6420 lb of 29.6 wt% Na_2SO_4 solution

Initial F = 6420 lb					Final P (lb)				$Na_2SO_4 \cdot 10H_2O$
	mass fr.					$\dfrac{lb}{mol}$	*MW*	*lb*	*mass fr*
Na_2SO_4	0.296				Na_2SO_4	1	142	142	0.441
H_2O	0.704				water	10	18	180	0.559
	1.000							322	1.000

Mother liquor M (lb)

	mass fr.
Na_2SO_4	0.161
H_2O	0.839
	1.000
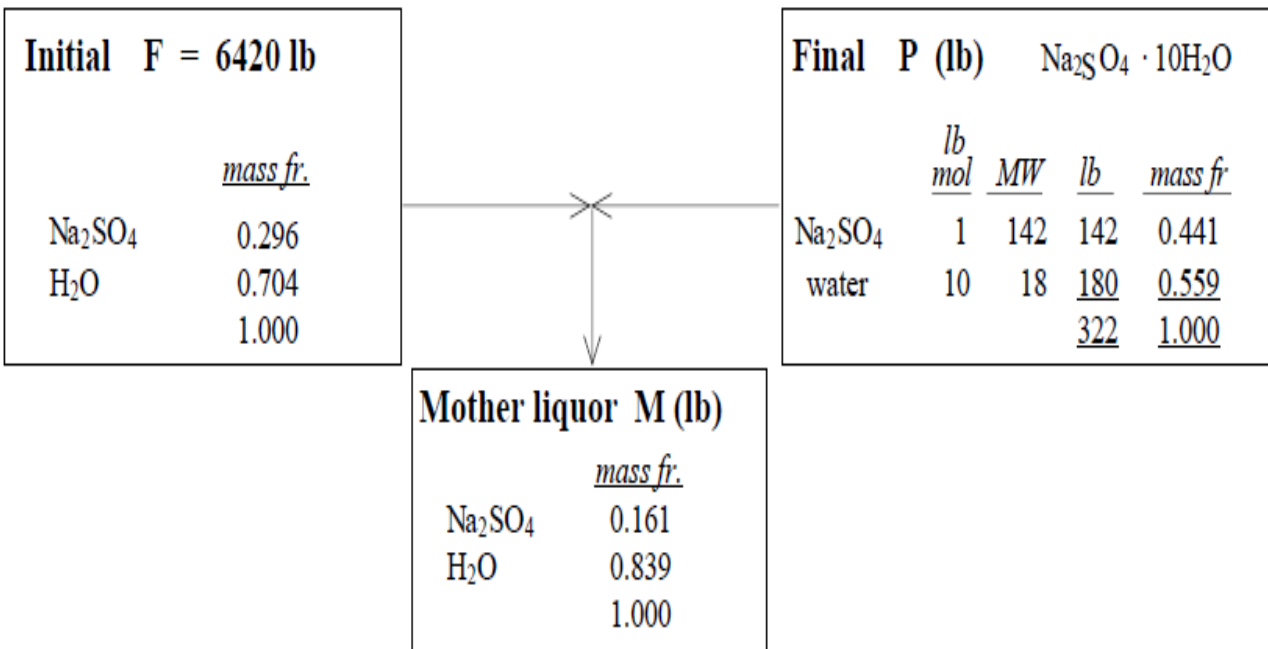
Accumulation   =   In   -   out

Total:	P	-	F	=	0	-	M	(1)
Na_2SO_4:	0.441P	-	0.296 F	=	0	-	0.161 M	(2)

from (1)   P = 6240 - M

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

M = 3330 lb   P = 3100 lb

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Use H$_2$O balance as a check

H$_2$O balance: 0.704 F = 0.551 P + 0.839 M

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

Problem 2.9 Dryer: In the processing of the fish, after the oil is extracted, the fish cake is dried in rotary drum dryers, finely ground, and packed. The resulting product contains 65% protein. 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.

Solution

Basis: 100 kg water evaporated
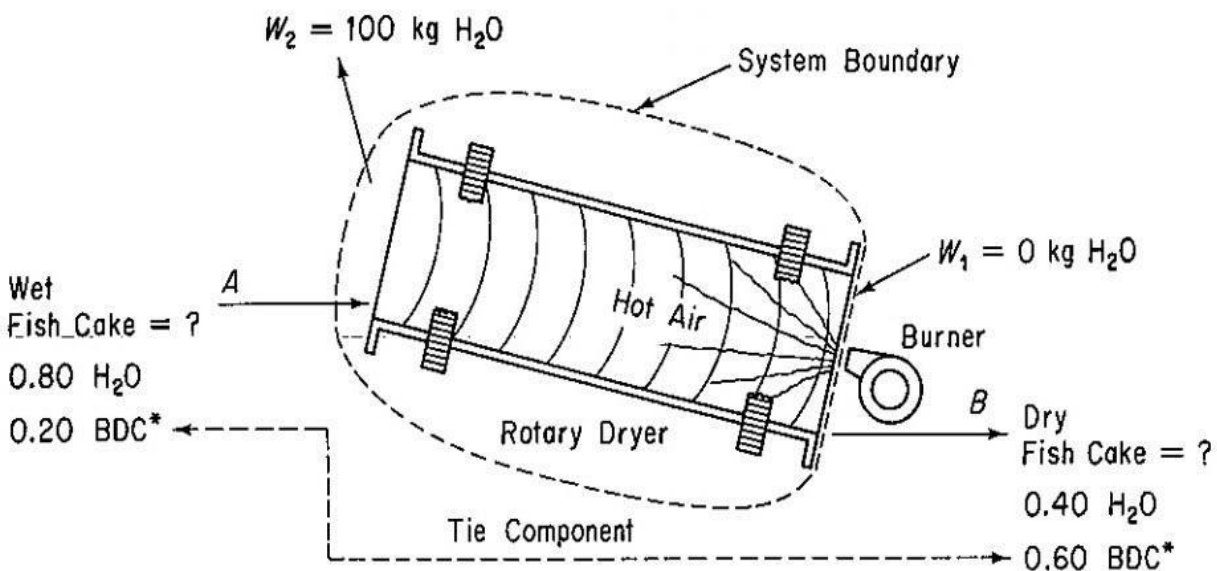
*Bone Dry Cake

Overall material balance:

Input = Output

$A + W_1 = B + W_2$

$A + 0 = B + 100$ ⟹ $A = B + 100$ .... (1)

BDC material balance:

Input = Output

$(0.2)(A) = (0.6)(B)$ ⟹ $B = (1/3) A$ ....(2)

Sub. Eq. (2) into (1):

$A = (1/3) A + 100$ ⟹ $A = 150$ kg initial cake

$B = (1/3) A = (1/3)(150) = 50$ kg

Problem 2.10. Membrane unit: Separation of Gases Using a Membrane:

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 below illustrates a nano porous 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?
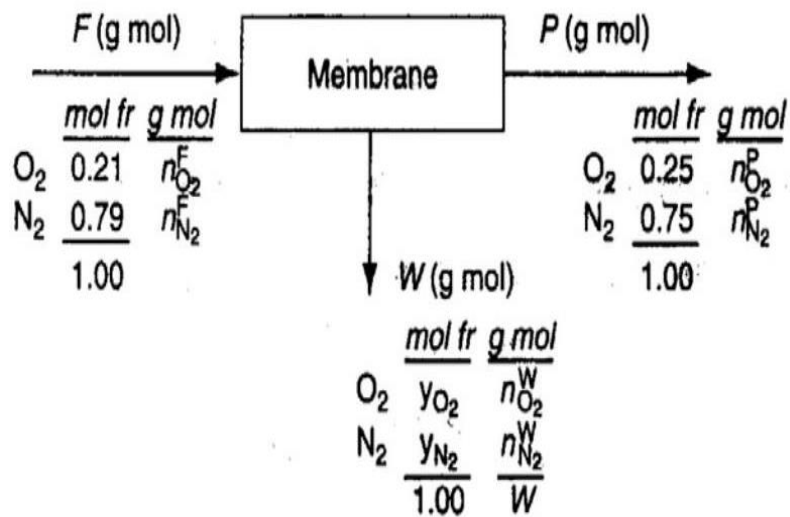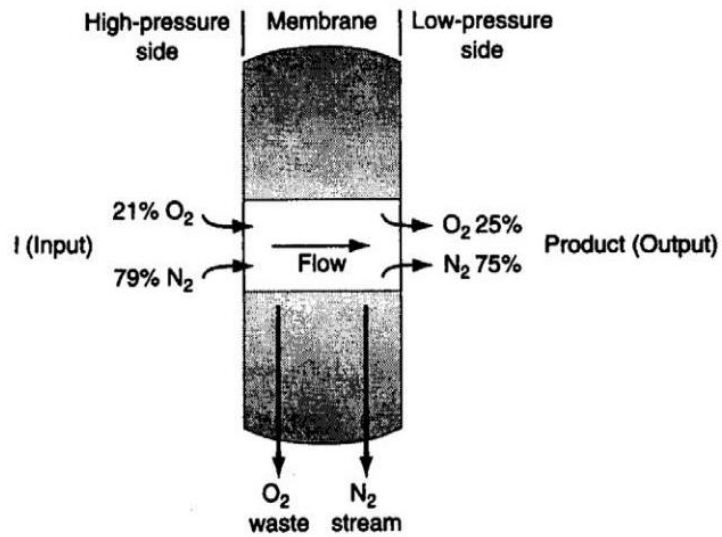
Basis: F=100 g mole

Input = Output

F = P + W

W = 80% F = 0.8 x 100 = 80 g mole

P= 20 g mole

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

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

$y_{O_2}^P = n_{O_2}^P/P = 0.25$ $n_{O_2}^P = 0.25P = 5$ gmole

$y_{N_2}^P = n_{N_2}^P/P = 0.75$ $n_{N_2}^P = 0.75P = 15$ gmole

Oxygen Material Balance (O_2 M.B):

$0.21\ (100) = 0.25P + y_{O_2}^W\ (80)$

$0.21\ (100) = 0.25(20) + n_{O_2}^W \implies n_{O_2}^W = 16$ gmole

Nitrogen Material Balance (N_2 M.B):

$0.79\ (100) = 0.75P + y_{N_2}^W\ (80)$

$0.79\ (100) = 0.75(20) + n_{N_2}^W \implies n_{N_2}^W = 64$ gmole

Mole fraction of O_2 in waste, $y_{O_2}^W = \dfrac{16}{16+64} = 0.2$

Mole fraction of N_2 in waste, $y_{N_2}^W = \dfrac{64}{16+64} = 0.8$

Problem 2.11: Mixer unit: It is required to prepare 1250 kg of a solution composed of 12 wt.% ethanol and 88 wt.% water. Two solutions are available, the first contains 5 wt.% ethanol, and the second contains 25 wt.% ethanol. How much of each solution are mixed to prepare the desired solution?
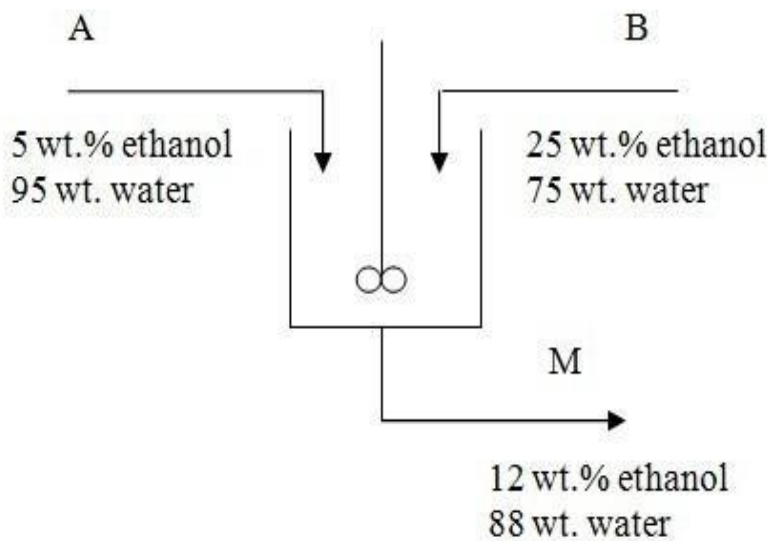
Solution:

1.   Ethanol balance

Input = output

$$A\left(\frac{5}{100}\right) + B\left(\frac{25}{100}\right) = M\left(\frac{12}{100}\right)$$

$$0.05\ A +\ 0.25\ B = 0.12\ M$$

$$A = \left(\frac{150 - 0.25\ B}{0.05}\right) = 3000 - 5\ B \ldots\ldots\ldots\ldots (1)$$

2.   Water balance

Input = output
$$0.95\ A +\ 0.75\ B = 0.88\ M = 0.88\ (1250) = 1100$$
$$0.95\ A +\ 0.75\ B = 1100 \ldots\ldots\ldots\ldots (2)$$
Sub. (1) in (2)

$$0.95(300\text{-}5\ B) + 0.75\ B = 1100$$
$$2850 - 4.75 + 0.75\ B = 1100$$
$$4\ B = 1750 \ldots\ldots\ldots\ldots\ldots \qquad B = \underline{437.5\ kg}$$

Sub. B in (1): $\qquad$ A= 3000 – 5(437.5) = \underline{812.5 \text{ kg}}

3. **Checking:** Total material balance (T.M.B.), Input = A + B = 437.5 + 812.5 = 1250 kg

$$\text{Output} = M = 1250 \text{ kg}$$

Problem 2.12:

Mixing of streams Solved by both Compound and Atom Balance Steady state, no reaction

$m_1 (lb_m) = 2195 \ lb_m$
$0.750 \ lb_m C_2H_5OH / lb_m$
$0.250 \ lb_m \ H_2O / lb_m$

Process Unit

$m_3 (lb_m)$
$0.600 \ lb_m C_2H_5OH / lb_m$
$0.400 \ lb_m \ H_2O / lb_m$

$m_2 (lb_m)$
$0.400 \ lb_m C_2H_5OH / lb_m$
$0.600 \ lb_m \ H_2O / lb_m$
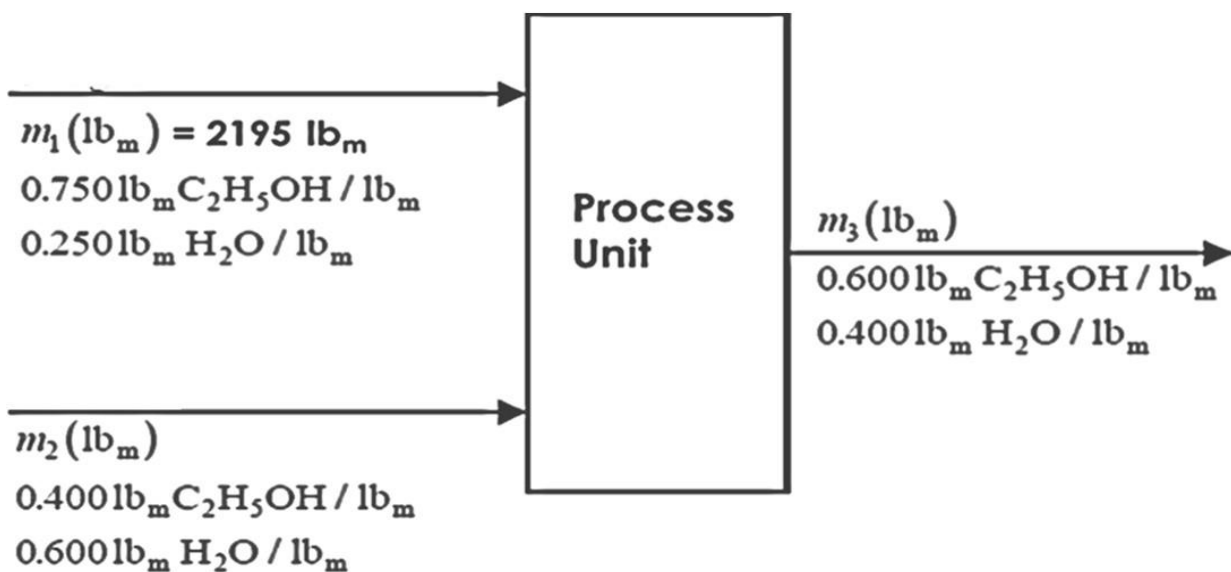
$$[\text{ACCUMULATION}] = [\text{INPUT}] - [\text{OUTPUT}] + [\text{GENERATION}] - [\text{CONSUMPTION}]$$

Compound Balance	Atomic Balance
Overall bal.: $m_1+m_2 = m_3$ C_2H_5OH bal.: $m_1*0.45+m_2*0.40 = m_3*0.60$ H_2O bal.: $m_1*0.25+m_2*0.60 = m_3*0.40$ Solve this: $m_1 = 2195$ lbm; $m_2 = 1646$ lbm; $m_3 = 3841$ lbm	Overall: $m_1+m_2 = m_3$ C balance: $m_1*(2*0.750)+m_2*(0.40*2) = m_3*(0.60*2)$ H bal: $m_1*0.75*6+m_1*0.25*2+m_2*0.40*6+m_2*0.60*2$ $=m3*0.6*6+ m_3*0.40*2$ O bal: $m_1*0.75*1+m_1*0.25*1+m_2*0.40*1+m_2*0.60*1$ $= m_3*0.60*1+ m_3*0.40*1$ Solving: $m_2 = 1646$ lbm; $m_3 = 3841$ lbm

Problem 2.13: You are asked to prepare a batch of 18.63% battery acid as follows. A tank of old weak battery acid (H_2SO_4) solution contains 12.43% H_2SO_4 (the remainder is pure water). If 200 kg of 77.7% H_2SO_4 is added to the tank, and the final solution is to be 18.63% H_2SO_4, how many kilograms of battery acid have been made? See Figure below.

Solution:

Overall material balance:

Input = Output

$A + F = P$

$200 + F = P$ ....(1)

H_2SO_4 material balance:

$(0.777)(200) + (0.1243)(F) = (0.1863)(P)$ ....(2)

H_2O material balance:

$(0.223)(200) + (0.8757)(F) = (0.8137)(P)$ ....(3)

From equation(1), $P = 200 + F$

Sub. Equation (1) in (2):

$(0.777)(200) + (0.1243)(F) = (0.1863)(200 + F)$
$155.4 + 0.1243\ F - 37.26 = 0.1863\ F$
$F = 1905.5\ kg$ & $P = 2105.5\ kg$

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SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – III - Material Balance with Chemical Reaction – SCHA1304

3. INTRODUCTION

When chemical reactions occur, in contrast with physical changes of material such as evaporation or dissolution, you want to be able to predict the mass or moles required for the reaction(s), and the mass or moles of each species remaining after the reaction has occurred. Reaction stoichiometry allows you to accomplish this task. The word stoichiometry (stoi-ki-om-e-tri) derives from two Greek words: stoicheion (meaning "element") and metron (meaning "measure"). Stoichiometry provides a quantitative means of relating the amount of products produced by chemical reactions to the amount of reactants.

Stoichiometric coefficients:

The numbers that are precede the chemical substances involved in the chemical reaction equation are known as " stoichiometric coefficients". These coefficients represent quantity of any reactant that is theoretically required for complete conversion of other reactants.

Stoichiometric ratios:

The ratio between any stoichiometric coefficients in a balanced chemical equation is known as " stoichiometric ratio".

As an example the reaction of nitrogen and hydrogen to produce ammonia:

$N2 + 3H_2 \rightarrow 2NH_3$
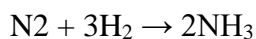
The stoichiometric ratios of $N_2/H_2 = 1/3$, $N_2/NH_3 = 1/2$ and $H_2/NH_3 = 3/2$

3.1 LIMITING AND EXCESS REACTANTS:

In most industrial processes, the quantities of reactants input are not in exact stoichiometric proportions as fixed by the reaction equation. It is generally desirable that some of the reacting materials be present in excess quantity over the amounts theoretically required for combination with other reactants.

a. 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 and it has smallest maximum extent of reaction.

b. The excess reactant:

Is the reactant that is present in excess amount over the stoichiometric requirement equivalent to that of the limiting reactant and it has highest maximum extent of reaction that of the limiting reactant. If the reaction does not proceed to completion, all the reactants called excess reactants.

Limiting reagent/reactant

Limiting reagent - the reactant that would be first depleted if a reaction proceeded to completion

A reactant is limiting if it is present in less than its stoichiometric proportion relative to all other reactants

Identifying the limiting reactant :

[this procedure is valid for any number of reactants]

1. Select the reactant with the lowest stoichiometric coefficient .If there is more than

one reactant with the same "lowest" coefficient, e.g.,

A + B + 2C→ D
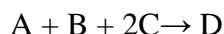
select the one with the smallest number of moles fed.

2. Set up stoichiometric ratios with the stoichiometric coefficient identified above as the denominator. In doing so, all your stoichiometric ratios should be > 1.

3. Set up the corresponding ratios using actual feed values.

Compare each set of ratios:

$$\left(\frac{n_x}{n_y}\right)_{feed} \quad vs. \quad \left(\frac{n_x}{n_y}\right)_{stoichiometric}$$

IF

$$\left(\frac{n_x}{n_y}\right)_{feed} \geq \left(\frac{n_x}{n_y}\right)_{stoichiometric} \quad \textbf{reactant } x \textbf{ not limiting}$$

IF

$$\left(\frac{n_x}{n_y}\right)_{feed} < \left(\frac{n_x}{n_y}\right)_{stoichiometric}$$

reactant *x* limiting

Problem 3.1

Example: $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8\,H_2O$
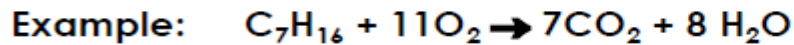
Given 1 gmol of C_7H_{16} and 12 gmol of O_2 . Identify the limiting reactant.

$$\left(\frac{n_{O_2}}{n_{C_7H_{16}}}\right)_{stoichiometric} = \frac{11}{1} \qquad \left(\frac{n_{O_2}}{n_{C_7H_{16}}}\right)_{feed} = \frac{12}{1}$$

O_2 in excess;

$$\left(\frac{n_{O_2}}{n_{C_7H_{16}}}\right)_{feed} > \left(\frac{n_{O_2}}{n_{C_7H_{16}}}\right)_{stoichiometric}$$

O_2 in excess;

C_7H_{16} limiting

$$f_{xs} = \frac{n_{O_2,feed} - n_{O_2,stoichiometric}}{n_{O_2,stoichiometric}} = \frac{12-11}{11} = 0.09$$

Other definitions:

$$A + B \rightarrow C + D$$
$$C + B \rightarrow E + D$$
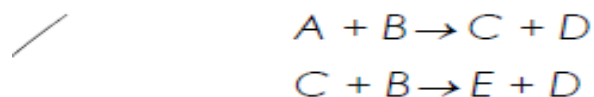
further reaction of desired product C; undesired reaction

- ► If C is the desired product, then want to minimize second reaction from taking place.
- ► Second reaction uses up reactant B and desired product C; it also produces undesired product E.
- ► Let A be the limiting reactant

$$conversion\,of\,A = \frac{mol\ A\ reacted}{mol\ A\ fed} \qquad conversion\,of\,B = \frac{mol\ B\ reacted}{mol\ B\ fed}$$

4

$$selectivity = \frac{mol\ C\ in\ output}{mol\ E\ in\ output}$$

$$yield = \frac{total\ mole\ of\ products}{mol\ A\ fed}$$

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

$$yield\ of\ c = \frac{mol\ C\ in\ output}{mol\ A\ fed}$$

$$efficiency = \frac{mol\ C\ in\ output}{mol\ A\ reacted}$$

Percent excess:

It is the excess quantity of any reactant expressed as a percent of the stoichiometric amount theoretically required to react completely with the limiting reactant according to the chemical equation.

$$\%\ excess = \left[\frac{amount\ of\ the\ excess\ reactant\ feed - \substack{amount\ of\ the\ excess\ reactant\ required \\ to\ react\ with\ the\ limiting\ reactant}}{\substack{amount\ of\ the\ excess\ reactant\ required \\ to\ react\ with\ the\ limiting\ reactant}} \right] \times 100$$

$$\%\ excess = \left[\frac{Feed - Theoritical\ amount\ required}{Theoritical\ amount\ required} \right] \times 100$$

Fractional conversion: the fraction of reactant that has reacted.

Fractional conversion = (moles reactant reacted)/(moles reactant fed in)

Percentage conversion: (fractional conversion) × 100 %

Yield: Reactions, in general, do not go to 100% conversion of the reactant into the desired product. This is because of side reactions taking place as well as thermodynamic limitations (see below).

"Yield" is used to measure how effective a reaction is in converting reactant to the desired product. It has several possible definitions, so it is important to always note which one is being used. Often, yield is defined as

$$\text{Yield} = \frac{\textit{moles of desired product formed}}{\textit{moles of desired product that would have been formed if there were no side reactions and if complete conversion of the limiting reactant had taken place}}$$

Selectivity: Selectivity measures how effective a reaction is in producing the desired product relative to undesired products that result from side reactions.

$$\text{Selectivity} = \frac{\textit{moles of desired product formed}}{\textit{moles of undesired product formed}}$$

Problem 3.2 : In the combustion of heptane, CO_2 is produced. Assume that you want to produce 500 kg of dry ice per hour, and that 50% of the CO_2 can be converted into dry ice, as shown in

Figure 4.1. How many kilograms of heptane must be burned per hour?
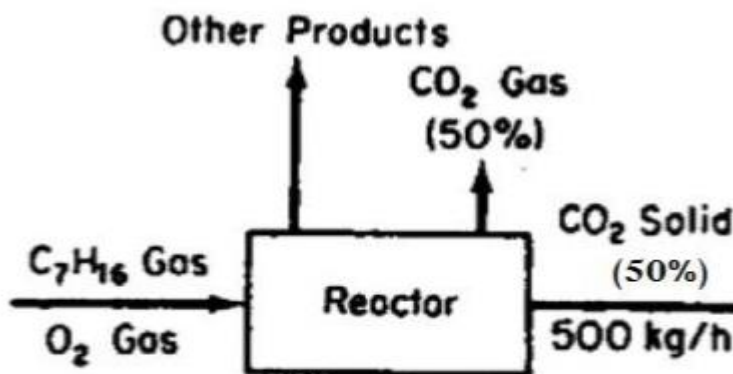
Figure 4.1

Solution:

The chemical equation is:

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$$
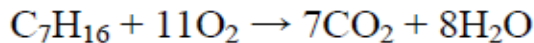
Basis: 500 kg dry ice (equivalent to 1 hr)

M.wt. of $CO_2 = 44$ kg/kgmol & $C_7H_{16} = 100.1$ kg/kgmol

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

$$\left| \frac{100.1 \text{ kg } C_7H_{16}}{1 \text{ kg mol } C_7H_{16}} = 325 \text{ kg } C_7H_{16} \right.$$

Problem 3.3 :A limestone analyses (weight %)

$CaCO_3 = 92.89\%$

$MgCO_3 = 5.41\%$

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?

Solution: chemical reactions are:
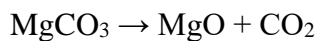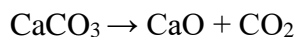
$CaCO_3 \rightarrow CaO + CO_2$

$MgCO_3 \rightarrow MgO + CO_2$

M.wt. of $CaCO_3 = 100.1$ Ib/Ibmol, $MgCO_3 = 84.32$ Ib/Ibmol, $MgO = 40.32$ Ib/Ibmol, $CaO = 56.08$ Ib/Ibmol and $CO_2 = 44$ Ib/Ibmol

Basis: 100 Ib of limestone
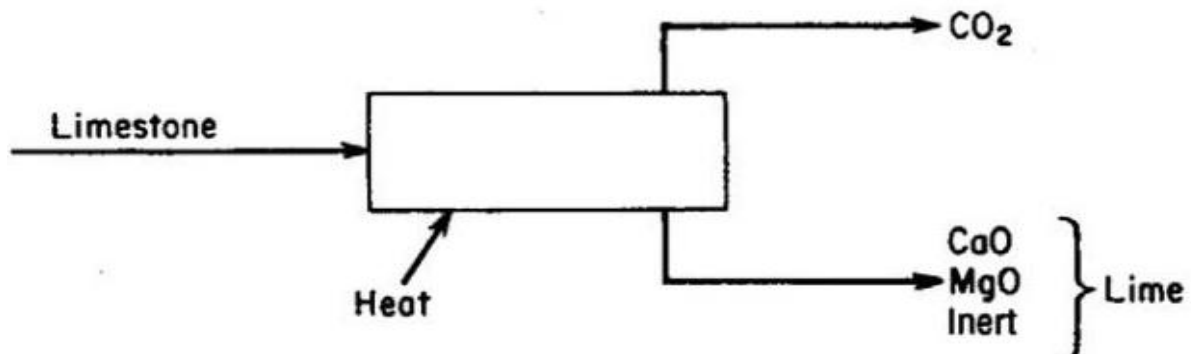
Figure 3.2

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

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

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

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

The production of CO_2 is:

$$0.9280 \text{ lb mol CaO is equivalent to } 0.9280 \text{ lb mol } CO_2$$
$$0.0642 \text{ lb mol MgO is equivalent to } \underline{0.0642} \text{ lb mol } CO_2$$
$$\text{Total} \qquad\qquad 0.992 \ \text{ lb mol } CO_2$$

$$\frac{0.992 \text{ lb mol } CO_2}{} \left| \frac{44.0 \text{ lb } CO_2}{1 \text{ lb mol } CO_2} \right. = 44.65 \text{ lb } CO_2$$

or Ib CO_2 = 100 - 56.33 = 44.65 Ib CO_2

1 ton = 2000 Ib

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

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

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

Problem 3.4 : If you feed 10 grams of N_2 gas and 10 grams of H_2 gas into a reactor:

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

b. What is the limiting reactant?

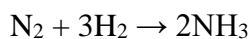c. What is the excess reactant?

Solution:

The chemical reaction is:

$N_2 + 3H_2 \rightarrow 2NH_3$
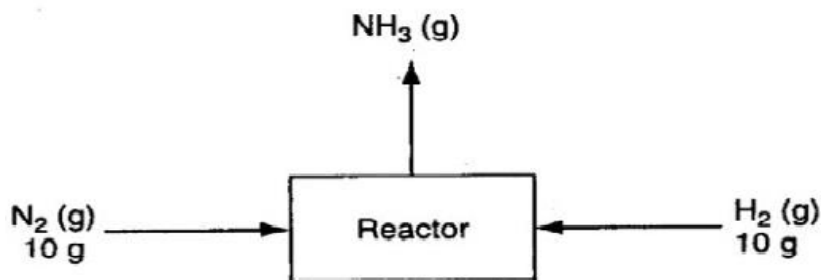
Figure 3.3

Next, write down the chemical equation, and get the molecular weights:

	$N_2(g)$	$+$	$3H_2(g)$	$\rightarrow$	$2NH_3(g)$
Given g:	10		10		0
MW:	28		2.016		17.02
Calcd. g mol:	0.357		4.960		0

The next step is to determine the limiting reactant by calculating the maximum extent of reaction based on the complete reaction of N_2 and H_2.

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

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

You can conclude that N_2 is the limiting reactant and H_2 is the excess reactant:

$$\% \text{ excess } (H_2) = \left[\frac{4.960 - 3(0.357)}{3(0.357)}\right] \times 100 = 363.12 \%$$

the maximum amount of NH_3 that can be produced is based on assuming complete conversion of the limiting reactant

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

3.2 CONVERSION AND DEGREE OF COMPLETION

In spite of using excess amount of some reactants, many industrial reactions does not go to the completion, i.e. part of the limiting reactant is reacted and the other part remains unchanged.

Degree of completion:

Is the fraction of the limiting reactant that is actually reacted and converted into products.

$$\text{Fractional degree of completion} = \left[\frac{\text{moles (or mass) of the limiting reactant that react}}{\text{moles (or mass) of the limiting reactant that introduce (input)}}\right]$$

Conversion:

Is the fraction of the feed or some key material in the feed (usually the excess reactant) actually reacted and converted into products.

$$\% \text{ Conversion} = \left[\frac{\text{moles (or mass)of feed (or a compound in the feed) that react}}{\text{moles (or mass)of feed (or a compound in the feed) that introduce (input)}} \right] \times 100$$

Note:

➤   The amount actually reacted is computed from the amount of product that is produced from the reaction.

➤   % conversion is dimensionless.

Problem 3.5: For the reaction $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

If 14.4 kg of CO_2 are formed in the reaction of 10 kg of C_7H_{16}, what is the percent of conversion of the C_7H_{16} to convert to CO_2?

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

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

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

Selectivity:

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

$$\text{Selectivity} = \left[\frac{\text{moles of desired product}}{\text{moles of undesired product}} \right]$$

Yield:

Yield (based on feed):

11

The amount (mass or moles) of desired product obtained divided by the amount of the key (frequently the limiting) reactant fed.

$$\text{Yield (based on feed)} = \left[\frac{\text{moles (or mass) of desired product}}{\text{moles (or mass) of limiting reactant fed (input)}}\right]$$
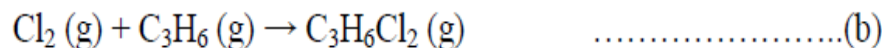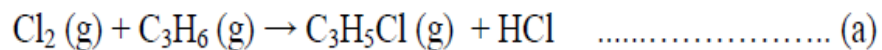
Yield (based on reactant consumed):
The amount (mass or moles) of desired product obtained divided by the amount of the key (frequently the limiting) reactant consumed.

$$\text{Yield (based on reactant consumed)} = \left[\frac{\text{moles (or mass) of desired product}}{\text{moles (or mass) of limiting reactant consumed (reacted)}}\right]$$

Problem 3.6

We have two reactions:

$$Cl_2 (g) + C_3H_6 (g) \rightarrow C_3H_5Cl (g) + HCl \quad \text{.......................} (a)$$
$$Cl_2 (g) + C_3H_6 (g) \rightarrow C_3H_6Cl_2 (g) \quad \text{........................}(b)$$

The species recovered after the reaction takes place for some time are listed in table below:

| Species	MW	gmol
Cl_2		141.0
C_3H_6, propylene	42.08	651.0
C_3H_5Cl, ally chloride	76.53	4.6
$C_3H_6Cl_2$, propylene chloride	112.99	24.5
HCl		4.6

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

a. How much Cl_2 and C_3H_6 were fed to the reactor in g mol?

b. What was the limiting reactant?

c. What was the excess reactant?

d. What was the fraction conversion of C_3H_6 to C_3H_5Cl?

e. What was the selectivity of C_3H_5Cl relative to $C_3H_6Cl_2$?

f. What was the yield of C_3H_5CI expressed in g of C_3H_5Cl to the g of C_3H_6 fed to the reactor?

g. What was the extent of reaction of the first and second reactions?

Solution:
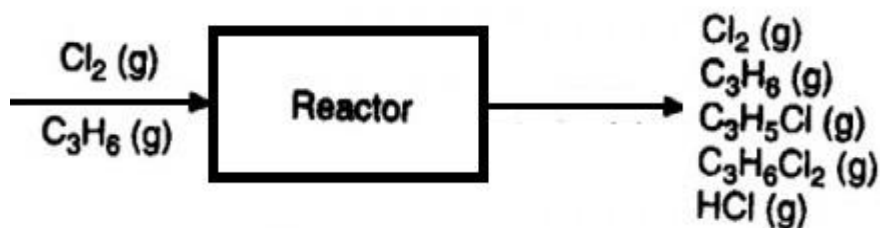
First calculate the g mol fed to the reactor (even if the amounts were not asked):

Reaction (a)

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

Reaction (b)

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

Total Cl_2 in product $\quad \frac{29.1}{141.0}$ g mol Cl_2 reacts

(a)   Total Cl_2 fed $\quad \underline{170.1}$

From the chemical equations you can see that if 29.1 gmol Cl_2 reacts by reaction (a) and (b), the same quantity of 29.1 gmol of C_3H_6 must react.

C_3H_6 in the product = 651.0 gmol

Total C_3H_6 fed = 651.0 + 29.1 = 680.1 gmol C_3H_6

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

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

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

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

(d) The fraction conversion of C_3H_6 to C_3H_5Cl was

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

(e) The selectivity was

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

(f) The yield was

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

(g) Because C_3H_5Cl is produced only by the first reaction, the extent of reaction of the first reaction is

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

Because $C_3H_6Cl_2$ is produced only by the second reaction, the extent of reaction of the second reaction is

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

Problem 3.7: Antimony is obtained by heating pulverized stibnite (Sb2S3) with scrap iron and drawing off the molten antimony from the bottom of the reaction vessel.

$$Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS$$
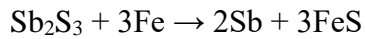
Suppose that 0.600 kg of stibnite and 0.250 kg of iron turnings are heated together to give 0.200 kg of Sb metal. Determine:
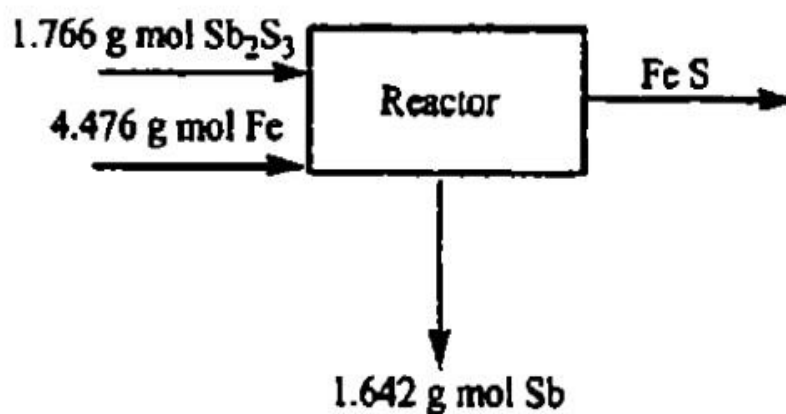
(a) The limiting reactant.

(b) The percentage of excess reactant.

(c) The degree of completion (fraction).

(d) The percent conversion based on Sb_2S_3.

(e) The yield in kg Sb produced/kg Sb_2S_3 fed to the reactor.

Solution:
The molecular weights needed to solve the problem and the gmol forming the basis are:

Component	kg	M.wt.	gmol
Sb_2S_3	0.600	339.7	1.766
Fe	0.250	55.85	4.476
Sb	0.200	121.8	1.642
FeS		87.91	

The process is illustrated as below:

15

a. Moles of Sb_2S_3 = (0.6 x 1000) / 339.7 = 1.77 gmol
    Moles of Fe = (0.25 x 1000) / 55.85 = 4.48 gmol

ξ_s^{max} (based on Sb_2S_3) = (-1.77/-1) = 1.776

ξ_s^{max} (based on Fe) = (-4.476/-3) = 1.492

Hence, the Fe is the limiting reactant and Sb_2S_3 is the excess reactant.
Theoretical Sb_2S_3 required to react with the limiting reactant = (4.476/3) = 1.492 gmol

b. % excess $= \left[\frac{1.776-1.492}{1.492}\right] = 18.4$ % excess Sb_2S_3

c. Although Fe is the limiting reactant, not all the limiting reactant reacts. We can compute from the 1.64 gmol of Sb how much Fe actually does reacts:

$$\frac{1.64 \text{ g mol Sb}}{} \left| \frac{3 \text{ g mol Fe}}{2 \text{ g mol Sb}} \right. = 2.46 \text{ g mol Fe}$$

If by the fractional degree of completion is meant the fraction conversion of Fe to products, then

Fractional degree of completion $= \frac{2.46}{4.48} = \boxed{0.55}$

(d) Let us assume that the percent conversion refers to the Sb_2S_3 since the reference compound is not specified in the question posed.

$$\frac{1.64 \text{ g mol Sb}}{} \left| \frac{1 \text{g mol } Sb_2S_3}{2 \text{ g mol Sb}} \right. = 0.82 \text{ g mol } Sb_2S_3$$

% conversion of Sb_2S_3 to Sb $= \frac{0.82}{1.77}(100) = \boxed{46.3\%}$

(e) The yield will be stated as kilograms of Sb formed per kilogram of Sb_2S_3 that was fed to the reaction

Yield $= \frac{0.200 \text{ kg Sb}}{0.600 \text{ kg } Sb_2S_3} = \boxed{\frac{0.33 \text{ kg Sb}}{1 \text{ kg } Sb_2S_3}}$

Problem 3.8 Aluminum sulfate can be made by reacting crushed bauxite ore with sulfuric acid, according to the following equation:

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO4)_3 + 3H_2O$$
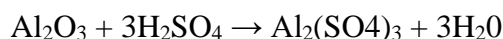
The bauxite ore contains 55.4% by weight of aluminum oxide, the remainder being impurities. The sulfuric acid solution contains 77.7% H_2SO_4, the rest being water.

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 used.

(a) Identify the excess reactant.

(b) What percentage of the excess reactant was consumed?

(c) What was the degree of completion of the reaction?

Solution:

Mass of Al_2O_3 input = (1080 x 0.554) = 598.32 lb

$\Longrightarrow$ moles of Al_2O_3 input = (598.32/101.96) = 5.87 lbmol

Mass of impurities input = (1080 x 0.4436) = 497.1 lb = output of impurities

Mass of H_2SO_4 input = (2510 x 0.777) = 1950.27 lb

$\Longrightarrow$ moles of H_2SO_4 input = (1950.27/98.1) = 19.88 lbmol

ξ^{max}(based on Al_2O_3) = (-5.87/-1) = 5.87

ξ^{max}(based on H_2SO_4) = (-19.88/-3) = 6.63

Hence, the Al_2O_3 is the limiting reactant and H_2SO_4 is the excess reactant.

Theoretical Al_2O_3 required to react with the limiting reactant = (4.476/3) = 1.492 gmol

a. % excess $= \left[\dfrac{19.88-(5.87 \times 3)}{(5.87 \times 3)}\right] = 12.89\%$ excess H_2SO_4

b. Moles of $Al_2(SO_4)_3$ produced = (1798/342.2) = 5.25 lbmol

The $Al_2(SO_4)_3$ actually formed indicates that:

$$\frac{5.25 \text{ lb mol Al}_2(SO_4)_3 \;\Big|\; 3 \text{ lb mol H}_2SO_4}{1 \text{ lb mol Al}_2(SO_4)_3} = 15.75 \text{ lb mol H}_2SO_4 \text{ was consumed}$$
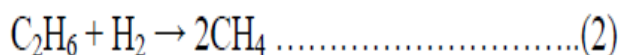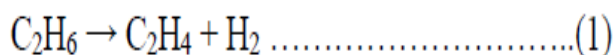
$$\frac{15.75}{19.88}(100) = 79.2\%$$

(c) The fractional degree of completion refers to the limiting reactant. For each mole of $Al_2(SO_4)_3$, 1 mole of Al_2O_3 was used:

$$\frac{5.25}{5.87} = 0.89$$

Problem 3.9

Ethylene (C_2H_4) can be produced by dehydration of ethane (C_2H_6). Methane can be produced as a by-product to the following reactions:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \; \text{.............................(1)}$$
$$C_2H_6 + H_2 \rightarrow 2CH_4 \; \text{............................(2)}$$

The composition (mol%) of the gases reaction product are given below:

Component	Percent
C_2H_6	35
C_2H_4	30
H_2	28
CH_4	7
Total	100

Calculate: (a) The selectivity of C_2H_4 relative to CH_4.

(b) The yield of C_2H_4 in kilogram moles of C_2H_4 per kilogram mole of C_2H_6.

Basis: 100 kg mol of products

(a) The selectivity (as defined) is

$$\frac{30 \text{ kg mol } C_2H_4}{7 \text{ kg mol } CH_4} = 4.29\frac{\text{mol } C_2H_4}{\text{mol } CH_4}$$

(b) The moles of C_2H_6 entering into the reaction can be determined from the C_2H_4 and the CH_4 formed.

$$\frac{30 \text{ kg mol } C_2H_4}{} \left| \frac{1 \text{ kg mol } C_2H_6}{1. \text{kg mol } C_2H_4} = 30 \text{ kg mol } C_2H_6 \right.$$

$$\frac{7 \text{ kg mol } CH_4}{} \left| \frac{1 \text{ kg mol } C_2H_6}{2 \text{ kg mol } CH_4} = 3.5 \text{ kg mol } C_2H_6 \right.$$
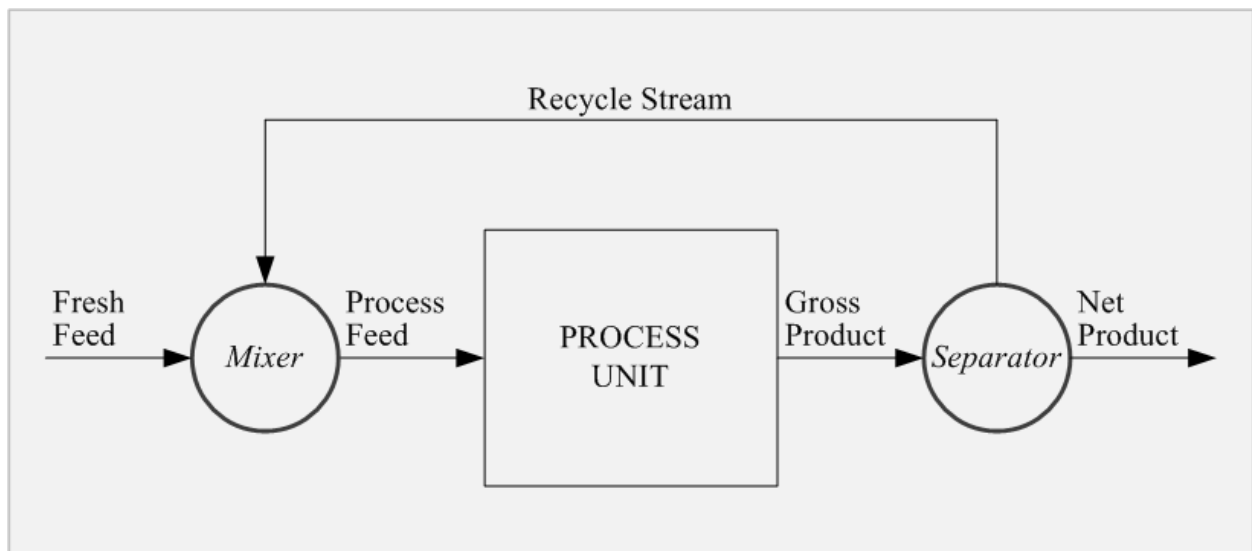
$$\overline{33.5 \text{ kg mol } C_2H_6}$$

Total $C_2H_6 = 33.5 + 35 = 68.5$ kg mol.

$$\frac{30 \text{ kg mol } C_2H_4}{68.5 \text{ kg mol } C_2H_6} = 0.44\frac{\text{kg mol } C_2H_4}{\text{kg mol } C_2H_6}$$
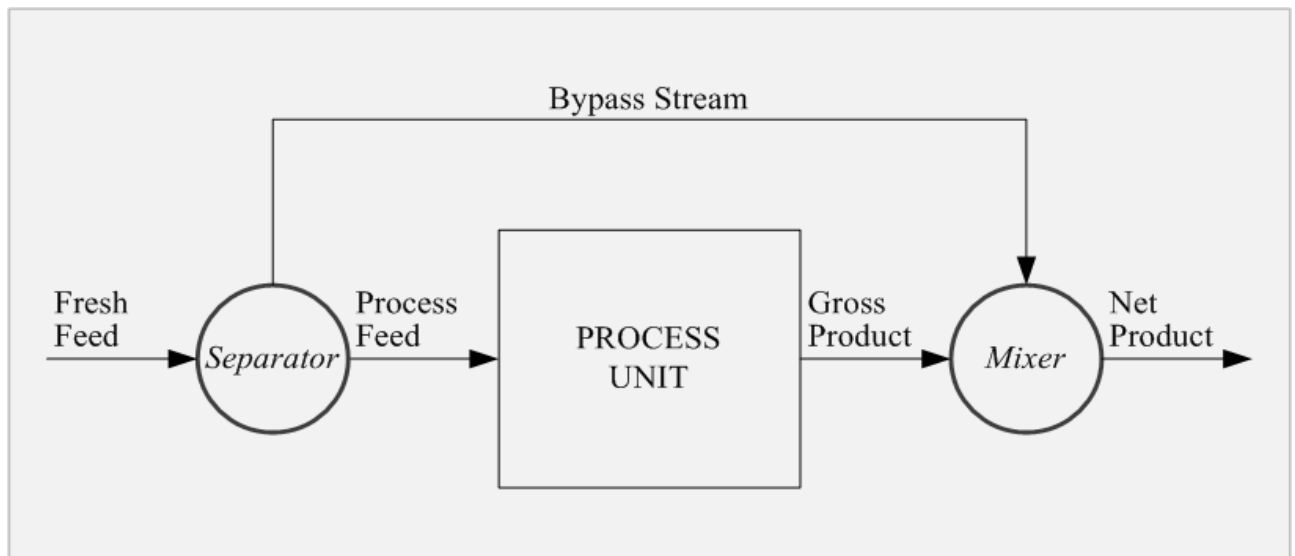
3.3 RECYCLE STREAM

Recycle stream is a term denoting a process stream that returns material from downstream of a process unit back to the process unit.

3.4 BYPASS STREAM

Bypass stream is a stream that skips one or more stages of the process and goes directly to another downstream stage.

3.5 PURGE STREAM

Purge stream is a stream bled off to remove an accumulation of inerts or unwanted material that might otherwise build up in the recycle stream.
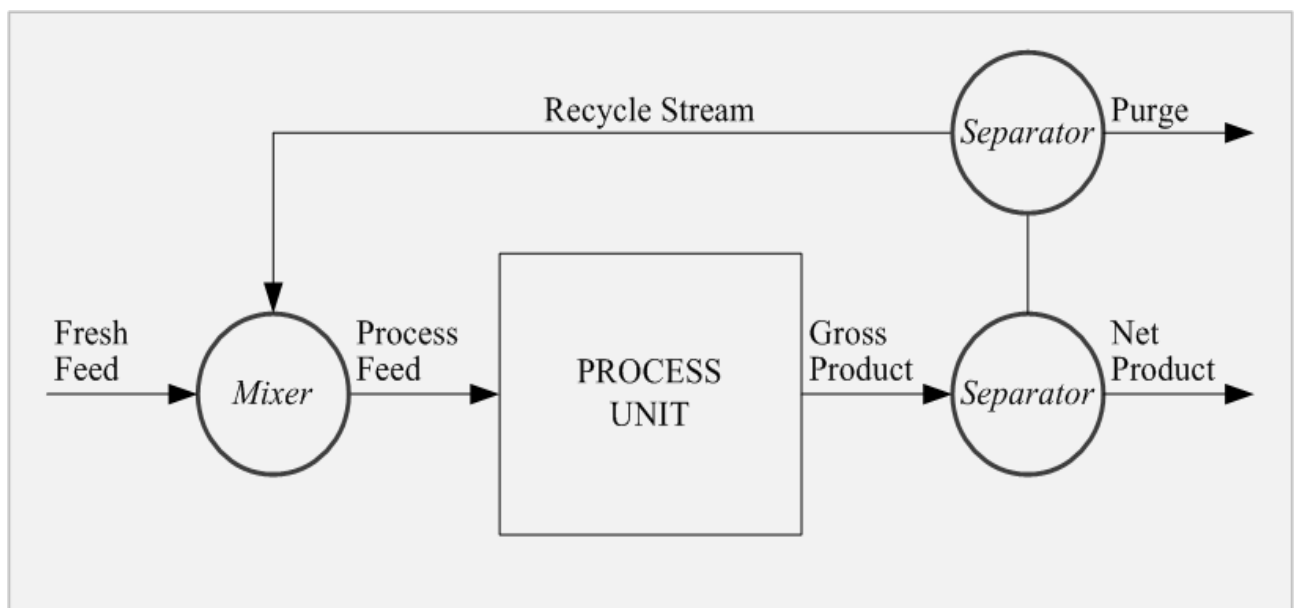
Problem 3.10. Distillation of Benzene and Toluene. A distillation column separates 10,000 kg/hr of a mixture containing equal mass of benzene and toluene. The product D recovered from the condenser at the top of the column contains 95% benzene, and the bottom W from the column contains 96% toluene.

The vapor V entering the condenser from the top of the column is 8000 kg/hr. A portion of the product from the condenser is returned to the column as reflux R, and the rest is withdrawn as the final product D. Assume that V, R, and D are identical in composition since V is condensed completely.

Find the ratio of the amount refluxed R to the product withdrawn D. Distillation of Benzene and Toluene
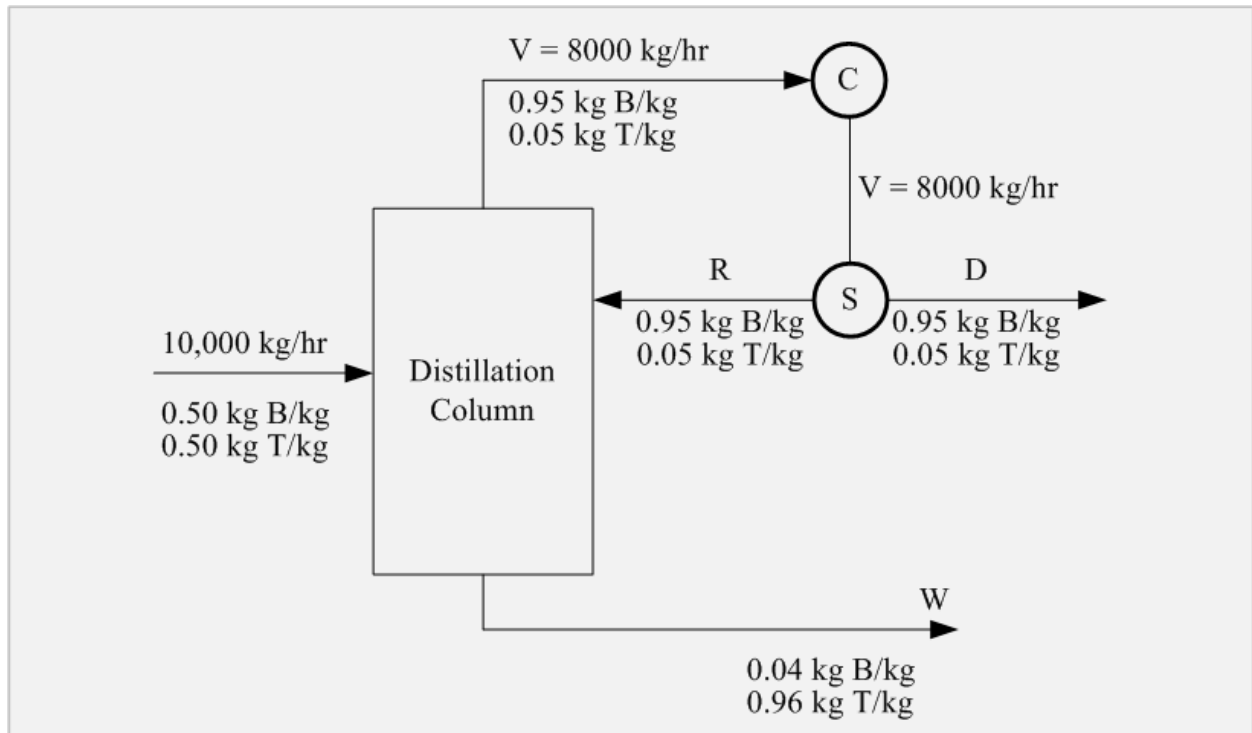
Overall Process

Total Balance: $10,000 = D + W$

Benzene Balance: $10,000(0.50) = D(0.95) + W(0.04)$

Solving simultaneously, $D = 5050$ kg/hr ; $W = 4950$ kg/hr

Total balance around the separator:

$8000 = R + D$

$R = 2950$ kg/hr

Ratio $(R/D) = (2950/5050) = 0.58$

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SCHOOL OF BIO AND CHEMICAL

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – V - Energy Balance – SCHA1304

5.1 Introduction

What is energy?

- Strength/ability to work which is derived from the utilization of physical or chemical resources, especially to provide light and heat or to work machines.
- In physics, energy is the quantitative property that must be transferred to an object in order to perform work on.
- The common symbol for energy is the uppercase letter E. The standard unit is the joule, symbolized by J.

Conversion: Although energy cannot be created or destroyed, it can be converted from one form to another.

Transport: Energy can also be transferred from one point to another or from one body to another one.

Carrier: Energy transfer can occur by flow of heat, by transport of mass, or by performance of work

Why we should know about energy

- How much power is required to pump certain amount of liquid from a storage vessel to a process unit. It will be helpful to design the pump motor
- How much energy is required to convert certain amount of liquid at a particular temperature to steam at another temperature
- You know hydrocarbon mixture is distilled to produce a liquid and a vapor useful product. The energy input to the distillation column based on which it is assessed how much it is required for a certain amount of steam to be supplied to process certain amount of feed mixture
- A highly exothermic chemical reaction takes place in a continuous reactor. If there is a certain % of conversion is to be achieved, at what rate of energy to be supplied from the reactor to keep the contents in the reactor at a constant temperature? That must be known

➢ How much coal must be burned each day to produce enough energy to generate the steam to run the turbines to produce enough electricity to meet the daily power requirements of a city.

➢ If a chemical process is executed with several units like a number of reactors, a number of compressors, distillation column, mixing tanks, evaporators, filter presses, and other materials handling and separation process unit. Each of the unit either requires or releases energy.

➢ How can the process operation be designed to minimize the total energy requirement?

Energy conservation (The First Law of Thermodynamics)

➢ The law of conservation of energy says that energy is neither created nor destroyed.

➢ When we use energy, it doesn't disappear. It changes from one form of energy into another. Example:

➢ A car engine burns gasoline, converting the chemical energy in gasoline into mechanical energy.

➢ Solar cells change radiant energy into electrical energy.

➢ Heat and light can be converted into mechanical energy, chemical energy, and electrical energy and back again.

➢ Energy changes form, but the total amount of energy in the universe remains the same.

Different Forms of Energy

➢ Kinetic Energy: The energy of motion.

➢ Potential Energy: Due to the position of the system in a potential field.

➢ Thermal energy: It refers to several distinct thermodynamic quantities, such as the internal energy of a system; heat or sensible heat, which are defined as types of energy transfer

Kinetic Energy

➢ The energy associated with an object's motion is called kinetic energy.

➢ It is the energy carried by a moving system because of its velocity.

➢ The kinetic energy KE of a moving object of mass m, traveling with speed v, is given by

$$KE = \frac{1}{2}\dot{m}v^2 \Rightarrow \left(\frac{kg}{s}\right)\left(\frac{m}{s}\right)^2 \left|\frac{N}{kg\,m/s^2}\right|\frac{J}{N\cdot m}\left|\frac{W}{J/s}\right| = W$$

Problem 5.1: Water flows from a large lake into a process unit through a 0.02 m inside diameter pipe at a rate of 2.0 m³/h. Calculate the change in kinetic energy for this stream in joules per second.

Solution:

➤ First, calculate the mass flow rate from the density and volumetric flow rate, and, next, determine the velocity as the volumetric flow rate divided by the pipe inner cross-sectional area.

➤ The rate of change in kinetic energy is calculated by

$$\Delta KE = \frac{1}{2}\dot{m}\Delta v^2 = \frac{1}{2}\dot{m}(v_2^2 - v_1^2)$$

$$\dot{m} = \rho\dot{V} = \frac{1000\,kg}{m^3}\left|\frac{2\,m^3}{h}\right|\frac{h}{3600\,s} = 0.56\,kg/s$$

The water exit velocity (v_2) is calculated from the volumetric flow rate divided by pipe inner cross-sectional area of the exit of the pipe (A).

The surface of the lake being large, the water surface can be assumed to be almost stagnant. Accordingly, the initial velocity is negligible ($v_1 = 0$):

$$v_2 = \frac{\dot{V}}{A = \frac{\pi D^2}{4}} = \left(\frac{2.00\,\frac{m^3}{h}\left|\frac{h}{3600\,s}\right|}{\frac{3.14 \times (0.02\,m)^2}{4}}\right) = 1.77\,m/s$$

$$\Delta KE = \frac{1}{2}\dot{m}(v_2^2 - v_1^2) = \frac{1}{2}\left(0.56\,\frac{kg}{s}\right)\left(\left(1.77\,\frac{m}{s}\right)^2 - 0\right)\left(\frac{1\,N}{\frac{kg\,m}{s^2}}\right)$$

$$\times \left(\frac{1\,J}{1\,N\,m}\right) = 0.88\,J/s$$

Problem 5.2: A liquid is pumped from a storage tank through a tube of 2.5 cm inner diameter at the rate of 0.005 m³/s. What is the specific kinetic energy of the water? Assume density of water 1000 kg/m³

Solution:

Mass rate of water = Volumetric flowrate X Density = 0.005 X1000 = 5 kg/s

Cross sectional area of pipe: $= \Pi(d^2)/4 = \Pi\ (0.025)2/4 = 0.000491\ m^2$

Velocity of liquid = Volumetric flow rate/ cross-sectional area

(0.005 m³/s)/0.000491 m² = 4.07 m/s

Kinetic energy rate = ½ m.v² = ½ X5 X (4.07)²= 41.41 J/s

Kinetic energy per unit mass = Kinetic energy rate/mass flow rate = 41.41/5 = 8.28 J/kg.

Potential energy

Potential energy (P) is energy the system possesses because of the body force exerted on its mass by a gravitational or electromagnetic field with respect to a reference surface. Potential energy for a gravitational field can be calculated from

$$\Delta PE = \dot{m}g(z_2 - z_1)$$

where

m = mass of the body

z = the distance from the reference surface

The symbol (hat) means potential energy per unit mass (or sometimes per mole)

- ➢ Potential energy is energy that is not "in use" (stored and is available to do work.
- ➢ If an object can fall, it has gravitational potential energy.
- ➢ The chemical energy in fossil fuels is considered potential energy until released.
- ➢ Fossil fuels have chemical potential energy from chemical bonds which store energy taken long ago from the sun.
- ➢ Biomass and batteries also have chemical potential energy.

Problem 5.3: Water is pumped at a rate of 5.0 kg/s from a point 100.0 m below the earth's surface to a point 100.0 m above the ground level. Calculate the rate of change in potential energy.

Solution

Taking the surface of the earth as a reference, the distance below

the earth's surface is negative ($z_1 = -100.0$) and above the surface is positive ($z_2 = +100$):

$$\Delta PE = \dot{m}g(z_2 - z_1)$$

Substituting the values,

The rate of change of potential energy (PE) = 5*9.81*(100-(-100)) =

9810 J/s =9.81 Kw

Energy Balance

$$Accumulation = Input - Output$$

$$Final\ system\ energy - Initial\ system\ energy$$
$$= Net\ energy\ transfered\ to\ the\ system\ (in - out)$$

The energy balance for a closed system can be expressed as

$$\Delta U + \Delta KE + \Delta PE = Q - W$$

where

Q = heat

W = Work

U = internal energy,

KE = kinetic energy and

PE = potential energy.

The energy balance for an open process system can be expressed as

$$\Delta \dot{U} + \Delta K\dot{E} + \Delta P\dot{E} + \Delta(P\dot{V}) = \dot{Q} - \dot{W}_s$$

5.2 ENTHALPY

Qualitatively, it is a thermodynamic property of a system capable to do non-mechanical work and capable to release heat. Or you can say

The enthalpy is a measurement of energy in a thermodynamic system, which is equivalent to the total heat content of a system.

It is the function of state and its value depends only on the starting and final state of the system.

Quantitatively, it is the sum of the internal energy and the product of the pressure and volume of a thermodynamic system.

$$H = U + PV$$

Evaluation of Enthalpy Change

The change in enthalpy can occur because of
  - ➢ Change in temperature,
  - ➢ Change in phase,
  - ➢ Mixing of solutions and reactions.

Sensible heat

- ➢ Sensible heat is the heat transferred to raise or lower the temperature of a material in the absence of phase change.
- ➢ The sensible heat change is determined by using a property of matter called the specific heat capacity at constant pressure or constant volume, (C_P)or (C_v) (unit is J/mol/K) or (cal/g/°C)

Heat Capacity

$$C_P(T) = \left(\frac{\partial \hat{H}}{\partial T} \right)_P$$

$$C_V(T) = \left(\frac{\partial \hat{U}}{\partial T} \right)_V$$

Specific heat capacities for most substances vary with temperature where the values of C_P vary for the range of the change in temperature

$$C_p = a + bT + cT^2 + dT^3$$

$$C_V = a + bT$$

C_P and C_V have units of energy per amount per temperature interval, where the amount of material may be measured in molar or mass units (e.g. units of heat capacity could be J/(kg $^\circ$C), J/(mol $^\circ$C), J/mol/K) or (cal/g/$^\circ$C) etc). The coefficient depends on nature of substance. The coefficients you can get from the appendix of the text book given for the course

For ideal gases, $Cp = CV + R$.   For liquids and solids, $Cp = Cv$.

Specific heat capacity for mixtures

The overall heat capacity of the mixture Cp, mix can be approximated as the sum of heat capacity contributions from the separate components of the mixture,

$$C_{P,mix}(T) = \sum_{\substack{all\ mixure \\ components}} x_i C_{P,i}(T) \qquad\qquad C_{V,mix}(T) = \sum_{\substack{all\ mixure \\ components}} x_i C_{V,i}(T)$$

the index i ranges over all of the components of the mixture. xi is the mass fraction (if using heat capacities expressed per mass of material) or mole fraction (if using heat capacities expressed per mole of material) of component i in the mixture, and C_p or $_{v,i}$ is the heat capacity of species i in its pure form.

Enthalpy Change as a Result of Temperature

If CP is constant

$$\Delta H = mC_p(T - T_{ref})$$

If C_P is changing with temperature

$$\Delta \dot{H} = \dot{m} \int_{T_{ref}}^{T} C_p dT$$

Heat capacities for most substances vary with temperature where the values of C_P vary for the range of the change in temperature

$$C_P = a + bT + cT^2 + dT^3$$

The coefficients you can get from the appendix of the text book given for the course. The coefficient depends on nature of substance

Problem 5.4: What is the change in the enthalpy of 100 g/s brine solution heated in a counterflow heat exchanger from 20°C to 80°C, if the average heat capacity at constant pressure is 3.12 kJ/kg K?

Solution

The change in enthalpy as a function of specific heat is given by

$$\Delta \dot{H} = \dot{m} \int_{T_{ref}}^{T} C_p dT$$

Since the heat capacity (C_P) is constant, the equation is simplified to

$$\Delta \dot{H} = \dot{m} C_p (T - T_{ref})$$

The change in enthalpy transport rate is then

$$\Delta \dot{H} = (0.1)(3.12)((80 + 273) - (20 + 273)) = 18.72 \, kJ$$

Heat of solution

Enthalpies of mixing are often expressed in terms of heat of solution.

It is the change in enthalpy that results from dissolving one mole of solute in certain moles of liquid solvent at constant T.

In the limit when 1 mole of solute is dissolved in an infinitely large amount of solvent, the heat of solution approaches a limiting value known as the heat of solution at infinite dilution.

Enthalpy Calculations with Phase Changes

Phase changes (example, evaporation and melting), are accompanied by relatively large changes in internal energy and enthalpy, as bonds between molecules are broken and reformed.

Latent heat: Heat transferred to or from a system, causing change of phase at constant temperature and pressure, is known as latent heat.

Latent heat of vaporization, which is the heat required to vaporize a liquid; Latent heat of fusion, which is the heat required to melt a solid; and

Latent heat of sublimation, which is the heat required to directly vaporize a solid.

Latent heats are, in general, f (pressure, temperature). However, they depend much more strongly on temperature than on pressure. Therefore, when calculating heat associated with a change of phase, it is important to ensure that the latent heat value used for the calculation is that for the actual temperature at which the phase transformation occurs.

Remember that latent heat of vaporization at 30 $^{\circ}$C is not same as at 100 $^{\circ}$C.

5.4 HEAT OF FORMATION

Change of enthalpy with chemical reactions

To take account of possible energy changes caused by a reaction, in the energy balance you have to incorporate (in the enthalpy of each individual constituent at operating condition) an additional quantity termed as the standard heat (really enthalpy) of formation, heat released or absorbed by chemical reaction (experimentally).
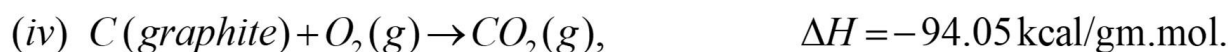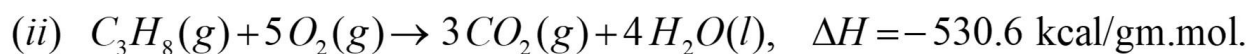
Standard Heat of Formation (Definition)

The standard heat of formation of a compound is the enthalpy change associated with the formation of 1 mol of the compound at 25°C and 1 atm from its elemental constituents as they are normally found in nature (e.g.(s), O2(g), N2(g), H2(g) are the most important elemental constituents).

The heat of formation is zero in the standard state for each element ((C(s), O2(g), N2(g), H2(g)), at 25°C and 1 atm.

Problem 5.5: Standard heat of formation from standard heat generation/absorption by reaction (that experimentally estimated)
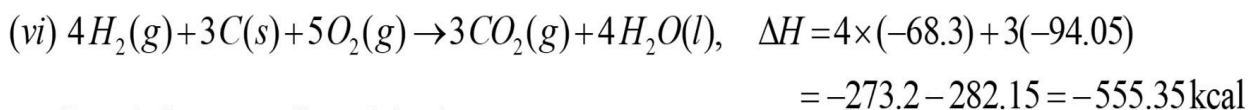
The following enthalpy changes are observed experimentally for the reaction below at 25°C in standard state. Calculate the standard heat of formation of propylene.

$(i)\quad C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g),\qquad\qquad \Delta H = -29.6 \text{ kcal/gm.mol.}$

$(ii)\quad C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l),\quad \Delta H = -530.6 \text{ kcal/gm.mol.}$

$(iii)\quad H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l),\qquad\qquad \Delta H = -68.3 \text{ kcal/gm.mol.}$

$(iv)\quad C(graphite) + O_2(g) \rightarrow CO_2(g),\qquad\qquad \Delta H = -94.05 \text{ kcal/gm.mol.}$

Adding (i) and (ii) and cancelling common constituents from both the sides,

$(v)\ C_3H_6(g) + H_2(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)\quad \Delta H = -29.6 + (-530.6) = -560.2 \text{ kcal}$

Multiplying reactions (iii) and (iv) by 4 and 3 respectively and then adding,

$(vi)\ 4H_2(g) + 3C(s) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l),\quad \Delta H = 4 \times (-68.3) + 3(-94.05)$

$$= -273.2 - 282.15 = -555.35 \text{ kcal}$$

~~action (vi) Reaction (v) gives~~

Reaction (vi)- Reaction (v) gives,

$$(vii)\ 3\,C(s) + 3\,H_2(g) - C_2H_6(g) = 0$$

or, $\quad 3\,C(s) + 3\,H_2(g) \rightarrow C_2H_6(g), \qquad \Delta H = -555.35 - (-560.2)$
$$= 4.85\ \text{kcal}$$

Reaction (vii) is the formation reaction of propylene.

Reaction (vii) is the formation reaction of propylene.

Heat of formation is 4.85 kcal/gm mol

Problem 5.6: Standard heat of formation from standard heat generation/absorption by reaction (that experimentally estimated)

On the basis of the data and the chemical reactions given below, find the heat of formation of $ZnSO_4$ from the elements:

(1) $Zn + S\,(rhomb.) \rightarrow ZnS, \qquad \Delta H = -44\ \text{kcal/kg mol.}$
(2) $2ZnS + 3\,O_2 \rightarrow 2ZnO + 2SO_2, \quad \Delta H = -221.88\ \text{kcal/kg mol.}$
(3) $2\,SO_2 + O_2 \rightarrow 2SO_3, \qquad \Delta H = -46.88\ \text{kcal/kg mol.}$
(4) $ZnO + SO_3 \rightarrow ZnSO_4 \qquad \Delta H = -55.10\ \text{kcal/kg mol.}$

Solution

Basis: 1 kg mol of $ZnSO_4$

Reactions:

(1) $Zn + S\,(rhomb.) \rightarrow ZnS, \qquad \Delta H = -44\ \text{kcal/kg mol.}$
(2) $2ZnS + 3\,O_2 \rightarrow 2ZnO + 2SO_2, \quad \Delta H = -221.88\ \text{kcal/kg mol.}$
(3) $2\,SO_2 + O_2 \rightarrow 2SO_3, \qquad \Delta H = -46.88\ \text{kcal/kg mol.}$
(4) $ZnO + SO_3 \rightarrow ZnSO_4 \qquad \Delta H = -55.10\ \text{kcal/kg mol.}$
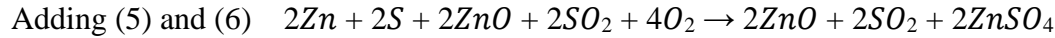
Multiplying reaction (1) by 2 and adding to reaction (2),

(5) $2\,Zn + 2\,S + 2\,ZnS + 3\,O_2 \rightarrow 2\,ZnS + 2\,ZnO + 2\,SO_2, \qquad .$
or $\ 2\,Zn + 2\,S + 3\,O_2 \rightarrow 2\,ZnO + 2\,SO_2 \quad \Delta H = -2(44) + (-221.88)\ \text{kcal}$
$$= -309.88\ \text{kcal}$$

Mul

tiplying reaction (4) by 2 and adding to reaction (3), $\qquad$ Eq.(6)

$$2\,ZnO+2\,SO_3+2\,SO_2+O_2 \rightarrow 2\,ZnSO_4+2\,SO_3$$

or, $\quad 2\,ZnO+2\,SO2+O_2 \rightarrow 2\,ZnSO_4 \qquad \Delta H=2(-55.10)+(-46.88)$

$$=-110.20-46.88=-157.08\,\text{kcal}$$

Adding (5) and (6) $\quad 2Zn+2S+2ZnO+2SO_2+4O_2 \rightarrow 2ZnO+2SO_2+2ZnSO_4$

Cancelling the common terms from both the sides,

$$2\,Zn+2\,S+4O_2 \rightarrow 2\,ZnSO_4$$

$$\Delta H=-309.88+(-157.08)=-466.96\,\text{kcal}$$

$$\Delta H=\text{heat of formation of two mol of } ZnSO_4$$
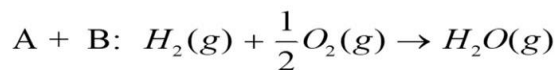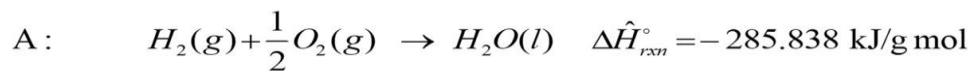
Hence, heat of formation in kcal per kg mol of $ZnSO_4$

$$=-\frac{466.96}{2}=-233.48$$

Problem 5.7: Heat of Formation Including a Phase Change If the standard heat of formation for H_2O (l) is -285.838 kJ/g mol and the heat of evaporation is +44.012 kJ/g mol at 25°C and 1 atm, what is the standard heat of formation of H_2O (g)?

Solution: Basis: 1 g mol of H_2O

We shall proceed as to add the known chemical equations and the phase transitions to yield the desired chemical equation and carry out the same operations on the enthalpy changes.

$$\Delta \hat{H}^\circ_{rxn}=\sum \Delta \hat{H}^\circ_{f\,\text{products}}-\sum \Delta \hat{H}^\circ_{f\,\text{reactants}}$$

A: $\qquad H_2(g)+\dfrac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta \hat{H}^\circ_{rxn}=-285.838$ kJ/g mol

B: $\qquad H_2O(l) \qquad\qquad \rightarrow H_2O(g) \quad \Delta \hat{H}^\circ_{vap}=+44.012$ kJ/g mol

A + B: $H_2(g)+\dfrac{1}{2}O_2(g) \rightarrow H_2O(g)$

$$\Delta \hat{H}^\circ_{rxn\,A}+\Delta \hat{H}^\circ_{vap}=\Delta \hat{H}^\circ_{rxn\,H_2O(g)}=\Delta \hat{H}^\circ_{f\,H_2O(g)}=-241.826 \text{ kJ/g mol}$$

5.5 HESS'S LAW

If a set of reactions can be manipulated through a series of algebraic operations to yield the desired reaction, then the desired heat of reaction can be obtained by performing the same algebraic operations on the heats of reaction of the manipulated set of reactions

Based on Hess' law, the molar enthalpy of solution is equal to the sum of the enthalpies of formation of products minus reactants.

Problem 5.8

Standard molar enthalpy of formation $(NaCl(s))= -411.2$ kJ/mol

Standard molar enthalpy of formation $(Na+(aq))= -240.1$ kJ/mol

Standard molar enthalpy of formation $(Cl-(aq))= -167.2$ kJ/mol

Standard enthalpy of solution =

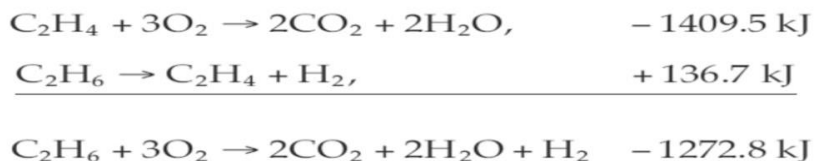-240.1 kJ mol-1 -167.2 kJ mol-1 $+411.2$ kJ mol-1 $= 3.9$ kJ/mol

Problem 5.9: Calculate the heat of reaction for C_2H_6 from the following reactions:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H^o_{Rx1} = -1409.5 \text{ kJ/mol}$$

$$C_2H_4 + H_2 \rightarrow C_2H_6, \quad \Delta H^o_{Rx2} = -136.7 \text{ kJ/mol}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad \Delta H^o_{Rx3} = -285.5 \text{ kJ/mol}$$

Solution

Subtracting second reaction from the first reaction on one mole basis

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O, \qquad -1409.5 \text{ kJ}$$
$$\underline{C_2H_6 \rightarrow C_2H_4 + H_2, \qquad\qquad\quad +136.7 \text{ kJ}}$$

$$C_2H_6 + 3O_2 \rightarrow 2CO_2 + 2H_2O + H_2 \qquad -1272.8 \text{ kJ}$$

The resulting reaction is added with the third one

Accordingly, the heat of combustion of C_2H_6 is -1558.3 kJ

$$C_2H_6 + 3O_2 \rightarrow 2CO_2 + 2H_2O + H_2 \quad -1272.8 \text{ kJ}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad\quad\quad\quad\quad\quad -285.5 \text{ kJ}$$

$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \quad -1558.3 \text{ kJ}$$
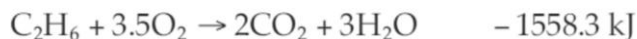
Standard Heat of reaction from standard heat of formation

The standard heat of reaction is calculated as the difference between the product and reactant enthalpies (heat of formation) when both reactants and products are at standard conditions, that is, at 25°C and 1 atm.

Heat of reaction at standard condition can be expressed

$$\Delta H^o_{rxn} = \sum_{Products} n_i \Delta \hat{H}^o_{f,i} - \sum_{Reactants} n_i \Delta \hat{H}^o_{f,i}$$

The symbol "o" denotes standard conditions.

For an example: If reaction like

$$aA + bB \rightarrow cC + dD$$

$$\Delta H^o_{rxn}[\text{kJ/mol}] = c\Delta \hat{H}^o_{f,C} + d\Delta \hat{H}^o_{f,D} - a\Delta \hat{H}^o_{f,A} - b\Delta \hat{H}^o_{f,B}$$
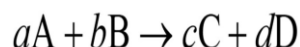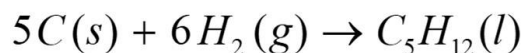
Standard Heat of Combustion

The standard enthalpy of combustion is the enthalpy change when 1 mol of a reactant completely burns in excess oxygen under standard thermodynamic conditions. The standard heat of combustion of a species i, $\Delta Hc,i$, is the enthalpy change associated with the complete combustion of 1 mol of species i with oxygen at

25°C and 1 atm.

 For complete combustion

All the carbon forms CO_2 (g), All the hydrogen forms H_2O (l), All the sulfur forms SO_2 (g), and All the nitrogen forms NO_2 (g).

Problem 5.10

$$5C(s) + 6H_2(g) \rightarrow C_5H_{12}(l)$$

Carbon, hydrogen, and pentane can all be burned, and their standard heats of combustion can be determined experimentally.

The standard heat of reaction from standard heat of combustion can be calculated as

$$\Delta H^\circ_{Rx} = 5\,\Delta H^\circ_{c,C(s)} + 6\,\Delta H^\circ_{c,H_2(g)} - \Delta H^\circ_{c,C_5H_{12}(l)}$$

If any reactants or products are combustion products (i.e., CO_2, H_2O, SO_2), their heats of combustion are equal to zero.

The standard heat of reaction can also be calculated from standard heat of formation as

$$\Delta H^0_{Rx} = \Delta H^0_{f,C_5H_{12}(l)} - 5\Delta H^0_{f,C(s)} - 6\Delta H^0_{f,H_2(g)}$$

Problem 5.11

Problem: Calculate the standard heat of reaction as follows from the standard heat of formation and standard heat of combustion

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$
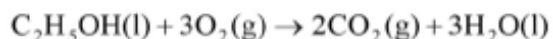
Given that standard heats of formation of Ethanol, CO_2 and H_2O are respectively: −277.63, −393.51 and −285.84 and heat combustion of ethanol is −1366.91.

Solution

➤ From the standard heat of formation:

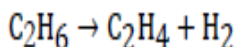ΔH^o_{Rx}(kJ/mol) $= 3(-285.84) + 2(-393.51) - (-277.63) - 3\,(0) = -1366.9$ kJ/mol

➤ From the standard heat of combustion:

ΔH^o_{Rx}(kJ/mol) $= -1366.9$ kJ/mol$+3(0) - 2(0) - 3(0) = -1366.9$ kJ/mol

Results are same in both cases

Problem 5.12

Problem: Calculate the standard heat of reaction from the dehydrogenation of ethane using the standard heats of combustion

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

The standard heat of combustion for C_2H_6, C_2H_4, H_2 are -1559.9, -1410.99 and -285.84 respectively

$$\Delta H^o_{Rx} = \Delta H^o_{c,C_2H_6} - \Delta H^o_{c,C_2H_4} - \Delta H^o_{c,H_2}$$

Solution: Substituting the values of standard heat of combustion yields

$$\Delta H^o_{Rx}(kJ/mol) = -1559.9 - (-1410.99) - (-285.84) = -136.93 \; kJ/mol$$

Problem 5.13

Compute the heat of reaction of the following reaction from standard heat of combustion data:

$$C_2H_5OH(l) + CH_3COOH(l) \rightarrow C_2H_5OOCCH_3(l) + H_2O(l)$$
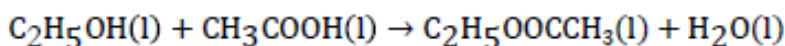
Ethyl alcohol   Acetic acid   Ethyl acetate

Basis: 1 g mol of C_2H_5OH

Tabulated data	$C_2H_5OH(l)$	$CH_3COOH(l)$	$C_2H_5OOCCH_3(l)$	$H_2O(l)$
$\Delta \widehat{H}^o_c$ per g mol at 25° C and 1 atm (kJ/g mol)	- 1366.91	- 871.69	- 2274.48	0

$$\Delta H^o_{rxn} = \sum_{Reactants} n_i \Delta \hat{H}^o_{c,i} - \sum_{Products} n_i \Delta \hat{H}^o_{c,i}$$

$$\Delta H^o_{rxn} = -[((-1366.91) + (-2274.48)) - (-871.69 - 0)] = +35.9 \; kJ/g \; mol$$

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